ported in this paper have proton nmr corresponding to a cis configuration while the previously reported complexes[1–5] have proton nmr indicative of the trans stereochemistry.

Conclusion

In view of the work done with *cis*-$[\mathrm{Ir(py)_4Cl_2}]\mathrm{Cl}$,[20–22] the hexapyridine complexes,[6,12,23–25] the $[\mathrm{Ru(py)_4bipy}]^{2+}$ (bipy = 2,2′-bipyridine) complex,[26] and the $[(\mathrm{Ru(py)_4})_2\mathrm{ox}](\mathrm{BF_4})_2$ complex,[12] it is not surprising that a relatively stable *cis*-$\mathrm{Ru(py)_4X_2}$ ($\mathrm{X^-} = \mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$) series can be rather easily prepared. However, as has been suggested by other workers,[12,27] the cis isomer does seem to be less stable than the trans. Indications of this come from the following observations. The cis isomer, upon recrystallization from hot pyridine, is converted largely to the trans form. A solution of the cis isomer in methylene chloride when exposed to air turns green. The proton nmr shows a merging of the two sets of 2- and 6-proton resonances to form a single doublet. Upon reduction of the green solution, the trans isomer is formed.

Whatever the form of and reason for the instability of the cis isomer with respect to the trans, it seems clear that the success of this work depended on the use of the oxalate ligand. The oxalate group forces the complex to adapt a cis configuration and can be replaced under conditions which leave the configuration of pyridine ligands unaltered.

Acknowledgment.—The use of the Shell Research and Development Co. Beckman IR-11 spectrophotometer, an NSF fellowship (1968–1972) for D. W. R., and financial support through NSF Grant GP5322X are gratefully acknowledged.

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N,N,N‴,N‴-Diglycylethylenediaminetetraacetic Acid. A New Cobalt(II) Oxygen Carrier[1,2]

BY R. NAKON AND A. E. MARTELL*

Received April 9, 1971

The formation, stability, and properties of a new cobalt(II) chelate oxygen carrier, formed from Co(II) and diglycylethylenediaminetetraacetic acid, $\mathrm{H_4L}$, are described. One mole of oxygen is absorbed per 2 mol of metal chelate, $\mathrm{CoL^{2-}}$, to form the oxygen complex. Potentiometric data indicate that two hydrogen ions are released per ligand upon oxygenation, indicating ionization of the amide hydrogens, with formation of a complex having the composition $\mathrm{Co_2O_2(H_{-2}L)_2^{8-}}$. Ligand protonation constants, the formation constant of the 1:1 unoxygenated complex, and the formation constant of the oxygenated chelate are reported. Facile equilibrium with molecular oxygen, rapid pH equilibrium, and relative slowness of an irreversible reaction to a cobalt(III) complex of the ligand make this oxygen carrier a convenient model system for further study of the nature of oxygen complexes of cobalt(II) peptides in solution.

Introduction

Cobalt(II) complexes of dipeptides have been known to absorb oxygen for some time.[3–7] Recently Nakon and Martell[8] have elucidated the nature of the solution species of the glycylglycinatocobalt(II) system, showing that the chelate having a 1:1 molar ratio of ligand to metal ion forms a binuclear complex in which the amide group of the ligand undergoes proton dissociation on oxygenation and in which there are μ-peroxo and μ-hydroxo bridges between two $\mathrm{Co^{3+}}$ ions. The chelate having a 2:1 molar ratio of ligand to metal ion forms a μ-peroxo bridge between two $\mathrm{Co^{3+}}$ ions but does not form a μ-hydroxo bridge on oxygenation, and only one ligand per metal ion undergoes amide proton dissociation. Because of a relatively rapid irreversible side reaction to form a cobalt(III)–glycylglycine species, oxygen equilibrium data have not been obtained. The purpose of this paper is to describe a new oxygen-carrying chelate compound formed from Co(II) ion and a new ligand, *N,N,N‴,N‴*-diglycylethylenediaminetetraacetic acid, $\mathrm{H_4L}$, I. In the absence of oxygen this ligand forms the normal chelate compounds $\mathrm{CoHL^-}$ (II) and $\mathrm{CoL^{2-}}$ (III), described previously.[9] In the

[1] Abstracted in part from a dissertation submitted by R. S. N. to the Faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This work was supported by a fellowship granted to R. S. N. by the Petroleum Research Fund, administered by the American Chemical Society.

