This value of K_a agrees well with the literature value[12] under similar conditions.

Discussion

The decomposition of diaquocob(II)aloxime in 0.01 *M* acetate buffer occurs in a first-order process showing a dependence on $[H^+]$ slightly greater than first-order (*ca.* 1.1–1.2 order) between pH 4.8 and 6.1. The likely role of H^+ in this process is the protonation of *both* oxygens of the dimethylglyoxime ligands thereby destroying the O---H---O hydrogen bonding which lends such great stability to these complexes. Independent evidence exists for the importance of such protonation in $Co^{III}(dmg)_2$ complexes.[13,14]

The rate of reduction of RCl^{2+} was found to be the same whether or not acetate was present, suggesting that any interaction between ~0.01 *M* acetate and cob(II)aloxime is slight.

The rate constants summarized in Table I show a wide range ($\sim 3 \times 10^4$) in reactivity between the different $Co(NH_3)_5X^{2+}$ complexes. The very slow reaction rate of $Co(NH_3)_5H_2O^{3+}$ was referred to previously, and we have also found that $Co(NH_3)_6^{3+}$ reacts too slowly to measure (*i.e.*, decomposition of $Co(dmg)_2(H_2O)_2$ is the only process seen).

Except for $Co(NH_3)_5OH^{2+}$, the product determinations referred to above establish that all the reactions proceed by an inner-sphere mechanism; we presume the hydroxo complex reacts in the same fashion. The basis of this claim rests on the assumption that anation of $Co(dmg)_2(H_2O)_2^+$ by X^- in a medium similar to the present one does not occur rapidly. The kinetics of the anation reactions were not studied, but inappreciable quantities of the complex $Co(dmg)_2(H_2O)X$ were found in the control experiments.

The order of effectiveness of the halide ions as bridging ligands ($Br^- > Cl^- \gg F^-$) is reflected in the respective values of the second-order rate constants or more precisely by the relative stabilities of the respective transition states according to Haim.[15] Both these observations demonstrate the "soft acid" or "class b" character of $Co(dmg)_2(H_2O)_2$ in the transition states and also presumably in the free complex.

Generally, a high rate ratio for reduction of an azido complex compared to the N-bonded thiocyanato complex can be expected,[16] provided the reductant exhibits hard-acid character. For example, the rate constant ratio is 1.5×10^4 for the reductions of $(NH_3)_5CoN_3^{2+}$ and $(NH_3)_5CoNCS^{2+}$ by Cr^{2+}.[17] The ratio for the reduction of the same two complexes by the soft acid $Co(CN)_5^{3-}$ is 1.5.[7] For $Co^{II}(dmg)_2(H_2O)_2$ the ratio is 26, again indicating a tendency toward soft-acid character.

Considering the rate constants found for certain other Co(II)–Co(III) reactions, the present reactions appear rather rapid. We note that $Co(dmg)_2(H_2O)_2$ is a low-spin complex,[17] and the electron is transferred from and into an e_g orbital.

Indeed it has been observed[18] that $Co(dmg)_2(H_2O)$ reacts very rapidly with $Fe(CN)_6^{3-}$, at a specific rate $\geq 3 \times 10^7\ M^{-1}\ sec^{-1}$. This reaction produces a new anionic species which we presume to be $[(NC)_5FeCN\text{-}Co(dmg)_2H_2O]^{3-}$ by analogy with $Co(CN)_5^{3-}$ reactions.[19] The observation of this reaction and the importance of the inner-sphere mechanism for the $Co(NH_3)_5X^{2+}$ reactions necessarily implicate rapid axial ligand exchange for the complex $Co(dmg)_2(H_2O)_2$.

One practical benefit of the present reactions should also be noted. They can provide a convenient synthetic method for $Co(dmg)_2(H_2O)X$ complexes. This is particularly useful for the fluoro complex, which is difficult to prepare by other methods.

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(13) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 6041 (1963).

(14) A. Adin and J. H. Espenson, *Chem. Commun.*, 753 (1971).

(15) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

(16) J. H. Espenson, *ibid.*, **4**, 121 (1965).

(17) J. P. Candlin, J. Halpern, and D. Z. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

(18) A. Adin, unpublished experiments.

