resonances for bibenzyl, toluene, benzyl alcohol, and benzaldehyde are observed at 2.92 (CH_2), 2.34 (CH_3), 4.47 (CH_2), and 10.0 (CH) ppm, respectively, relative to internal TMS.

The inorganic products were separated on columns (8 × 1 cm) of Sephadex SP-C25 (H^+) after the reaction solution had been flushed with a stream of air for 1 min. Three chromium complexes were separated. A blue species is eluted with 0.5–0.6 M $HClO_4$ and was identified as $Cr(OH_2)_6^{3+}$ from its electronic spectrum. Two higher charged polymers, green-blue and green, are eluted in that order with 0.1 M $HClO_4$, and these two species also are formed as the major products in the air oxidation of aqueous Cr^{2+}. Total chromium was determined spectrophotometrically as chromate after oxidation by alkaline hydrogen peroxide.

The presence of chromium(II) in the reaction solutions was confirmed by comparison of the spectra of the solutions in the 570-nm region before and after exposure to air. If chromium(II) is present, there is a substantial increase in absorbance when it is oxidized.

Blank experiments, which relate to the homolysis product study in the absence of O_2, show that our procedure for the air oxidation of chromium(II) in 0.98 M $NaClO_4$ and 0.01 M $HClO_4$ yields ~15% $Cr(OH_2)_6^{3+}$ and 85% higher charged polymers. The amount of the blue-green polymer is about 35% under both conditions, and the main change is the production of more green polymer and less $Cr(OH_2)_6^{3+}$ at the higher acidity. These polymeric species are probably the bis(μ-hydroxo) and μ-hydroxo chromium(III) dimers of 4+ and 5+ charge, respectively.

Kinetic Methods. The reactions were followed by the decrease in absorbance at 358 nm recorded on a Cary 219 spectrophotometer equipped with a thermostated cell holder and standard water circulation and temperature control system. The concentrations of $(H_2O)_5CrCH_2C_6H_5^{2+}$ were in the range of (2–10) × 10^{-5} M, and the observations were made in 50 or 100 mm pathlength cells. An appropriate volume of the perchloric acid–sodium perchlorate reaction medium was placed in the cell, and the cell was closed with serum caps and purged for 30 min with a stream of argon that had been passed through a scrubber of aqueous chromium(II) perchlorate to remove dioxygen. Then Cr^{2+} was added if required, and the solution was equilibrated at the desired temperature before the addition of $(H_2O)_5CrCH_2C_6H_5^{2+}$. All reagents that are sensitive to dioxygen were handled by standard syringe techniques under an argon atmosphere.

Instrumentation. The electronic spectra were recorded on a Cary 219 spectrophotometer and the NMR spectra on a Bruker AM 300 system.

Acknowledgment. We acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada. P.K. thanks N. Copernicus University for granting a leave to do this work.

Registry No. $(H_2O)_5CrCH_2C_6H_5^{2+}$, 34788-74-4; chromium(II) perchlorate, 21359-99-9; benzyl bromide, 100-39-0.

Contribution from the Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Cadiz, Cadiz, Spain, and Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Kinetics and Mechanism of the Decomposition of Cobalt Dioxygen Complexes of the Binucleating Macrocyclic Ligand BISBAMP

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Received December 20, 1988

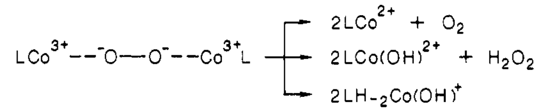
The kinetics of the decomposition of cobalt dioxygen complexes with the ligand 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo-[23.3.1.1^{11,15}]triaconta-1(28),11,13,15(30),25(29),26-hexaene, BISBAMP, has been studied at 50.0 °C between p[H] 9 and 12. Under these conditions, dioxygen complexes $Co_2LO_2(OH)_2^{2+}$ and $Co_2LO_2(OH)_3^+$ are present in solution and undergo irreversible metal-centered autoxidation to form Co(III) complexes. From the p[H] dependence of the observed rate constants, a mechanism is proposed in which both complexes decompose by two parallel pathways that correspond to direct aquation and base-catalyzed hydrolysis of a cobalt–dioxygen coordinate bond. Preliminary results are also described that indicate extensive dehydrogenation of BISBAMP upon reaction with Cu(I) in the presence of dioxygen.

Introduction

Cobalt dioxygen complexes have been shown to decompose according to the three processes illustrated in Scheme I for the case of a neutral pentadentate ligand L. The first process consists of the reversible decomposition of the dioxygen complex to dioxygen and the original Co(II) complex. This reaction occurs rapidly in acidic solutions for dioxygen complexes containing basic ligands, which are not usually stable at low pH. The proposed mechanism implies the formation of a mononuclear dioxygen complex intermediate, and it is essentially the inverse of the mechanism that operates for the formation of binuclear dioxygen complexes.[1,2]

Under neutral or basic conditions, cobalt dioxygen complexes are generally stable enough to be characterized, but they decompose slowly by either a metal-centered or a ligand-centered autoxidation process. Metal-centered autoxidation leads to the formation of Co(III) complexes with H_2O_2 release.[3-5] The reaction is base-catalyzed, and a mechanism has been proposed[5] in which deprotonation of a coordinated nitrogen activates the hydrolysis of the Co(III)–O_2 bond in a manner similar to that of the well-established dissociative conjugated-base mechanism for the base hydrolysis of Co(III) complexes. Although irreversible metal-centered autoxidation is the most common decomposition reaction of cobalt dioxygen complexes, ligand-centered oxidative dehydrogenation may occur when certain requirements are met. The process is essentially oxidative dehydrogenation of the ligand and leads to the formation of a binuclear Co(II) complex of the oxidized ligand, LH_{-4} (**2**).[6] If this complex is stable it can reoxygenate to form a new dioxygen complex, but hydrolysis of the C=N bond formed in the previous step may occur to give an aldehyde with reduced complexing ability.[7,8] Ligand-centered autoxidation is also base-catalyzed, and the proposed mechanism implies the homolytic cleavage of the O–O bond. According to previous observations by Martell et al.,[5] in order that degradation occur as a ligand-centered dehydrogenation process, the C=N

Scheme I



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† Universidad de Cadiz.