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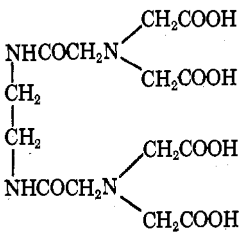
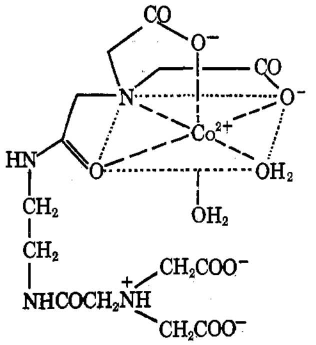
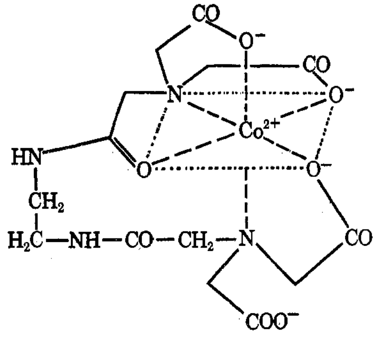

I, H_4L


II, $CoHL^-$


III, CoL^{2-}

presence of oxygen it has now been found that the cobalt complex undergoes amide proton dissociation in marked contrast to its behavior in the absence of oxygen.

Experimental Section

Potentiometric Measurements.—A Beckman research model pH meter was used to determine hydrogen ion concentration in all potentiometric titrations, which were carried out in a double-walled titration cell of 50-ml capacity. The temperature of all solutions was maintained at 25.0 ± 0.05° by circulation of thermostated water through the outer jacket of the potentiometric cell. The titration cell was fitted with glass and calomel extension electrodes, a microburet delivery tube, and gas (nitrogen and oxygen) inlet and outlet tubes.

The ionic strengths of the experimental solutions were maintained at 0.10 M by the addition of an appropriate amount of KNO_3. The solutions were stirred through the use of a magnetic stirrer and/or the bubbling of oxygen or nitrogen through them. Both stirring and gas supply were stopped when a reading was taken. However, the solutions were always under positive nitrogen or oxygen pressure to prevent contamination from the atmosphere.

The glass extension electrode was calibrated by titration of acetic acid and hydrochloric acid with sodium hydroxide to give $-\log [H^+]$ values directly. For the acetic acid titration, the actual hydrogen ion concentrations were determined on the basis of data tabulated by Harned and Owen.[10] In this investigation pH is defined as the logarithm of a concentration, $-\log [H^+]$, instead of the usually employed activity function, $-\log a_{H^+}$, which cannot be determined precisely and which cannot be used directly in most calculations.

Reagents.—A pure sample of diglycylethylenediaminetetraacetic acid was supplied by Dr. R. Motekaitis. The stock cobalt(II) nitrate solution was prepared with Baker Analyzed grade hexaaquocobalt(II) nitrate. The cobalt(II) solution was standardized by direct titration with ethylenediaminetetraacetic acid (EDTA) according to the procedure described by Schwarzenbach.[11] The cobalt(II) solution was nitrogenated before standardization and always kept under nitrogen.

Warburg Measurements.—Oxygen absorption experiments to determine the stoichiometry of the oxygenated species were performed on a Warburg apparatus, Gilson Medical Electronics, No. 8058. The oxygen stoichiometric experiments were performed at 25.0° on solutions of 1:1 molar ratios of ligand to metal ion at 0.10 M KNO_3. Enough sodium hydroxide solution was added to make the $-\log [H^+]$ value of the resultant solution about 11. The amount of base needed was calculated from potentiometric titration curves in the presence of excess oxygen. After the solutions in the Warburg flask reached equilibrium under an oxygen atmosphere, the cobalt(II) in the side arm was added to the basic ligand solution. Readings were taken at appropriate time intervals and the time of mixing was taken as time zero.

