plexes. The overall titration equation for 2:1 solutions is

$$2Co^{II}(H_2L_2)^{2+} + {}^1/_2O_2 + 6OH^- \rightarrow 2Co^{III}L_2^- + 7H_2O$$

where L represents GlyGly with an ionized amide nitrogen coordinated to metal ion. The product Co(III) complexes for both 2:1 and 1:1 solutions exhibit an absorption maximum at 520 nm, identical with earlier results with excess ligand and consistent with four nitrogen donors.[2,8] The nearly half absorption magnitude for the 1:1 solution suggests disproportionation to yield the same Co(III) dipeptide complex as in the 2:1 solution. The disproportionation observed in the 1:1 solutions confirms earlier suggestions that at least three nitrogen donors are required for oxygenation and oxidation of Co(II) complexes in the presence of amine and peptide ligands.[2,3] Because ionization of amide hydrogens in a 2:1 dipeptide-cobalt(II) complex has been shown to be cooperative in the presence of oxygen,[2,8] both amide hydrogens undergo deprotonation in formation of binuclear peroxo and final red Co(III) complexes.

Experimental Section

Commercial dipeptides were weighed out as required and the purity was checked by titration on a Radiometer combination titrimeter-titrigraph. Analytical reagent grade $Co(NO_3)_2 \cdot 6H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ were employed. Titrations under nitrogen were performed as described previously.[8] CD spectra were recorded on a Durrum-Jasco 5 instrument. All molar absorptivities and differential molar absorptivities between left and right circularly polarized light are based upon the molar concentration of cobalt ion. Pmr spectra were recorded on a Varian HA-100 spectrometer and are reported in hertz downfield from external TMS. ABC pmr spectra were analyzed by the program LAOCOON II.[22] All pH values recorded are meter readings uncorrected for the presence of any D_2O. Two to one molar ratios of dipeptide and Co(II) (at 0.1 or 0.2 *M*) were used for the pmr experiments. Usually the D_2O solution for the pmr experiments was diluted with H_2O to 0.02 or 0.04 *M* cobalt for CD and absorption spectra. For the Gly-L-His studies cobalt concentrations of 2.5–10 m*M* were employed for each ratio of ligand to metal ion. All experiments were performed throughout at room temperature, near 25°.

Efforts were made to account quantitatively for dipeptides as Co(III) complexes by utilizing $Co(CH_3COO)_2 \cdot 4H_2O$ as the Co(II) starting material with twice as much dipeptide. Results of the comparisons of areas under the methyl peaks of dipeptides with that due to a known amount of acetate are not completely satisfactory but do appear to indicate some loss of dipeptide. For instance, in the first three solutions of Table I only 75–90% of the alanyl methyl groups are accounted for as Co(III) products yet no other peaks appear in the well-defined pmr spectra. Lower percentages were obtained by this method for Gly-L-Ala. Lower percentages are accompanied by a reduced molar absorptivity at 520 nm. In comparing CD results of dipeptide Co(III) complexes, the magnitudes should probably be scaled to the same ϵ value at 520 nm.

Registry No. $Co^{III}(L\text{-}AlaGly)_2^-$, 37380-88-4.

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Mono- and Dibridged Peroxo Complexes of Cobalt(III)[1]

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Received January 26, 1973

The binuclear peroxocobalt(III) complex formed by oxygenation of solutions containing 2 mol of L-2,3-diaminopropionate/mol of Co(II) becomes dibridged at pH >9 with formation of a μ-hydroxo bridge. The hydroxo bridge forms most rapidly at high pH. The suggestion that from 310 to 450 nm two maxima appear in monobridged peroxocobalt(III) complexes and only one maximum in dibridged complexes is supported. Similar circular dichroism patterns of peroxo bis complexes fall into oppositely signed sets with L-2,3-diaminopropionate and L-2,4-diaminobutyrate in one set and L-histidine in the other. In contrast the bis mononuclear Co(III) complexes of the three ligand systems exhibit similar patterns and identical signs. Conversion of the binuclear peroxo to mononuclear Co(III) complexes is facilitated by addition of H_2O_2 and, in separate experiments, unaffected by addition of the enzyme catalase. From CD and kinetic results, it is suggested that binuclear peroxo complexes may not be intermediates on the main pathway from Co(II) to mononuclear Co(III) complexes but only relatively unreactive complexes formed in a side reaction.