‡ Texas A&M University.

[1] Fallab, S.; Mitchel, P. R. In *Advances in Inorganic and Bioinorganic Mechanisms*; Academic Press: New York, 1984; Vol. 3, p 311.

[2] Wong, C. L.; Endicott, J. F. *Inorg. Chem.* **1981**, *20*, 2233, 1981.

[3] Shibahara, T.; Kuroya, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2834.

[4] Raleigh, C.; Martell, A. E. *J. Chem. Soc., Chem. Commun.* **1984**, 335.

[5] Raleigh, C.; Martell, A. E. *Inorg. Chem.* **1986**, *25*, 1196.

[6] Raleigh, C.; Martell, A. E. *Inorg. Chem.* **1985**, *24*, 142.

[7] Basak, A. K.; Martell, A. E. *Inorg. Chem.* **1986**, *25*, 1182.

[8] Basak, A. K.; Martell, A. E. *Inorg. Chem.* **1988**, *27*, 1948.

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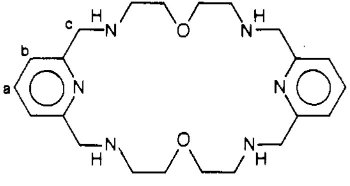
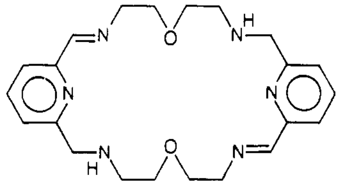
bond that forms must be stabilized by conjugation with an aromatic ring. Moreover, certain steric requirements are also necessary in order to avoid the more prevalent metal-centered process.

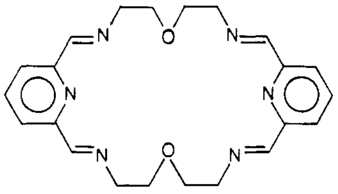
In a previous paper,[9] the formation of cobalt dioxygen complexes with the binucleating ligand 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23,3,1,$1^{11,15}$]triaconta-1(28),11,13,15(30),25(29),26-hexaene, BISBAMP (**1**), was reported. Three dioxygen complexes with formulas $Co_2LO_2(OH)_n$ (n = 1–3; L = BISBAMP) are formed in basic solution, but the monohydroxo complex is only a minor species in oxygenated solutions containing 2:1 molar ratios of Co:BISBAMP. The trihydroxo species is predominant at high pH values, with the dihydroxo complex being the major species at pH close to 9. The pyridine rings in the BISBAMP molecule are disposed in such a way that oxidative dehydrogenation would seem to be the probable autoxidation process to give a Co(II) complex of the partially oxidized ligand BISBAMP–4H, LH_{-4} (**2**). If this complex were to form a stable dioxygen adduct, the latter would decompose to give a cobalt(II) complex of BISBAMP–8H, LH_{-8} (**3**). Similar dehydrogenation reactions have been observed for other dicobalt polyamine dioxygen complexes, as noted above.[6-8] According to the observations by Nelson et al.[10] for the case of copper complexes of a closely related ligand in acetonitrile solutions, further dehydrogenation may occur at the ethylenic connecting units. In this paper we report a kinetic study of the decomposition process of Co–BISBAMP dioxygen complexes together with some observations on the formation and degradation of copper(I) complexes of BISBAMP.



BISBAMP, L (**1**)



BISBAMP-4H, LH_{-4} (**2**)



BISBAMP-8H, LH_{-8} (**3**)

Experimental Section

The synthesis of BISBAMP·6HCl and the formation of its cobalt dioxygen complexes have been previously reported.[9] From the species distribution–p[H] curves and the electronic spectra of dioxygen complex solutions at several pH values, calculated absorbance curves were obtained for the two main forms of the dioxygen complexes present in this system, $Co_2LO_2(OH)_n$ (n = 2, 3; L = BISBAMP).

Electronic spectra were recorded with a Perkin Elmer Model 553 fast scan UV/vis spectrophotometer. A Corning Model 250 ion analyzer fitted with glass and calomel reference electrodes was used for the p[H] measurements. p[H] is defined as $-\log [H^+]$. ^1H NMR spectra were recorded with a Varian XL 200 spectrometer with samples dissolved in $CDCl_3$, and TMS was used for reference. Infrared spectra were obtained with samples prepared as KBr disks.