Results

Potentiometric Data.—The potentiometric titration curves of solutions of the ligand (H_4L) and of a 1:1 molar ratio of ligand to cobalt(II) under nitrogen and oxygen atmospheres are presented in Figure 1. The ligand titration curve has two buffer regions separated by an inflection at $n = 2$, corresponding to the removal of the two carboxylic acid protons at low pH and the removal of the two zwitterionic protons at high pH. A final inflection at $n = 4$ corresponds to completion of the neutralization of the ligand. The protonation constants of the ligand at 25.0° and an ionic strength of 0.10 M (KNO_3) were calculated as $K_1 = 10^{7.31}\ M^{-1}$, $K_2 = 10^{6.15}\ M^{-1}$, $K_3 = 10^{2.70}\ M^{-1}$, and $K_4 = 10^{1.98}\ M^{-1}$. The titration curve for the solution containing a 1:1 molar ratio of ligand to cobalt(II) under a nitrogen atmosphere has inflections at $n = 3$ and $n = 4$, corresponding to the removal of the two carboxylic acid protons and one zwitterionic proton and the removal of the second zwitterionic proton in the second step. The following formation constants of the 1:1 chelates are $K_{ML} = 10^{8.5\pm0.1}$ and $K_{MHL} = 10^{6.9\pm0.1}\ M^{-1}$ at 25.0° and an ionic strength of 0.10 M (KNO_3)

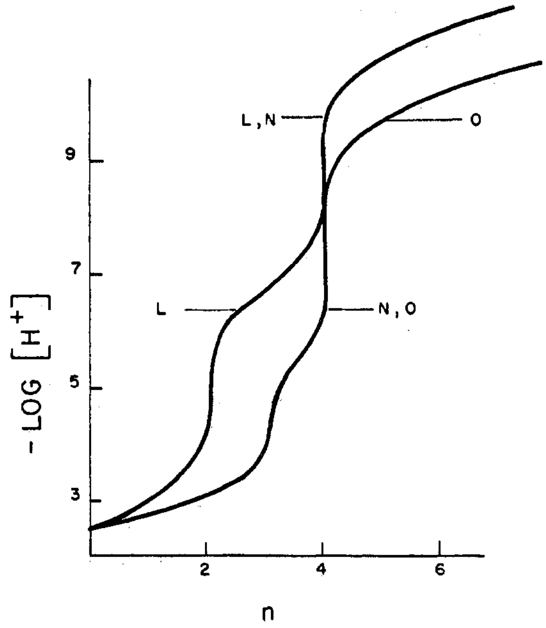


Figure 1.—Potentiometric equilibrium curves for 6.69 × 10^{-4} M diglycylethylenediaminetetraacetic acid (DGENTA, L) and a 1:1 molar ratio of DGENTA to cobalt(II) under nitrogen and oxygen atmospheres at 6.70 × 10^{-4} M metal ion at 25.0° in 0.10 M KNO_3; n = moles of base added per mole of ligand present; L = ligand without metal ion under nitrogen; N = ligand with metal ion under nitrogen; O = ligand with metal ion under oxygen.