Introduction

When formation of binuclear peroxo complexes of Co(III) from oxygen and Co(II) complexes results in release of an odd number of equivalents of acid for each 2 mol of metal ion, it was suggested that a μ-hydroxo bridge in addition to the peroxo bridge is formed yielding a dibridged binuclear complex.[2] In the group of ligands first investigated an odd number of acid equivalents was observed and a dibridged binuclear peroxo complex suggested for the bis complexes of diaminoethane, histamine, and glycinamide. A hydroxo bridge was also implied for the 1:1 complex with dien. The absence of μ-hydroxo bridges with the other ligands investigated was ascribed to steric hindrance, on the assumption that μ-hydroxo bridges would form unless inhibited by steric effects or lack of suitable coordination sites about the metal ions.[2] Although no evidence was obtained for a hydroxo bridge in the binuclear bis(histidine)complex formed at pH 10, features of the uv spectra of the binuclear complex formed in 1 *N* base[3] suggested to us the presence of a hydroxo bridge in the more basic solutions.[4] At about the same time, a hydroxo bridge was suggested on the basis of titration evidence for the binuclear triethylenetetramine (trien) complex.[5] With four coordination positions about each metal ion occupied by amino nitrogen donors and the fifth position involved in a peroxo bridge, a μ-hydroxo group bridging the sixth positions of each Co(III) ion is in keeping with the above idea. The hydroxo bridge also aids interpretation of kinetics of the overall oxygenation reaction for the

(1) This research was supported by a grant from the National Science Foundation.

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Co(II) chelate of trien.[6] Subsequently, the presence of hydroxo bridges in complexes with polyamine ligands with up to four nitrogen donors was confirmed by titration,[7] lending further support to the ideas expressed earlier.[2] An important point not recognized in the polyamine titration work[7] is the high cooperativity apparent in the titrations in the presence of oxygen. Because of the flatness of the titration curves, flushing with inert gas at most points in the acid buffer region decreases the concentration of dibridged peroxocobalt(III) species in favor of partially protonated ligand and aqueous Co(II).

The binuclear peroxo complex formed by admission of oxygen to solutions containing L-2,3-diaminopropionate (L-dampa) is relatively stable with a half-life of about 1 day for conversion to mononuclear Co(III) products.[2] In addition no protons are released upon formation of the peroxo complex at pH 8.3 ($n = 0$) so that studies of the effects of added acid are not complicated by explicit appearance of protons in the balanced equation for the oxygenation reaction. This paper reports properties of binuclear peroxocobalt(III) complexes of L-dampa produced upon oxygenation of Co(II) solutions.

Attempts have been made to test for the H_2O_2 that is presumably released as a binuclear peroxo complex of Co(III) dissociates into mononuclear complexes. Some but not the stoichiometric amount of H_2O_2 has been found with a cyclic tetramine,[8] while no H_2O_2 was found in final solutions with histidine as a ligand.[9] Polarographic waves assigned to H_2O_2 appear in solutions containing oxygenated complexes of L-histidine,[9] L-dampa, L-2,4-diaminobutyrate, and L-ornithine.[10] With bis(dipeptide) complexes the behavior is dependent upon the side chains, but in several cases, such as glygly, H_2O_2 is not detected nor is oxygen reemitted from the solution (even upon addition of catalase) on dissociation of binuclear peroxo into mononuclear complexes.[11] This paper describes several experiments in which H_2O_2 is added externally to solutions containing Co(II) and oxygenated species.

Results

Table I records the CD and absorption spectra obtained after bubbling oxygen through solutions containing 2 mol of anionic L-2,3-diaminopropionate (L-dampa) or 2–5 mol of *l*-1,2-diaminopropane (*l*-pn) per mole of Co(II) at the indicated pH. It is evident that the high pH 11.4 solution of L-dampa exhibits similar absorption and CD properties to the *l*-pn complex. Careful inspection of the absorption spectra of the L-dampa complexes indicates a shift to shorter wavelengths of both peaks upon increasing the pH. The shorter wavelength shoulder at about 300 nm at pH 11.4 is obscured by a stronger absorption band further in the ultraviolet region. The shift to shorter wavelengths of both peaks upon increase of pH is also evident in absorption spectra of the 2:1 L-histidinecobalt(III)-peroxo complex.[12] However, since the absorption spectra give the appearance of single- and double-peaked curves at longer than 310 nm, we shall refer to them in this way. As shown in the first part of the Discussion, an absorption curve that is double peaked between 310 and 450 nm indicates a monobridged peroxocobalt(III) complex and a single-peaked curve a dibridged peroxo complex with a hydroxide group providing the second bridge.