Kinetic Requirements. Solutions for kinetic experiments were prepared by mixing the corresponding volumes of BISBAMP and Co(II) standard solutions and diluting with water to a volume of 70.0 mL. Solid KNO_3 was added to provide 0.10 M KNO_3 supporting electrolyte. These solutions were prepared under argon atmosphere, and appropriate volumes of 0.0973 M KOH were added in every case to obtain the desired p[H] values between 9 and 12. Dioxygen was bubbled through the solutions for 1 h to form dioxygen complexes, and then the solutions were deoxygenated by passing argon through the solutions for 1 h more while the temperature was maintained at 25.0 °C. The total concentration of dioxygen complexes in these solutions was close to 2.0×10^{-4} M, with small differences caused by the volumes of KOH solution added and by the degree of dioxygen complex formation. Samples prepared in this way were observed not to decompose significantly before starting the kinetic runs and could be maintained in stable form for several hours in a refrigerator, when necessary.

The kinetic experiments were performed by circulating the solutions with an external peristaltic pump through a quartz flow cell thermostated at 50.0 °C under an argon atmosphere. Glass and reference electrodes were calibrated as previously described[9] to read high values of p[H] at 50.0 °C, and they were used for monitoring the p[H] as the reaction proceeded. The p[H] readings obtained were always constant within ±0.02 unit during all the experimental runs. Electronic spectra were recorded at fixed time intervals until no further changes were observed.

The rate constants were determined by linear least squares treatment of the ln ($A_t - A_\infty$) values vs time over three half lives. A_t and A_∞ represent the absorbance values at time t and at equilibrium. The wavelength chosen is 360 nm, which corresponds closely to the maximum absorbance of the charge-transfer band of the dioxygen complexes. In all cases, the correlation coefficient was greater than 0.99. Estimations of the errors were obtained by the use of Student's t-test[11] at 95% probability.

For determination of the p[H] dependence of the observed rate constants a FORTRAN program was used that minimizes the sum of the weighed squares of the residuals. The inverse of the squares of the estimated errors were used as weighting factors for every k_{obs} value.

Identification of Reaction Products. Solutions resulting from the decomposition of cobalt dioxygen complexes in the kinetic experiments do not reoxygenate when an oxygen atmosphere is restored, which seems to indicate a metal-centered autoxidation process. However, Co(III) complexes could not be isolated from the reaction mixtures, and the experiments were directed toward the identification of the ligand after the decomposition reaction.

BISBAMP·6HCl (0.154 g) and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 70 mL of distilled water. The p[H] was raised to 10.5 with 0.5 M NaOH solution, and O_2 was bubbled through the solution for 1 h in order to form the cobalt dioxygen complexes. The solution was digested under argon at 50.0 °C for 24 h in order to achieve complete decomposition. It was then concentrated to a volume of 10 mL and extracted with $CHCl_3$, and the NMR spectrum was recorded. The aqueous phase was treated with a solution of 2.50 g of Na_2H_2EDTA in 30 mL of water (NaOH solution was added to adjust the p[H] close to 10.5), and the resulting mixture was stirred for about 12 h at room temperature. After concentration to 5 mL, it was extracted with 50 mL of chloroform. The organic phase was concentrated to dryness and the residue dissolved in 0.5 mL of $CDCl_3$, and a new NMR spectrum was recorded.

Cu(I)–BISBAMP Complex. CuCl (0.014 g), BISBAMP·6HCl (0.044 g), and KOH (0.010 g) were placed in a reactor vessel thermostated to 50.0 °C, and argon was passed over the mixture for 2 h. Then 50 mL of anhydrous methanol were added, and the solution turned yellow in a few seconds as the solids dissolved. An oxygen atmosphere was established, and the solution was stirred at 50.0 °C for 24 h. The color changed to green-brown, and the solution was then concentrated to a volume of ca. 5 mL until a green solid appeared. The precipitate was filtered, washed with chloroform, and dried on the desiccator. A yield of 20 mg of green-brown solid was obtained.

In a separate experiment, the same reaction was studied, but the yellow solution obtained after addition of methanol was evaporated to dryness. The residue was dissolved in water (5 mL) and treated with EDTA (10 mL solution at pH 10). The mixture was stirred for about 12 h at room temperature, and then it was extracted with 50 mL of chloroform. The organic phase was concentrated to dryness, the resulting material was dissolved in 0.5 mL of $CDCl_3$, and its NMR spectrum was recorded.

Results

Kinetics of Cobalt Dioxygen Complex Decomposition. Aqueous solutions of cobalt dioxygen complexes of BISBAMP have a

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(9) Basallote, M. G.; Martell, A. E. *Inorg. Chem.* **1988**, *27*, 4219.

(10) Burnett, M. G.; McKee, V.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1980**, 829.

(11) Ott, L. *An Introduction to Statistical Methods and Data Analysis*; Duxbury Press: Boston, MA, 1984.

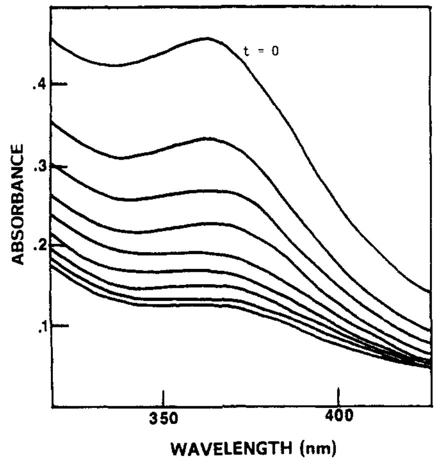
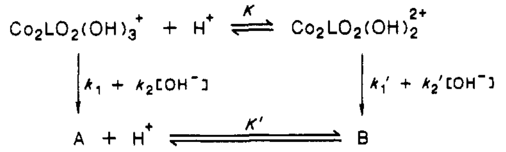


Figure 1. Variation of the UV–vis spectrum of Co(II)–BISBAMP dioxygen complexes with time ($[BISBAMP]_T = {}^1/_2[Co]_T = 1.98 \times 10^{-4}$ M; t = 50.0 °C; μ = 0.10 M KNO_3; p[H] = 11.32; time intervals = 20 min).