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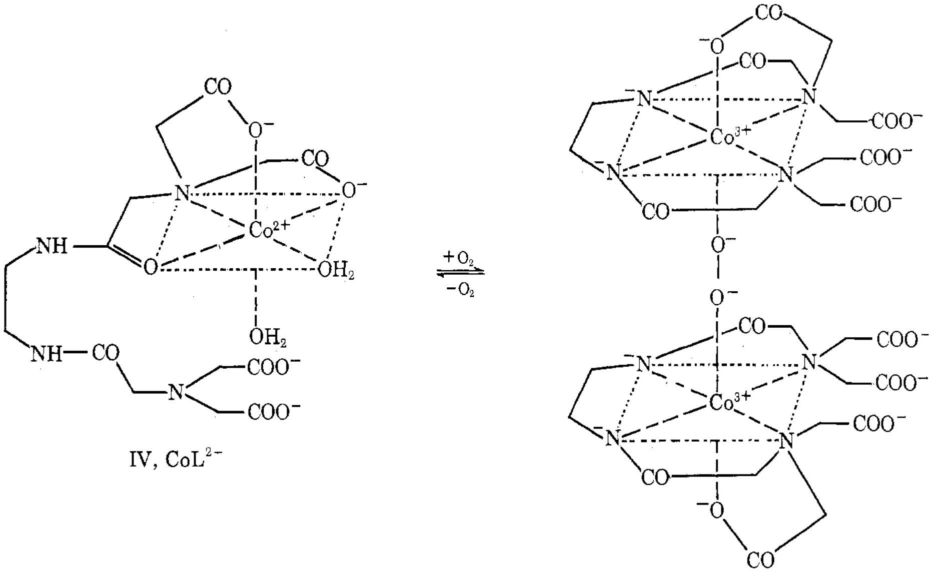
SCHEME I

OXYGENATION OF DIGLYCYLETHYLENEDIAMINETETRAACETATOCOBALT(II)



IV, CoL^{2-}

V, $Co_2O_2(H_{-2}L)_2^{8-}$

$$K_{ML} = [ML^{2-}]/[M^{2+}][L^{4-}]$$

$$K_{MHL} = [MHL^-]/[M^{2+}][HL^{3-}]$$

The 1:1 titration curve under an oxygen atmosphere is identical with the curve obtained under a nitrogen atmosphere up to the inflection at $n = 4$. The curve obtained under an oxygen atmosphere begins to deviate from the nitrogen atmosphere curve at high pH. The appearance of the typical brown color of the oxygen complex and the uptake of oxygen begin at the point where the curves begin to deviate. Since the pH is already very high, no additional inflection is observed beyond $n = 4$. The following formation constant at 25.0° and an ionic strength of 0.1 M (KNO_3) was calculated as $10^{-38.5\pm0.2}$ M^3 atm^{-1}

$$K_{O_2} = [MH_{-2}L(O_2)MH_{-2}L^{8-}][H^+]^4/[ML^{2-}]^2p_{O_2}$$

This formation constant is of course the same as that calculated if the protons dissociated from the oxygen complex were assumed to come from coordinated water rather than from peptide protons. However, the microscopic interpretation of peptide proton dissociation is assumed here, and the formulation $H_{-2}L^{6-}$ is ascribed to the ligand, for reasons given in the Discussion.

Oxygen Stoichiometry.—At pH 11, ionic strength 0.10 M (KNO_3), and 25.0°, a 1:1 solution of ligand to cobalt(II) absorbed 0.48 mol of oxygen per mole of metal ion or 96% of the theoretical value of 1 mol of oxygen per 2 mol of metal ion in the first 15 min. This stoichiometry is in agreement with that obtained in the oxygenation of other cobalt complexes[5,8] and is interpreted as involving a binuclear complex with the oxygen coordinated to two cobalt ions.

Discussion

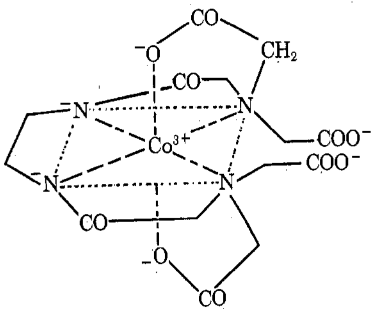
Co^{II}–DGENTA Complexes in the Absence of Oxygen.—The most probable structure for the cobalt–DGENTA chelate at low pH, $CoHL^-$, is indicated by II, for reasons described previously.[9] It is noted that, in spite of the considerable distance between the coordinated proton and coordinated metal ion in MHL^-, the affinity of Co^{2+} for L^{4-} (log K_{ML} = $10^{8.5}$) is considerably greater than for HL^{3-} (log K_{MHL} = $10^{6.9}$). For this reason coordination of the remote amino group and perhaps an adjacent carboxylate oxygen is suggested for ML^{2-}, to give a complex with an arrangement of donor groups similar to that indicated by III. Although this differs somewhat from the structure IV suggested previously,[9] the differences in stabilities of MHL^- and ML^{2-} were not discussed in the previous paper.