Table I. Absorption and CD Spectra of 2:1 Binuclear Peroxocobalt(III) Complexes

	Absorption			CD	
	pH	λ, nm	ϵ^a	λ, nm	$\Delta\epsilon^a$
L-2,3-Diaminopropionate	8.7	315	3430	268	+2.9
		385	3000	363	−2.8
				505	+0.8
	11.4			268	+2.6
				304	+2.8
		358	2500	378	−2.2
				428	−1.3
l-1,2-Diaminopropane	10.4			255	+4.4
				305	+4.4
		356	2180	370	−6.5
				425	−3.0
				540	+1.0
L-2,4-Diaminobutyrate	9.5–12.5	314	3900	268	+2.1
		370	2950	342	−0.7
				435	+0.4
				506	−0.6
				596	+0.6

[a] All absorptivities are per mole of metal ion.

Upon admission of oxygen to solutions containing 2 moles of L-dampa for 1 mol of Co(II), the double-peaked absorption curve characteristic of the monobridged species appears before the single-humped curve indicative of a dibridged complex. At pH 10.5 the double-peaked spectrum lasts for less than 1 min while at pH 9.2 several hours is required for its conversion to a single-peak curve. Thus the dibridged species forms more readily in basic solutions and the time dependence makes determination of even an apparent pK_a difficult. At all pH values appearance of a single-peaked spectrum is accompanied by uptake of 0.5 equiv of hydroxide/mol of cobalt. The uv peaks slowly lose intensity with time as product Co(III) complexes are produced.

Addition of acid to the peroxocobalt(III) complex of L-dampa at pH 8.7 results in a continuous decrease of the absorption spectrum indicating breakup into Co(II) complexes. Thus it does not seem possible to form a stable singly bridged complex with a protonated peroxo group with this ligand. A study was also made of the stability and properties of the dibridged L-dampa complex prepared at pH 10.6. Addition of some acid does not lead directly to a monobridged complex. Thus the reaction proceeding from mono- to dibridged complex does not appear as reversible. Addition of more acid to pH <6 results in breakup of the complex, as evinced by evolution of gas and decrease in ultraviolet absorption, leading to formation of Co(II) complexes. The reactions are reversible in that both mono- and dibridged peroxo complexes may be restored by addition of base and oxygen gas.

With L-histidine as the ligand a monobridged peroxo complex is stable from pH 8.3 to pH 10.4. The dibridged complex is fully formed only in 1 *N* NaOH. Addition of acid gives the same behavior as with L-dampa as the ligand. Our results with this ligand confirm those reported elsewhere.[3,12]

Proton magnetic resonance spectra of peroxo and product Co(III) complexes of dampa and of the peroxo complex of L-histidine all show too many peaks to be readily interpret-

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able. The complexity of the pmr spectra indicates that a distribution of isomers is present in all cases.

Extrema in absorption and CD spectra obtained upon admission of oxygen to solutions containing 2 mol of L-2,4-diaminobutyrate (L-damba) to 1 mol of Co(II) are also listed in Table I. For this ligand the spectra are independent of pH from pH 9.5 to pH 12.5. The absorption spectrum is characteristic of a monobridged species throughout the pH region. This result is consistent with no uptake of protons upon oxygenation. The CD spectra reported in Table I for the peroxo complexes of L-damba and L-dampa appear similar in the uv region, suggesting that the structure of the complexes may be similar. Some conclusions[10] regarding stabilities of L-damba and L-ornithine complexes may be incomplete as 2:1 solutions of these ligands do not yield fully formed complexes with Co(II) until a high pH is attained.