(19) A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

Importance of Asymmetric Nitrogens to the Circular Dichroism of Alkyl-Substituted Ethylenediaminediacetic Acid Complexes of Cobalt(III)[1]

BY CAROLYN W. MARICONDI AND BODIE E. DOUGLAS*

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Four Co(III) complexes containing *N*-alkyl-substituted ethylenediaminediacetic acid have been completely resolved, and their absorption and circular dichroism spectra are reported. Two of the complexes, *trans*-[Co(DMEDDA)en]I and *trans*-[Co(DEEDDA)en]I (containing, respectively, the *N,N'*-dimethyl- and *N,N'*-diethylethylenediamine-*N,N'*-diacetate ion), have been reported previously. The two corresponding complexes containing oxalate ion in place of ethylenediamine are new. Both ethylenediamine complexes give very similar absorption and circular dichroism spectra, as do the two oxalate complexes. The CD peak intensities of all the complexes, however, are less than half those of the corresponding unsubstituted-EDDA complexes. This reduction in intensities is attributed to a lower contribution to the asymmetry of the complexes from nitrogens in the *N*-alkyl-substituted EDDA's as compared to unsubstituted EDDA.

Introduction

In the course of recent studies to determine factors responsible for variations in intensities of circular dichroism (CD) bands within and between series of related complexes, a series of cobalt(III) complexes containing the tetradentate ligand ethylenediamine-*N,N'*-diacetate (EDDA) was prepared.[2,3] The geometrical

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(1) This work was supported by a research grant (GM-10829) from the Division of General Medical Studies, U. S. Public Health Service.

(2) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, **6**, 700 (1967).

(3) C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969).

isomers studied were those with the coordinated oxygens of the EDDA trans to one another. Complexes with EDDA and the bidentate ligands ethylenediamine, (*S*)-alanine, carbonate, oxalate, and malonate were resolved. Rotational strengths of the d–d transitions were found to be determined largely by the EDDA and to be quite insensitive to the bidentate ligand used. Also the rotational strengths observed were significantly greater than those for most cobalt(III) complexes with similar ligands. The present work is part of a study to find the reasons for the dominating influence of EDDA in these complexes by systematically varying the structure of the EDDA portion of the complex.

The complexes reported here were chosen to assess the importance of the asymmetric nitrogen centers of coordinated EDDA in determining the rotational strengths of EDDA complexes. The four compounds in the series contain *N*,*N'*-dimethylethylenediamine-*N*,*N'*-diacetate ion (DMEDDA) or *N*,*N'*-diethylethylenediamine-*N*,*N'*-diacetate ion (DEEDDA) and ethylenediamime (en) or oxalate ion (ox). The two complexes with ethylenediamine have been prepared before[4] and partially resolved (about 10%) by ion-exchange chromatography.[5] The CD curves of the partially resolved complexes showed significant changes in shape compared to the CD spectrum of $[Co(EDDA)en]^+$ but gave no information about changes in overall intensity. Complete resolutions of these and the corresponding oxalate complexes are reported here.

Experimental Section

The following compounds were prepared by the methods of Legg and Cooke:[4] barium *N*,*N'*-dimethylethylenediamine-*N*,*N'*-diacetate (**1**), barium *N*,*N'*-diethylethylenediamine-*N*,*N'*-diacetate (**2**), *trans*-*N*,*N'*-dimethylethylenediamine-*N*,*N'*-diacetato(ethylenediamine)cobalt(III) nitrate (**3**), and *trans*-*N*,*N'*-diethylethylenediamine-*N*,*N'*-diacetato(ethylenediamine)cobalt(III) nitrate (4).

The iodide salts of **3** and **4** were prepared by dissolving the nitrate salts in a small amount of water and adding a solution of NaI.

Preparation of $\mathbf{Ag[(+)_{546}\text{-}Co(EDTA)]}$.—Silver nitrate and $K[(+)_{546}\text{-}Co(EDTA)]\cdot 2H_2O$ in 3:1 molar proportions were dissolved in a few milliliters of water. Ethanol (95%) was added until a purple oil separated. The weakly colored liquid was decanted from the oil which was then washed with more ethanol. A few milliliters of warm water was added to the resulting gum. The mixture was stirred with a glass rod and red-purple crystals began to form before the gum had completely dissolved. These crystals were removed, washed with ethanol and acetone, and air-dried; yield *ca.* 80%.

Resolution of ***trans*-*N*,*N'*-Dimethylethylenediamine-*N*,*N'*-diacetato(ethylenediamine)cobalt(III) Iodide,** ***trans*-[Co(DMEDDA)en]I.**—Solid $Ag[(+)_{546}\text{-}Co[EDTA)]$ (4.6 g, 0.01 mol) and [Co(DMEDDA)en]I (4.5 g, 0.01 mol) were stirred in 20 ml of warm water for several minutes. AgI was removed and washed with 15 ml of warm water. Ethanol (60 ml of 95%) was added, and the solution was cooled in ice. Red-purple needles separated and were removed in several fractions for a total of 3.3 g with $\Delta\epsilon_{565} = -2.7$ assuming a 1:1 diastereomer, mol wt 668. A little acetone was added to the filtrate and about 2.2 g of red-purple flakes separated. After two recrystallizations from water and EtOH, these crystals had $\Delta\epsilon_{535} = +2.0$. The optical isomers were isolated by treating the diastereomers separately by the following procedure. One gram of diastereomer was dissolved in 25 ml of water, and the solution was placed on a small (2 × 38 cm) Dowex 1-X8 ion-exchange column in Cl^- form. The $[Co(EDTA)]^-$ was retained as a narrow band at the top of the column, and the DMEDDA complex was eluted with deionized water at 6 ml/min. The complex was obtained in 40 ml of water. This solution was evaporated under a stream of air at room temperature to a small volume and then filtered. The complex was precipitated by addition of EtOH to get the Cl^- salt or by addition of NaI solution to get the I^- salt. For the resolved isomers, $\Delta\epsilon_{548} = \pm 2.15$. *Anal.* Calcd for $[Co(C_{10}H_{22}N_4O_4)]Cl\cdot 3H_2O$: C, 29.2; H, 6.80; N, 13.6. Found: C, 29.23; H, 6.97; N, 13.33.