Table I. Observed Rate Constants for the Decomposition of Co–BISBAMP Dioxygen Complexes (t = 50.0 °C)

p[H]	10^3k_{obs}, s^{-1}	p[H]	10^3k_{obs}, s^{-1}
9.16	2.58 ± 0.44	10.33	0.44 ± 0.03
9.30	1.59 ± 0.17	10.87	0.32 ± 0.03
9.71	1.91 ± 0.07	11.13	0.29 ± 0.02
9.79	0.99 ± 0.06	11.32	0.30 ± 0.02
9.85	0.92 ± 0.06	11.55	0.34 ± 0.04
10.22	0.47 ± 0.04	11.94	0.34 ± 0.03

Scheme II



characteristic electronic absorption band at 360 nm. The intensity of this band decreases with time (Figure 1) as the first-order decomposition process takes place. The kinetics of the decomposition reaction has been studied from the decrease in absorbance at 360 nm. First-order rate constants obtained at 50.0 °C are included in Table I and show marked p[H] dependence. In previous studies,[4-8] changes in the observed rate constants with the p[H] have also been noted both for metal-centered and ligand-centered autoxidation reactions, but in all these cases the reaction proceeds faster with increasing p[H]. However, results in Table I and the plot in Figure 2 show that for the mixture of BISBAMP complexes the observed rate constants decrease with increasing p[H] to reach an almost steady value between p[H] 10.8 and 12.0. The reason for this apparent anomalous behavior is the existence of several dioxygen complexes in equilibrium. According to the species distribution diagram,[9] the monohydroxo-μ-peroxo complex is a minor species and its concentration is negligible under the conditions used for kinetic experiments. However, $Co_2LO_2(OH)_2$ and $Co_2LO_2(OH)_3$ are present in solution at considerable concentrations, and both of them are expected to decompose according to a rate law similar to that previously observed for other dioxygen complexes. The reaction mechanism shown in Scheme II is proposed, where A and B represent two reaction products in equilibrium. As the decrease in absorbance reflects the disappearance of both dioxygen complexes, the observed rate constants will really be

$$-\frac{d[Co_2LO_2(OH)_3^+]}{dt} - \frac{d[Co_2LO_2(OH)_2^{2+}]}{dt} = k_{obs}([Co_2LO_2(OH)_3^+] + [Co_2LO_2(OH)_2^{2+}])$$

Assuming that K represents a fast acid-base equilibrium, substitution of dioxygen complex concentrations for the expressions implied in Scheme II gives

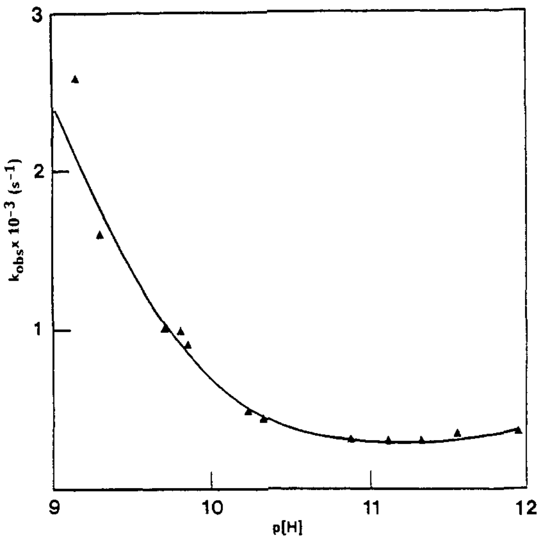


Figure 2. Representation of the p[H] dependence of the observed rate constants for the decomposition of the Co(II)–BISBAMP dioxygen complexes at 50.0 °C.

Table II. Rate Constants Obtained for the Decomposition of Co–BISBAMP Dioxygen Complexes (t = 50.0 °C, μ = 0.10 M (KNO_3))[a]

complex	rate constants
$Co_2LO_2(OH)_3^+$	$k_1 = 10^{-7}$ s^{-1}; $k_2 = 1.32 \times 10^{-3}$ M^{-1} s^{-1}
$Co_2LO_2(OH)_2^{2+}$	$k_1' = 4.35 \times 10^{-3}$ s^{-1}; $k_2' = 2.10$ M^{-1} s^{-1}

[a] For the definitions of rate constants see Scheme II.

$$k_{obs} = \frac{k_1 + k_2'KK_w + k_1'K[H^+] + k_2[OH^-]}{1 + K[H^+]} \tag{1}$$

Adjustment of data in Table I to an equation of the form

$$k_{obs} = \frac{a + b[H^+] + c[OH^-]}{1 + d[H^+]} \tag{2}$$

leads to $a = 2.43 \times 10^{-4}$, $b = 5.39 \times 10^6$, $c = 1.32 \times 10^{-3}$, and $d = 1.24 \times 10^9$. Comparison with eq 1 leads to the values included in Table II for the rate constants corresponding to the decomposition of both dioxygen complexes. The solid line in Figure 2 represents the theoretical curve calculated with the fitted parameters.