The product mononuclear Co(III) complex formed at pH 9.5-12 and room temperature from oxygenated solutions containing a 2:1 molar ratio of L-damba to metal ion displays a broad absorption band at 520 nm with ϵ 95. The CD spectrum exhibits extrema at 353, 512, and 580 nm with $\Delta\epsilon = +0.7, -1.9$, and $+1.3$, respectively. The CD sign pattern is identical with that reported for the mononuclear Co(III) complexes of L-histidine and L-dampa prepared by the oxygenation route.[2]

In order to assess the effects of any H_2O_2 generated by breakup of the binuclear peroxo complex to Co(III) products, H_2O_2 was added externally to solutions containing peroxo complexes with L-dampa. At pH 8.6, where the singly bridged complex predominates, and at pH 10.6, where the dibridged species occurs, addition of H_2O_2 markedly increases the rate of disappearance of uv absorption and formation of product Co(III) complexes. At both pH values the conversion takes place without a change in pH and appears to occur in two steps.

The effects of externally added H_2O_2 were studied on solutions containing a 2:1 molar ratio of L-dampa and Co(II) in the absence of prior or current treatment with oxygen. At pH 10.6 conversion to Co(III) products is complete in about 2 min. To attain maximum absorption due to Co(III) products about 0.5 mol of H_2O_2 is required for each mole of Co(II) originally present. At pH 8.6 the oxidation reaction takes more than 1 hr and there is a substantial build-up of a peroxo complexes, evidently from some Co(II) complex reacting with oxygen produced in early stages of H_2O_2 decomposition. The final Co(III) products of the H_2O_2 reaction in the absence of oxygen give the same absorption maximum (ϵ 90 at 510 nm) as the products from the reaction carried out in an oxygen atmosphere in the absence of H_2O_2.

As a binuclear peroxocobalt(III) complex dissociates into mononuclear complexes, H_2O_2 is presumably released. It has just been shown that the addition of external H_2O_2 speeds the production of a mononuclear complex from a peroxocobalt(III) complex of L-dampa. Addition of the enzyme catalase at pH 10.5 has no effect on the rate of conversion of the binuclear to mononuclear complexes with L-dampa as a ligand. Also the half-life of 18 min for the dissociation of the bis(diethylenetriamine)peroxo complex is unaffected at pH 11 by the addition of catalase to the solution. Control experiments with added H_2O_2 result in immediate evolution of gas upon addition of catalase.

Discussion

Oxygenated Co(II) complexes are binuclear and are better considered as bridged peroxo complexes of Co(III). Titration evidence indicates that the 2:1 complexes of L-dampa, L-histidine, and L-histidinamide at pH <10 are all monobridged. In all three cases absorption spectra of the peroxo complexes are double peaked with maxima about 320 and 380 nm. The uptake of a half-integer number of equivalents of base per mole of cobalt for the 2:1 complexes of en, glycinamide, and histamine indicates a dibridged species with a hydroxo as well as a peroxo bridge.[2] In the last three cases only singly peaked absorption spectra appear with a maximum near 360 nm. Thus we propose that the 310–450-nm absorption region of peroxocobalt(III) complexes exhibits two peaks when the complex is monobridged and one peak when the complex also contains a hydroxo bridge so that it is dibridged.

This conclusion correlating the number of absorption peaks with the number of bridges in peroxocobalt(III) complexes is further supported by and aids in the interpretation of the results reported in Table I. The single-peaked absorption spectrum of the *l*-pn complex is nearly identical with that of en, indicating that the former too is dibridged. For L-dampa the uptake of 0.5 mol of hydroxide ion to form the pH 11.4 peroxo complex indicates a dibridged species. The absorption spectrum at the high pH shows only a single peak and both the absorption and CD spectra of the 2:1 L-dampa complex at pH 11.4 are similar to those of the dibridged *l*-pn complex. Thus three lines of evidence—titration and absorption and CD spectra—support a dibridged structure for the high-pH and a monobridged species for the low-pH peroxocobalt(III) complexes of L-dampa. Both the 2:1 *l*-pn and L-dampa complexes at pH 11.4 contain four nitrogen donors about each cobalt ion and one oxygen and one hydroxo bridge. The high-pH peroxo complex of L-dampa may be viewed as having been formed from that at pH 8.7 by displacement of one bound carboxylate group on each metal ion in the peroxo-bridged binuclear complex by a hydroxo group. Like L-dampa, L-histidine in a 2:1 complex also exhibits characteristic absorption and CD spectra at pH 9 and 1 *M* base[2,3,12] that may be identified with mono- and dibridged peroxo complexes, respectively.[4]