Formation of the Oxygenated Complex.—The stoichiometric oxygenation experiments indicate that 1 mol of oxygen is absorbed per 2 mol of metal chelate. The titration curves show that the same species (III or IV) is formed under both oxygen and nitrogen atmospheres up to pH 9.5. At this pH the curve obtained under an oxygen atmosphere begins to deviate from the curve obtained under a nitrogen atmosphere. The appearance of an intense brown color (charge-transfer band), the uptake of oxygen, and the further release of proton indicate the formation of an oxygenated cobalt complex above pH 9.5.

It is not possible to discern an inflection point in this region but calculations of equilibrium constants indicate that two protons are released per cobalt(II) ion in the formation of the oxygen complex. The loss of four additional protons (two per cobalt ion) is probably due to the release of both of the amidic protons of both diglycylethylenediaminetetraacetic acid ligands. Oxygenation is pictured as occurring simultaneously with amide proton dissociation, as indicated by the conversion of IV to V (Scheme I). Similar oxygenation reactions of peptides with amide dissociation have been described previously.[5,8]

The general features and coordinate-bonding sites of the polynuclear oxygenated chelate V are indicated by both direct and indirect experimental evidence. Deprotonation of the amide protons of the ligands has been demonstrated above by analysis of the equilibrium data, so that the nitrogens joined by the ethylene bridge are trigonal,[7] negatively charged, and strongly coordinated, as are the peptide nitrogens in copper(II) and nickel(II) peptide complexes at high pH. Because of the presence of two adjacent trigonal nitrogen donors, the energetically and sterically favored conformation of the four nitrogen donors in V is planar. Since a binuclear complex, whose presence is demonstrated by equilibrium calculations as well as by the stoichiometry of the oxygenation reaction, is formed only on oxygenation, the oxygen must take up a bridging position between the cobalt atoms. The remaining two coordination positions, one per cobalt atom, are indicated as involving the binding of carboxylate groups attached to the terminal amino groups, since they are favorably positioned for such coordination.

The coordination of the oxygen to the cobalt atoms is pictured as involving the binding of a peroxo ligand to two Co(III) centers, formed by electron transfer from Co(II) to the oxygen. There are several types of evidence leading to this conclusion. The coordination of the ligand with displacement of amide protons is known not to occur with Co(II) at any pH but does occur with more strongly bound metal ions such as Ni(II), Cu(II), and Fe(III).[9] There can be no doubt that Co(III) would also form a complex with the ligand H_4L in such a manner as to displace peptide protons to give the chelate $CoH_{-2}L^{3-}$, VI. Thus it is seen that the formation of a binuclear complex of the type indicated by V, with Co(III) coordinated to peroxide and the hexanegative ligand $H_{-2}L^{6-}$, provides the only reasonable explanation for the properties of the oxygenated species and the unusually strong bonding of the multidentate organic ligand.



VI, Co^{III}–DGENTA chelate, $CoH_{-2}L^{3-}$

Reversibility of Oxygenation.—Throughout the high pH region where the nitrogen and oxygen titration curves deviate, the oxygenated species is completely reversible to molecular oxygen. Five to ten minutes of vigorous nitrogen flow into a solution of the oxygenated species results in the complete destruction of the brown color of the oxygen complex. The oxygen complex is then readily regenerated by increasing the oxygen pressure *via* exposure to air or bubbling oxygen into the solution. The process may be repeated many times with no apparent destruction of the oxygen carrier, the appearance and disappearance of the complex being followed spectrophotometrically.