The value obtained for log K (9.09) is in good agreement with that previously reported (9.45) from potentiometric data at 25.0 °C,[9] the difference being due mainly to the difference in temperature. It is clear from eq 1 that k_1 and k_2' cannot be determined directly. However, a resonable estimation made by considering the literature values[12] for related processes indicate that k_2/k_1 must be on the order of 10^4, and so an approximate value of 10^{-7} s^{-1} is included in Table II for k_1. This value does not represent a significant contribution to a, and so $k_2'KK_w$ is considered to be 2.43×10^{-4}, leading to a value of $k_2' = 2.10$.

Results in Table II indicate that $Co_2LO_2(OH)_2$ decomposes 10^3 times faster than $Co_2LO_2(OH)_3$ despite their similarities. Attempts to crystallize both complexes were unsuccessful, and in order to distinguish between them, their electronic spectra were calculated from spectra of solutions containing Co–BISBAMP dioxygen complexes over a range of p[H]. The composition of these solutions was obtained from the distribution curves,[9] and the results are shown in Figure 3. Although both dioxygen complexes present maxima between 300 and 400 nm, the patterns

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(12) Tobe, M. L. In *Advances in Inorganic and Bioinorganic Mechanisms*; Academic Press: London, 1983; Vol. 2.

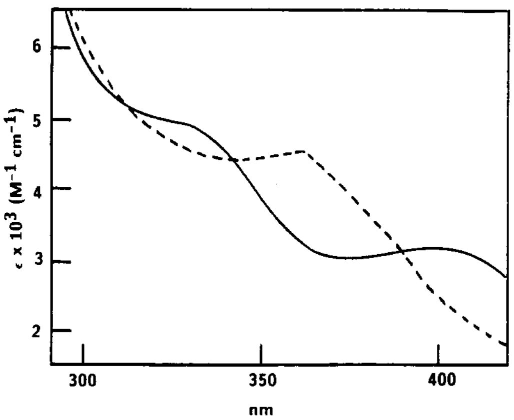

Figure 3. Calculated electronic spectra for Co(II)–BISBAMP dioxygen complexes: $Co_2LO_2(OH)_2^{2+}$ (—) and $Co_2LO_2(OH)_3^{+}$ (---).

Table III. ^1H NMR Spectra of BISBAMP·6HCl (**1**)[a] and the Extract of the Decomposition Product of Its Cobalt Dioxygen Complexes[b]

	chem shift, ppm	
	BISBAMP·6HCl	extract
a	7.80 (t, J = 7.7 Hz)	7.57 (t, J = 7.66 Hz)
b	7.34 (d, J = 7.7 Hz)	7.16 (d, J = 7.65 Hz)
c	4.37 (s)	3.90 (s)
d	3.31 (t, J = 4.9 Hz)	2.83 (t, J = 5.23 Hz)
e	3.82 (t, J = 4.9 Hz)	4.60 (t, J = 5.2 Hz)
NH		2.52 (s)

[a] D_2O. [b] $CDCl_3$

of their spectra are different. The spectrum of $Co_2LO_2(OH)_3$ shows only one maximum at 360 nm, which seems to indicate a doubly bridged μ-hydroxo-μ-peroxo structure.[1,13] On the contrary, the spectrum of $Co_2LO_2(OH)_2$ shows two maxima at 330 and 400 nm and is thus similar to those of nonplanar singly bridged μ-peroxo complexes.[13]

The solutions resulting from these kinetic experiments do not reoxygenate under an oxygen atmosphere, showing that a metal-centered autoxidation is the most probable process. However, Co(III) complexes could not be isolated from these solutions although repeated experiments under varying conditions were carried out. The low concentrations of reagents and the presumably high solubility of the reaction products are probably the reasons for the lack of crystallization. However, a ligand-centered decomposition leading to a ligand with reduced complexing ability cannot be completely ruled out, and attempts were made to isolate the probable oxidized ligands such as **2**, **3**, or related compounds. In fact the NMR spectrum of the product extracted with $CHCl_3$ before treatment with EDTA (see Experimental Section) has a resonance at 10.18 ppm, which seems to indicate the presence of aldehyde groups resulting from hydrolysis of C=N bonds. Moreover, the strong singlet corresponding to the protons in CH_2 groups of aminoethyl units of BISBAMP does not appear in the spectrum of the reaction product. Some other changes in the aromatic region and in the signals of protons in the ethylenic units also seem to indicate oxidative dehydrogenation of the ligand with subsequent hydrolysis to form aldehyde. However, the amount of extract is relatively small, and some impurities are also present. Attempts to prepare the (2,4-dinitrophenyl)hydrazone in separate experiments were unsuccessful, and it was concluded that the oxidative dehydrogenation which occurs is considerably incomplete. This interpretation was confirmed by the NMR spectrum of the product extracted with $CHCl_3$ after treatment with EDTA. The spectral data are compared in Table III with the data previously reported[9] for BISBAMP·6HCl, and the displacement of the signals can be easily explained by the difference in solvent employed and by partial protonation of BISBAMP in D_2O solution. The purity of this sample and the high yield (~70%) provide strong evidence that metal-centered autoxidation is the predominant process in the decomposition of Co–BISBAMP dioxygen complexes.