The examples of bis(L-diaminopropionate) and bis(L-histidine) complexes where the binuclear peroxo species is monobridged at low pH and dibridged in stronger base show that even when sufficient donor groups are present to inhibit formation of a hydroxo bridge, it may still form at high pH. Evidently from a pair of ligands on each metal ion the carboxylate groups that are bound at low pH are displaced by the hydroxo bridge in strong base. Since the peroxo and hydroxo bridge positions at each metal ion must be cis, a different isomer distribution of mononuclear product Co(III) complexes may be formed from mono- and dibridged peroxo precursors as the carboxylate groups are apparently cis in a dibridged complex. Though we noted similar absorption spectra for product Co(III) complexes obtained with L-dampa at several pH values, no definite conclusion about the identical isomer distribution seems possible due to the accompanying slow formation of dibridged from monobridged peroxo species so that we are unsure as to whether the product complexes had a common precursor. Furthermore, as suggested below, it seems probable that neither peroxo complex serves as a precursor.

The uv CD pattern displayed by both mono- and dibridged species of Table I is similar to that obtained for the 2:1 L-histidine-peroxo complexes except that the signs are inverted.[2,12] Since the *l*-pn absolute configuration corresponds to D-amino acids, two oppositely signed sets of peroxo com-

plexes exist: L-histidine and *l*-pn belonging to one set and L-dampa and L-damba to the other.

Information about the distribution of isomers of mononuclear 2:1 Co(III) complexes of L-dampa, L-damba, and L-histidine produced by room-temperature oxygenation of Co(II) solutions may be obtained by comparing product CD sign patterns[2] with those reported for the three separated isomeric complexes of each ligand. Even though a mixture of isomers is obtained in the oxygenation reaction, it is evident that the CD sign patterns for product Co(III) complexes of L-dampa, L-damba, and L-histidine are similar.[2] The CD patterns and signs for corresponding separated isomers of bis Co(III) complexes of L-dampa,[13] L-damba,[14] and L-histidine[15] are also similar. For all three ligand systems the CD sign pattern of the isomer with trans carboxylate groups nearly matches the pattern observed for the products of the oxygenation reaction. Thus the isomer with trans carboxylate groups appears to dominate the products of the room-temperature oxygenation reaction at the expense of the isomer with trans α-amino groups. A more quantitative analysis comparing absorption and CD spectra depends on knowing if all Co(II) originally in the solution is converted to a bis mononuclear Co(III) complex. In the case of dipeptide ligands the conversion appears to be less than 100%.[16]

The similar patterns and identical signs observed in the product mononuclear Co(III) complexes of three ligand systems and the lack of sign correspondence in the corresponding peroxo complexes may be due to a contribution to optical activity from inherent dissymmetry due to unequal populations of the two forms of the chiral peroxo group induced by stereoselectivity of the ligands involved. However the low values of the ratio $\Delta\epsilon/\epsilon$ and especially the similar areas under the CD curves of mono- and dibridged peroxo complexes despite the appreciably smaller dihedral angle in the latter complex argue against a significant contribution to optical activity from inherent dissymmetry and suggest that the populations of left- and right-handed screw senses of the peroxo group are nearly equal. An alternative explanation for the lack of sign correspondence in peroxo but not in mononuclear Co(III) complexes is that the latter do not, in all cases, arise from the former.

Hydrogen peroxide has been shown to be effective in promoting conversion of binuclear peroxocobalt(III) complexes into mononuclear complexes. No complex is expected to decompose H_2O_2 more rapidly than catalase, the most efficient enzyme known. The absence of rate changes upon addition of catalase to solutions presumably undergoing the dissociation reaction suggests that no H_2O_2 is produced. Formation of mononuclear complexes may involve direct oxidation of Co(II) species that are in equilibrium with the binuclear peroxo complex, rather than reaction of H_2O_2 with the latter.

The simplest interpretation of those systems in which no H_2O_2 can be detected nor oxygen reemitted upon formation of mononuclear Co(III) complexes is that these complexes are not formed from the binuclear peroxocobalt(III) complexes. The peroxo complexes, in these cases, are unreactive species formed in a side reaction. The pathway to mononuclear Co(III) complexes involves oxidation of Co(II) species without a binuclear peroxo species as an intermediate. Unreactive binuclear peroxocobalt(III) species appear to occur with 2:1 complexes of L-dampa, dien, histidine, and glycylglycine.