Resolution of ***trans*-*N*,*N'*-Diethylethylenediamine-*N*,*N'*-diacetato(ethylenediamine)cobalt(III) Iodide,** ***trans*-[Co(DEEDDA)en]I.**—The following compounds were combined and stirred 10 min in 10 ml of warm water: $[Co(DEEDDA)en]I\cdot H_2O$ (3.9 g), *d*-tartaric acid (0.5 g), and Ag_2(*d*-tart) (1.4 g). The AgI was removed and washed with 2 ml of water. The filtrate was left standing in the refrigerator for several days. Red needles (1 g) separated with $\Delta\epsilon_{558} = +1.5$, assuming a 1:1 diastereomer, mol wt 500. Addition of ethanol to the filtrate resulted in precipitation of the other diastereomer. One recrystallization of each diastereomer gave resolved fractions with $\Delta\epsilon_{558} = \pm 1.7$. The isolation procedure was the same as that used for the [Co(DMEDDA)en]I isomers. For the resolved isomers $\Delta\epsilon_{458} = \pm 1.8$. *Anal.* Calcd for $[Co(C_{12}H_{26}N_4O_4)]I\cdot H_2O$: C, 29.2; H, 5.68; N, 11.4; I, 25.8. Found: C, 29.35; H, 5.78; N, 11.28; I, 25.74.

Preparation of Sodium ***N*,*N'*-Dimethylethylenediamine-*N*,*N'*-diacetato(oxalato)cobaltate(III) Dihydrate,** $\mathbf{Na[Co(DMEDDA)ox]\cdot 2H_2O}$.—Ba(DMEDDA), 17 g, and $CoSO_4\cdot 7H_2O$, 14 g, were stirred together in 100 ml of warm water for 20 min. Analytical filter pulp was added and the mixture was filtered to remove $BaSO_4$. A mixture of oxalic acid dihydrate (6.3 g) and NaOH (2 g) in 170 ml of water and 4 g of activated charcoal were added to the filtrate. Air was bubbled through the mixture for 18–20 hr. The charcoal was removed and the purple filtrate was evaporated on a 60–80° water bath until solid separated. Evaporation and filtration were repeated several times. The collected solid was recrystallized from water; yield 6 g.

Resolution.—$(+)_{546}\text{-}[Co(en)_2ox]I$ (5 g) and silver acetate (2 g) were stirred for several min in 15 ml of warm water. The AgI was removed and washed with 10 ml of warm water. $Na[Co(DMEDDA)ox]\cdot 2H_2O$ (5.12 g) in 15 ml of water was added to the filtrate, and the solution was cooled in an ice bath for 3 hr. About 2 g of fluffy purple solid was removed, $\Delta\epsilon_{570} = -2.0$, assuming a 1:1 diastereomer, mol wt 615. The filtrate was left in the refrigerator overnight. Later fractions contained the other diastereomer and were recrystallized to give $\Delta\epsilon_{540} = +4.15$. The optical isomers of Na[Co(DMEDDA)ox] were obtained by dissolving the diastereomers in water separately and passing the solutions through a Rexyn 101 Analytical grade cation-exchange column in Na^+ form. The isolation procedure was comparable to that for the ethylenediamine complexes. For the resolved isomers, $\Delta\epsilon_{558} = \pm 2.72$. *Anal.* Calcd for $Na[Co(C_{10}H_{14}N_2O_8)]\cdot 2H_2O$: C, 29.4; H, 4.41; N, 6.86. Found: C, 29.41; H, 4.78; N, 6.51.