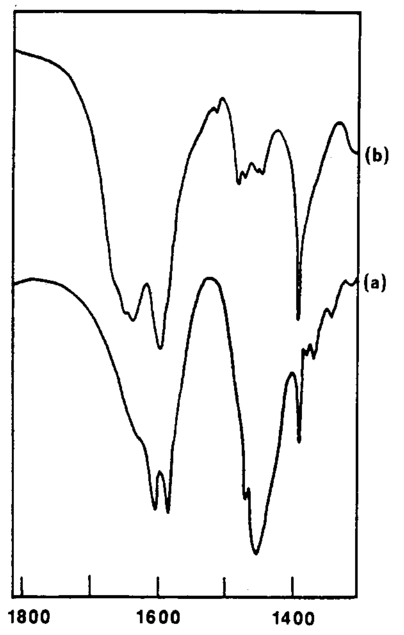

Figure 4. Infrared spectra of BISBAMP·6HCl (a), and the reaction product with CuCl (b).

Copper Complexes. Because of the low stability of Cu(I) complexes in aqueous solutions, the reaction between CuCl and BISBAMP was studied in anhydrous methanol. Reactions in this solvent normally lead to the formation of Cu(I) dimers with halide bridges,[14] and the yellow solution that forms initially under an argon atmosphere must contain binuclear Cu(I)–BISBAMP complexes. In fact, the observed color changes are similar to those observed previously by Nelson et al.,[10] and the infrared spectrum of the solid (Figure 4) shows the band at 1640 cm^{-1} which is considered indicative of oxidative dehydrogenation. The spectrum of BISBAMP·6HCl is also included in Figure 4 for comparison. The two bands appearing over 1600 cm^{-1} in the spectrum of BISBAMP·6HCl correspond to the pyridine ring stretching vibrations (C=N and C=C).[15] This part of the spectrum is clearly different from that in the case of the copper reaction product, with a new band at 1640 cm^{-1} considered by Nelson et al.[10] to indicate the formation of C=N bonds upon dehydrogenation. These changes may also be due to dehydrogenation with formation of C=C bonds or to coordination to the metal ion. However, this last possibility can be discarded because pyridine complexes do not show sufficient displacement.[16] In any case, the changes observed in the band seem to indicate oxidative dehydrogenation of the ligand, with formation of either C=N or C=C bonds. Moreover, the intensity of the band at 1450 cm^{-1} decreases considerably and nearly disappears. Because this band corresponds mainly to CH_2 bending, extensive dehydrogenation of the molecule or elimination of the 1,5-diaza-3-oxapentane units seems to occur.

These observations are confirmed by the NMR spectrum of the product extracted with $CHCl_3$. The spectrum does not show a signal corresponding to protons in CH=N or CHO groups that are expected in primary dehydrogenation products, showing that the decomposition process goes further than the simple dehydrogenation reactions implied in **2** and **3**. Extensive decomposition of organic ligands upon formation of Cu(I) complexes has been shown to be a very complicated process leading to highly frag-

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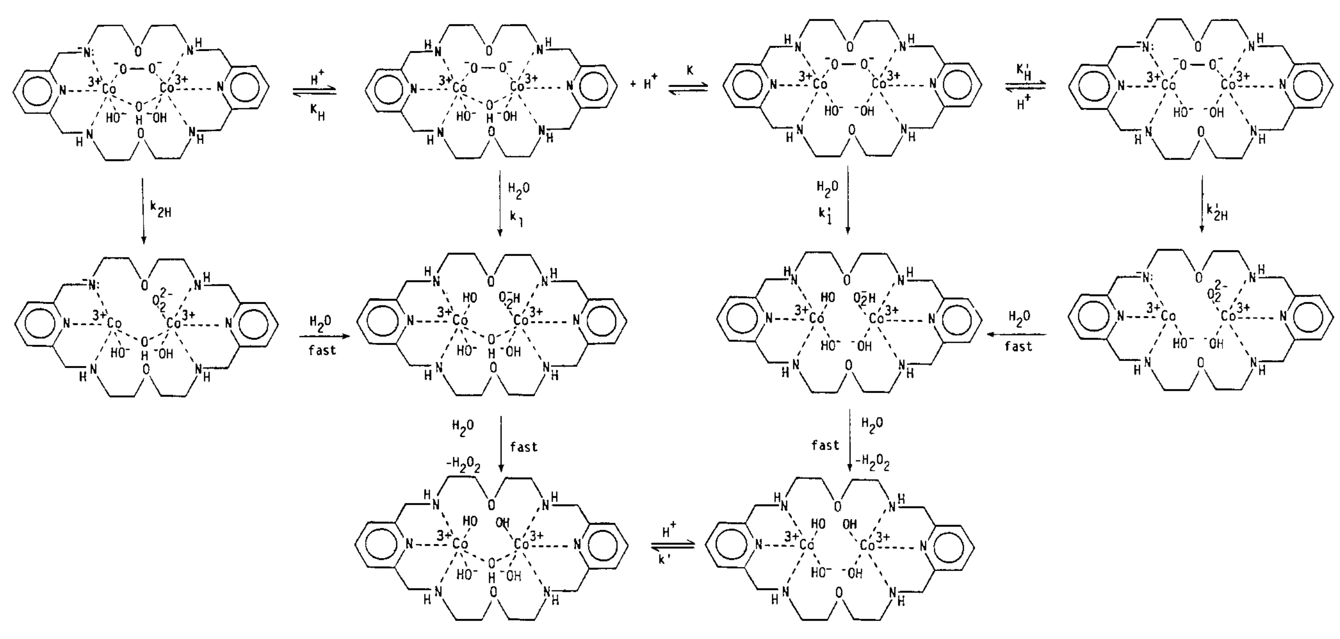
(13) Miskowski, V. M. *Comments Inorg. Chem.* **1987**, *6*, 193.