Two main routes are envisaged for formation of mononuclear Co(III) from Co(II) complexes. In those systems where H_2O_2 is detected or O_2 reemitted, binuclear peroxocobalt(III) complexes occur as reactive intermediates. When H_2O_2 and O_2 are not observed the binuclear peroxocobalt(III) complex is a dead end undergoing no further reaction on a time scale where the Co(II) complex undergoes oxidation by another route. A system contains a sufficient number of species so that the two routes may interact: production of some H_2O_2 initially by the first path may provide a stimulus for the second. With many ligands both pathways may coexist. If the equilibrium for the oxygenation reaction strongly favors the binuclear complex, there will be little Co(II) complex in solution to react by the second route. If the peroxo complex is also unreactive or reacts slowly, it will appear as the stable species in the system.

The reactions that may occur are

$$2Co^{II}L_2 + O_2 \rightleftarrows (Co^{III}L_2)_2O_2 \rightarrow 2Co^{III}L_2^+ + H_2O_2$$

$$2Co^{II}L_2 + H_2O_2 \rightarrow 2Co^{III}L_2^+$$

Our suggestion is that for many ligand systems the second reaction does not occur to an appreciable extent compared to last for the formation of monomeric Co(III) products.

Thus both structural and kinetic lines of evidence suggest that binuclear peroxo complexes formed in oxygenation of Co(II) complexes are not the precursors of all mononuclear Co(III) product complexes. CD sign patterns of bis mononuclear Co(III) complexes of L-dampa, L-damba, and L-histidine are all similar, while the CD signs for the peroxo complexes of the three ligand systems are not identical. Predominance of trans carboxylate groups in bis mononuclear Co(III) complexes even when the peroxo complex is dibridged and contains of necessity cis carboxylate groups indicates that the peroxo complex is not the immediate precursor of all the slowly formed mononuclear Co(III) products. Experiments where H_2O_2 or catalase are added to a peroxo complex and others where oxygen uptake and release have been measured[11] are most easily accounted for by assuming that mononuclear Co(III) complexes are produced directly from Co(II) complexes without the active intervention of binuclear peroxo complexes. The peroxo complexes appear as relatively unreactive species produced in a side reaction. This proposal does not exclude oxidation of oxidizable ligands when coordinated to the coordination sphere of an oxygenated Co(II) complex.

The suggestion that the oxygenated species is not on the main oxidation pathway may be even more applicable to other metal ion systems. For example, the stability of oxyhemoglobin seems less surprising if it is considered as an unreactive by-product not on the main pathway for oxidation of iron(II) hemoglobin to iron(III) methemoglobin. For hemoglobin the suggestion is strengthened by the spin states of the three species: reduced hemoglobin and methemoglobin are high-spin complexes while oxygenated hemoglobin is a low-spin complex.

Experimental Section

Materials and methods are identical with those already described in several publications from this laboratory.[2,4,16]

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Registry No. Co_2(L-dampa)$_4O_2$, 40354-51-6; [Co_2(L-dampa)$_4$(O_2)(OH)]$^-$, 40354-52-7; [Co_2(*l*-1,2-diaminopropane)$_4$(O_2)(OH)]$^{3+}$, 40273-29-8; [Co_2(L-2,4-diaminobutyrate)$_4$(O_2)(OH)]$^-$, 40354-53-8; H_2O_2, 7722-84-1.

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Hydrolytic Reactions in Carbonate Systems Containing Tetradentate Macrocyclic (N_4) Complexes of Cobalt(III)[1]

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Received February 13, 1973

The mechanisms of base hydrolysis of bidentate carbonate have been examined in cobalt(III) complexes containing methyl-substituted tetradentate (nitrogen donor) macrocyclic ligands. The reactions have been found to proceed in two stages: (I) the formation of a ring-opened Co(N_4)$OHCO_3$ intermediate and (II) the formation of product *trans*-Co(N_4)$(OH)_2^+$. In the case that N_4 = Me_6[14]dieneN_4, Co(N_4)$OHCO_3$ could be generated in sufficient concentration that it could be partially characterized; the evidence suggests that this reaction intermediate is formed irreversibly and has a trans geometry. Acid hydrolysis of Co(Me_6[14]dieneN_4)CO_3^+ was found to be much slower than acid hydrolysis of Co(Me_6[14]dieneN_4)$OHCO_3$, making possible the determination of the relative concentrations of these complexes and permitting the isotopic composition of the ring-opened species to be determined in ^{13}C–^{18}O double-labeled tracer experiments. The latter experiments demonstrated that cobalt–oxygen bond breaking occurred in the ring-opening step. Three different isomeric tetramine complexes have also been examined. These complexes exhibited the same general pattern of reactivity in base hydrolysis as the Co(Me_6[14]dieneN_4)CO_3^+; however, for these Co(Me_6[14]aneN_4)CO_3^+ complexes the ring-opened intermediate did not reach a sufficient concentration to permit its characterization. It was possible to sample unreacted tetraamine carbonate in order to determine from an ^{18}O tracer study that there could be no labile ring-opening preequilibrium involving carbon–oxygen bond breaking in the base hydrolysis. The decarboxylation of the tetraamine complexes was found to be reversible both in acid and in base. The role of ligand stereochemistry in determining the net reactivity is discussed in terms of nucleophillic scavenging for a five-coordinate ring-opened intermediate. The plausibility of such a process was demonstrated in experiments which showed that the rate of acid hydrolysis varied markedly with the anionic composition of the medium.