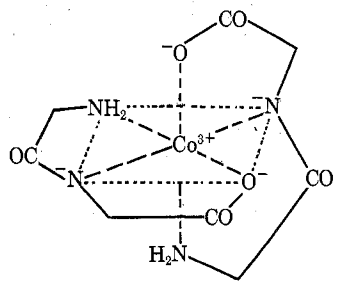
If the pH is not controlled but allowed to reach its own level, the dissociation of the oxygenated species by passing nitrogen gas through its solution results in an increase of pH. Conversely, the formation of the oxygenated species occurs with a corresponding decrease in pH. The pH increase accompanying the dissociation of the oxygen complex ceases as the pH attains that of a corresponding solution of the Co–DGENTA complex prepared under nitrogen. Oxygenation of a solution of Co–DGENTA prepared under nitrogen results in a decrease in pH which ceases as the pH nears that of a corresponding solution of the oxygen complex. These observations indicate a perfectly reversible system. The pH and oxygen pressure determine the amount of the oxygen complex that will form. An increase in pH and/or an increase in oxygen pressure will result in increased formation of the oxygenated species. Similarly a decrease in pH and/or a decrease in oxygen pressure will result in the reduction of the concentration of the oxygen complex.

The readily reversible oxygen equilibrium in the Co–DGENTA system may be explained by the proton affinities of the deprotonated amido moieties in the oxygenated complex V. The very high basicity of these donor groups, as evidenced by the fact that they cannot be deprotonated in aqueous solution in the absence of oxygen except by strong coordination with a small number of metal ions, results in formulas IV and V representing two states of nearly equivalent energy that are interconvertible by protonation and deprotonation, even at very high pH. It is also interesting to note that deprotonation of the amide protons is necessary for oxygenation, for only in this manner is it possible to provide the two additional negative nitrogen donors required to produce a sufficiently strong ligand field to facilitate the conversion

$$Co^{2+}\cdots O{=}O\cdots Co^{2+} \longrightarrow Co^{3+}{-}\bar{O}{-}\bar{O}{-}Co^{3+}$$

For the polyamine cobalt complexes described previously,[5,12,13] complete coordination and oxygenation take place at much lower pH, where protonated forms of the ligand predominate in solution. For these compounds increasing the pH to about 10 results in such a large shift of the equilibrium to the oxygenated species that only an infinitesimal concentration of the simple cobalt(II) complex can be present. Under these conditions the rate of high pH deoxygenation by removal of free oxygen from the solution is so slow as to be virtually undetectable.[12] Thus one of the interesting characteristics of the DGENTA system is its facile oxygen equilibrium at high pH.

Side Reactions.—The irreversible reaction to what is probably a cobalt(III) chelate is remarkably slow for the oxygenated Co–DGENTA complex, V, taking weeks for appreciable reaction to occur at room temperature, compared to a few hours for the previously studied cobalt–peptide systems.[6] A probable structure for the irreversible cobalt(III) product is shown by formula VI, indicated as a fully coordinated species in which six of the eight donor groups of the ligand are coordinated to the metal ion. A similar complex VII of glycylglycine and Co(III), containing two ligand



VII, bis(glycylglycinato)cobalt(III) chelate, $Co(H_{-1}L)_2^-$

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(12) F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, **92**, 2687 (1970).

(13) R. S. Nakon and A. E. Martell, *J. Inorg. Nucl. Chem.*, in press.

anions, each with a negative deprotonated amide group, has been demonstrated[7] as the irreversible cobalt(III) reaction product for the cobalt(II)–glycylglycine–oxygen system.

The facile equilibrium with molecular oxygen, the slowness of the irreversible reaction, and the rapid equilibrium resulting in the formation of the oxygenated complex make the Co(II)–DGENTA–oxygen system a convenient oxygen carrier for further study and provide a convenient model for the elucidation of the structure and reaction mechanisms of cobalt(II) peptide oxygen carriers.