(14) Munakata, M.; Kitagawa, S. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Ed. Karlin, K. D., Zubieta, J., Eds.; Academic Press: New York, 1983.

(15) Balaban, A. T.; Badilescu, S.; Badilescu, I. I. In *Physical Methods in Heterocyclic Chemistry*; Gupta, R. R., Ed.; Wiley: New York, 1984.

(16) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

Scheme III[a]

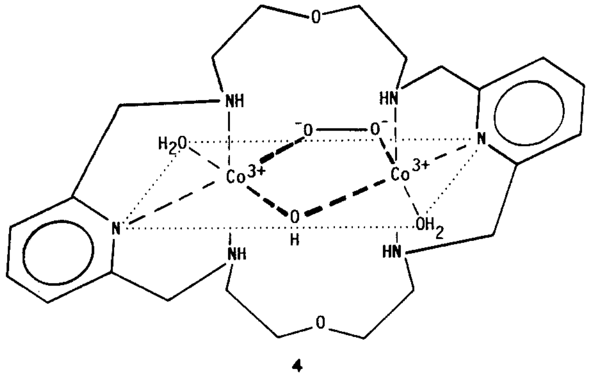


[a] K_H and K_H' represent equilibrium constants for deprotonation of nitrogen in both dioxygen complexes. k_{2H} and k_{2H}' represent the rate constants corresponding to dissociation of the Co(III)–O_2 bond for both deprotonated compounds. For comparison with other constants used in this paper $k_2 = K_Hk_{2H}$ and $k_2' = K_2'k_{2H}'$.

mented products.[17] In this sense, the modifications observed in the signals of aromatic protons clearly indicate some additional reaction of groups at the 2,6-positions of the pyridine rings, in addition to those occurring in the connecting bridges between the pyridine units.

Discussion

The results obtained in the kinetic study of the decomposition of Co–BISBAMP dioxygen complexes confirm that metal-centered and ligand-centered decomposition processes are two competing reactions for the decomposition of dioxygen complexes in basic solutions. Depending on the characteristics of the complexes involved, one of these processes usually predominates. For the case of BISBAMP complexes a metal-centered process is the main reaction leading to the irreversible formation of Co(III) complexes. Although the presence of pyridine rings in the molecule of BISBAMP leads us to expect oxidative dehydrogenation, steric requirements for that process probably are not met, perhaps because the 1,5-diamino-3-oxapentane linking units are not long enough to allow the flexibility needed for the ligand to adopt the conformation required for oxidative dehydrogenation. CPK models suggest that formation of BISBAMP binuclear complexes is only possible if both pyridine rings adopt a configuration similar to **4**, with the coordinated nitrogen donors in a vertical plane and the coordinated oxygens in a generally horizontal planar configuration. The same configuration of BISBAMP must also be present in the single-bridged complex, although in this case there is a OH coordinated to every Co(III) ion. Although the α-CH_2 groups are sufficiently close to the coordinated dioxygen for dehydrogenation to take place, as is the case for similar ligands previously described,[6-8] the five-atom bridges between the BAMP moieties are not sufficiently flexible to allow formation of the required trigonal bonding arrangement about each aliphatic nitrogen donor. Models show that these five-atom bridges are extensively distorted out of the vertical plane of the pyridine rings, thus rendering dehydrogenation difficult, as was observed earlier for much simpler but analogous cobalt dioxygen complexes.[4,18]



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Scheme III illustrates the suggested reaction pathways for the decomposition of $Co_2LO_2(OH)_2$ and $Co_2LO_2(OH)_3$. For both cases there are two parallel pathways corresponding to the aquation and base hydrolysis of the starting material, in a manner similar to that of the extensively studied hydrolysis of Co(III) complexes. Because of the high basicity of the solutions used for the kinetic studies, an OH^- ion may enter in the coordination site previously occupied by O_2, and HO_2^- would be the predominant form of peroxide coordinated to one Co(III) ion. The lack of evidence of accumulation of a hydroperoxo–Co(III) complex intermediate seems to indicate that the hydrolysis of the second Co–O bond is a fast process that probably goes through a Co(II) intermediate. In this sense, some "anomalously" fast substitution reactions at Co(III) centers coordinated to μ-peroxo bridges have been suggested as occurring through Co(II) intermediates.[19] As a result of the second hydrolytic step, H_2O_2 would be released. Hydrogen peroxide has been detected in previous studies,[20] but some problems exist for its quantitative determination because of its disproportionation to form O_2 and H_2O, a process that seems to be promoted by the catalase-like activity of the cobalt complexes in the medium.[20]

The difference in reactivities of $Co_2LO_2(OH)_2$ and $Co_2LO_2(OH)_3$ can be rationalized if one takes into consideration their electronic spectra. The spectra suggest different structures for these complexes, with a single μ-peroxo bridge in the case of $Co_2LO_2(OH)_2$ and a double μ-hydroxo–μ-peroxo bridge for $Co_2LO_2(OH)_3$. Decomposition of singly bridged dioxygen complexes to Co(II) and O_2 has been found to occur faster than that

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(17) Patch, M. G.; McKee, V.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 776.

(18) Raleigh, C. J.; Martell, A. E. *J. Coord. Chem.* **1985**, *14*, 139.