Introduction

There have been few attempts to probe the relationships between ligand stereochemistry and the chemical reactivity of coordination complexes.[2] The methyl-substituted macrocyclic tetraamines prepared by Curtis[3-7] clearly have considerable potential for stereochemical alteration of reaction rate and possibly even reaction mechanism. In a previous study Kernohan and Endicott[8] argued that the inertness of Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^{3+} [4] to acid hydrolysis most probably resulted from a stereochemical "protection"[9] of the bidentate carbonate group. This view of the observed, large variations in carbonate hydrolysis rates[10] has been elaborated by Dasgupta and Harris[11] and subjected to further critical evaluation and reinterpretation by Poon.[12]

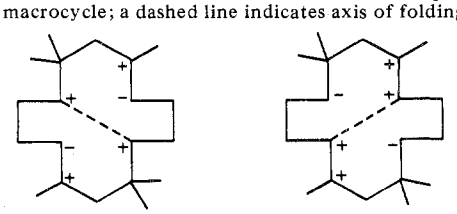
The present study was originally undertaken to examine the significance of stereochemical factors in the base hydrolyses of bidentate carbonate. Preliminary observations[8] had indicated that the net hydrolysis rate in basic solution was similar for the Co$(en)_2CO_3^+$ [13,14] and Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+ complexes although a number of details of their respective reactions appeared to be different. It was thus something of a paradox that due to steric interference with carbonate chelate ring opening the rates of

(1) (a) Partial support of this research by the Public Health Service (Grants AM 08737 and AM 14341) is gratefully acknowledged. (b) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; see Abstracts, No. INOR 62.

(2) For example see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(3) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(4) In the present study we use a contracted form of the abbreviations proposed by Busch and coworkers[5] for these ligands. Thus Me_6[14]dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; C(5,12)-*rac*-Me_6[14]aneN_4 = C(5,12)-*rac*-5,7,7,12,14,14-Me_6[14]aneN_4 = C(5,12)-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; C(5,14)-*meso*-Me_6-[14]aneN_4 = C(5,14)-*meso*-5,7,7,12,12,14-Me_6[14]aneN_4 = C(5,14)-*meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. The two different configurational isomers of the folded C(5,12)-*rac*-Me_6[14]aneN_4 ligand are distinguished by prefixes α (for VfCC[5,6]) and β (for VfEE[5,6]); see diagrams below (a plus sign at an asymmetric center indicates the H atom at the center lies above the plane of the flattened macrocycle; a dashed line indicates axis of folding)



VfCC VfEE

(5) V. L. Goedkin, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, 94, 3397 (1972).

(6) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 3397 (1971).

(7) N. A. P. Kane-Maguire, J. F. Endicott, and D. P. Rillema, *Inorg. Chim. Acta*, 6, 443 (1972).

(8) J. A. Kernohan and J. F. Endicott, *J. Amer. Chem. Soc.*, 91, 6977 (1969).

(9) In the original paper[8] this "protection" was considered to be thermodynamic, *i.e.*, the stability of the bidentate carbonate relative to the *cis*-aquocarbonato complexes.

(10) For a review see K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 70, 171 (1970).

(11) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 93, 91 (1971).

(12) C. K. Poon, *Coord. Chem. Rev.*, in press.

(13) M. E. Farago, *Coord. Chem. Rev.*, 1, 66 (1966).

(14) D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, 91, 6626 (1969).