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Racemization and Hydrogen Exchange in the *trans*-Bis(diethylenetriamine)cobalt(III) Ion

BY GRAEME H. SEARLE* AND F. RICHARD KEENE

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The rates of hydrogen exchange and racemization at the secondary N–H center in the *trans*-$[Co(dien)_2]^{3+}$ ion with coupled chelate rings have been measured, and rates and activation parameters are compared with previous results. The close correspondence of the kinetic results with those for the single chelate ring complex $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ of identical cationic charge indicates that the coupling of chelate rings across the secondary N–H center in the dien complex has little effect on either process. It is still difficult however to decide on the details of the nitrogen inversion process. Comparisons with the other asymmetric nitrogen systems previously studied involve variations of more than one structural parameter, but it appears that the electronegative trans substituent X in *sym*-$[Co(trenen)X]^{2+}$ has a greater effect on the kinetics than does the extensive chelate ring coupling.

Introduction

The three geometric isomers of $[Co(dien)_2]^{3+}$ (dien = diethylenetriamine) have recently been separated, and the two dissymmetric forms u-cis[1a] and trans resolved into their optical isomers.[1b] The trans isomer (Figure 1) is of particular interest because the dissymmetry arises essentially from the chiralities of the C_2 related bond pairs in the two dien ligands, as typified and uniquely described[2] by the two secondary N–H bonds at the secondary nitrogen centers.

Coordination of amines to cobalt(III) considerably reduces the rate of nitrogen–hydrogen dissociation from that in corresponding organic quaternary ammonium salts. Coordination of an unsymmetrically substituted secondary amine NHR_1R_2 to a metal generates an asymmetric center at the donor nitrogen atom, and the proton-exchange rate is sufficiently slow at suitably low pH to restrict inversion at that nitrogen center. Optical resolution of the resulting asymmetric complex thus becomes feasible, and a number of such optical separations have now been achieved.

dien is a symmetrically substituted secondary amine so that *trans*-$[Co(dien)_2]^{3+}$ does not contain an asymmetric donor atom. However racemization will result if one of the secondary N–H bonds adopts the alternative disposition (Figure 1). This process is equivalent to inversion of configuration at the asymmetric nitrogen center in the situation Co–NHR_1R_2, and we henceforth use the term "inversion" to describe the analogous configurational change about a secondary nitrogen center in *trans*-$[Co(dien)_2]^{3+}$ despite the absence of asymmetry. This configurational change must involve N–H dissociation and will be accompanied by conformational inversion in each of the adjacent chelate rings.

These phenomena provide an unequivocal method for establishing the geometric configurations of the two dissymmetric forms, since the optical rotatory powers derive from different chiral sources in the u-cis and trans isomers. The u-cis, whose optical activity arises essentially from a configurational effect, should be optically stable in base, but the racemization of the trans isomer should be OH^- catalyzed. It was thus necessary to establish the OH^- dependence of the racemization of the trans isomer, and this prompted the present study of the kinetics of both racemization and hydrogen exchange under a variety of conditions in the hope of further elucidating the mechanistic steps involved in the racemization.

Recently the kinetics of racemization and deuteration have been studied by Buckingham and Sargeson and coworkers for several cobalt(III) complexes where the sole source of asymmetry resides in a coordinated secondary amine N atom. For the three complexes $[Co(NH_3)_4sarc]^{2+}$,[3] $[Co(NH_3)_4(N\text{-Meen})]^{3+}$,[4] and *trans*,-*trans*-$[Co(N\text{-Meen})_2(NO_2)_2]^{+}$ [5] (sarc = sarcosinato anion; *N*-Meen = *N*-methylethylenediamine) the rates of proton exchange were several orders of magnitude faster than the respective rates of racemization, and both measured processes were described by rate laws of similar form, $R = k[\text{complex}][OH^-]$.

The two mechanisms which have been proposed by

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[1] (a) The three geometric isomers of $[C(dien)_2]^{3+}$ have been designated s-cis (or symmetrical-facial), u-cis (or unsymmetrical-facial), and trans (or meridional). (b) F. R. Keene and G. H. Searle, *Inorg. Chem.*, **11**, 148 (1972); F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, *J. Chem. Soc. D*, 784 (1970).

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