(19) Sasaki, Y.; Suzuki, K. Z.; Matsumoto, a.; Saito, K. *Inorg. Chem.* **1982**, *21*, 1825.

(20) Menif, R.; Martell, A. E. *Inorg. Chem.*, in press.

Inorg. Chem. **1989**, *28*, 3499–3503 **3499**

of doubly bridged compounds.[1,21] The results in the present work indicate that the same behavior is true for the case of metal-centered autoxidation processes. Doubly bridged dioxygen complexes seem to undergo slower decomposition reactions, probably because the rigidity caused by the double bridge makes dissociative processes more difficult.

The results obtained for the decomposition of BISBAMP in the presence of copper(I) clearly indicate mechanisms that are different from those observed with cobalt(II). Although there is no conclusive evidence that the decomposition of BISBAMP occurs through the formation of copper dioxygen complexes, this seems to be the most plausible route. In general, the synthesis of copper dioxygen complexes presents many complications, and only recently has their existence been clearly demonstrated.[22] Additional work is needed to determine the requirements for formation and decomposition of copper dioxygen complexes with various types of coordinating ligands.

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Registry No. $Co_2LO_2(OH)_2^{2+}$, 121574-26-3; $Co_2LO_2(OH)_3^{+}$, 121574-27-4.

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(21) Zehnder, M.; Macke, H.; Fallab, S. *Helv. Chim. Acta* **1975**, *58*, 2306.

(22) Jacobson, R. R.; Tyeklar, Z.; Faroog, A.; Karlin, K. D.; Liiu, S.; Zubieta, J. *J. Am. Chem. Soc.*, in press.

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Potentiometry of Mixtures: Metal Chelate Stability Constants of 1-Hydroxy-3-oxapentane-1,2,4,5-tetracarboxylic Acid and 3,6-Dioxaoctane-1,2,4,5,7,8-hexacarboxylic Acid

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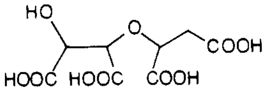
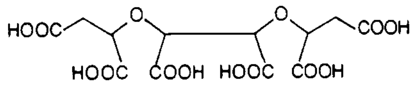
A novel and unique method is described in which potentiometric p[H] determinations of stability constants are made on two solutions containing mixtures of 1-hydroxy-3-oxapentane-1,2,4,5-tetracarboxylic acid (TMS) and 3,6-dioxaoctane-1,2,4,5,7,8-hexacarboxylic acid (TDS), along with known concentrations of other ligands as minor impurities. This report provides experimental evidence that the method works well because of successful determination of metal ion equilibrium constants for the reaction of TMS and TDS with 11 metal ions—Cu^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}. The validity of the method described for the potentiometric determination of equilibrium constants in mixtures is demonstrated by carrying out the same procedures on a pure aqueous solution of TDS.

Introduction

Maleic anhydride reacts with tartaric acid to yield a useful chelating mixture the principal components of which are tartaric monosuccinic acid, TMS (1-hydroxy-3-oxapentane-1,2,4,5-tetracarboxylic acid), and tartaric disuccinic acid, TDS (3,6-dioxaoctane-1,2,4,5,7,8-hexacarboxylic acid). Since the synthesis creates asymmetric carbon centers at α-succinate positions, several forms of each ligand are possible. Protonation constants and mononuclear metal ion formation constants are not expected to differ greatly for such pairs of stereoisomers.



TMS



TDS

In practice, the physical separation of pure TMS and TDS from the mixture formed is difficult. However, analytical HPLC has provided complete analyses of the components present. After the removal of extraneous inorganic ions and salts, each solution was found to contain tartaric acid, malic acid, maleic acid, and fumaric acid, in addition to TMS and TDS. The analyses provided not only the qualitative identification of each component but also quantitative determinations of the percentage compositions of the mixtures.

The purpose of this research was to determine the protonation constants and stability constants of TMS and TDS on mixtures where the complete separation of each component had not been accomplished. Since quantitative investigations of such mixtures, as well as of the pure ligands themselves, have not been described in the literature previously, the success and limitations of this study represent a new procedure for stability constant determinations. The development of such a technique for the study of complex mixtures is made possible by the use of iterative methods and the FORTRAN program BEST,[1] which places no constraints on the number and types of components present or the number and types of species formed in complex systems studied by potentiometric measurements of p[H] (p[H] = −log [H^+]).

Table I. Compositions of Reaction Mixtures Investigated

	fractional concn	
species	TMS-rich	TDS-rich
TMS	0.738	0.370
TDS	0.053	0.623
tartaric acid	0.134	0.007
malic acid	0.020	
maleic acid	0.031	
fumaric acid	0.024	

Experimental Section

Mixtures of two considerably different ratios of TMS and TDS concentrations were investigated. HPLC analyses (accuracy <1%) of the mixtures were performed by Procter and Gamble Co., Inc. The complete results of the analysis for the components present in these TMS-rich and TDS-rich solutions are displayed in Table I.

The basic experimental plan is to make parallel measurements in TMS-rich and TDS-rich solutions followed by data analysis accomplished in the following steps: (1) refinement of the TMS constants by using TMS-rich data; (2) refinement of the TDS constants by using TDS-rich data; (3) iteration of the calculations between steps 1 and 2 until the calculated equilibrium constants become constant.

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(1) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403; Motekaitis, R. J.; Martell, A. E. *Determination and Use of Stability Constants*; VCH Publishers: New York, 1988.