Preparation and Resolution of Sodium ***N*,*N'*-Diethylethylenediamine-*N*,*N'*-diacetato(oxalato)cobaltate(III) Trihydrate,** $\mathbf{Na[Co(DEEDDA)ox]\cdot 3H_2O}$.—The preparation of this complex was similar to that for Na[Co(DMEDDA)ox] with Ba(DEEDDA) replacing Ba(DMEDDA). The resolution procedure was also similar to that for the corresponding dimethyl complex. It was found that the less soluble diastereomer sometimes separates too quickly upon cooling, forming a jelly which cannot be filtered. This jelly can be avoided by rewarming the solution, adding a little water, and cooling more slowly. If, after dilution, no solid separates, a few drops of 95% ethanol can be added to start crystallization. For the resolution with $[(+)_{546}\text{-}Co(en)_2ox]I$, $\Delta\epsilon_{575} = -1.5$ for the less soluble diastereomer, assuming mol wt 645.

After removal of the less soluble diastereomer, the more soluble one separates as a silky paste when the solution is evaporated to a small volume and then cooled in ice. This paste cannot be filtered and dried conveniently so this isomer is best obtained using $[(-)_{546}\text{-}Co(en)_2ox]I$ as the resolving agent.

The optical isomers were isolated by the same procedure as for the DMEDDA complex. Pure samples had $\Delta\epsilon_{564} = \pm 2.42$. *Anal.* Calcd for $Na[Co(C_{12}H_{18}N_2O_8)]\cdot 3H_2O$: C, 31.8; H, 5.30; N, 6.18. Found: C, 32.0; H, 5.40; N, 6.32.

Spectra.—The absorption spectra were measured on a Cary Model 14 recording spectrophotometer using a tungsten lamp. The CD spectra were recorded with a Roussel-Jouan Dichrograph using a Sylvania Sun Gun light source. Concentrations were about 10^{-3} *M* and spectra were taken at room temperature.

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[4] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

[5] J. I. Legg and B. E. Douglas, *ibid.*, **7**, 1452 (1968).

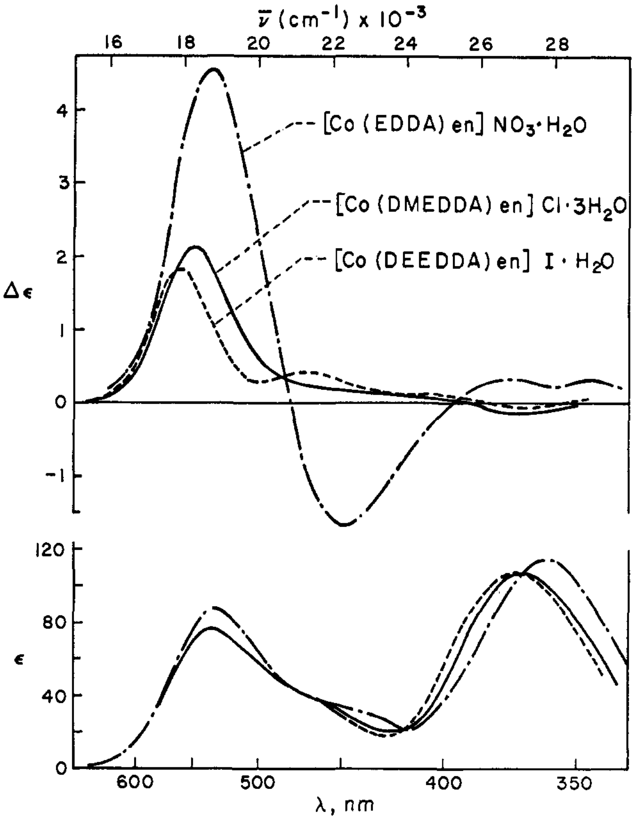

Figure 1.—Absorption and circular dichroism spectra of [Co(EDDA)en]NO$_3$·H$_2$O[2] and the corresponding complexes of *N,N'*-dimethyl- and *N,N'*-diethylethylenediamine-*N,N'*-diacetic acid.

The trans geometry of *N,N'*-dialkyl-substituted EDDA in the complexes was verified by pmr spectra[3] obtained on a Varian A-60 spectrometer (60 MHz) using D$_2$O as solvent.

Analyses.—Elemental analyses were performed by Alfred Bernhardt, Elbach, West Germany. The number of molecules of water of hydration was checked by determining the weight lost upon drying at 60° in a vacuum oven.

Results and Discussion

Circular dichroism and absorption spectra of the cobalt(III) complexes of ethylenediamine or oxalate ion and EDDA, DMEDDA, and DEEDDA are shown in Figures 1 and 2. The curves shown (lowest energy CD band positive) are for the isomers assigned the $\Lambda(C_3)$ absolute configuration[3] (Figure 3). For this chirality the EDDA nitrogens are in the *RR* configuration. The EDDA nitrogens in the $\Delta(C_3)$ isomer are in the *SS* configuration so the CD curves of the two optical isomers are mirror images of one another.

The basis for the assignment of absolute configuration of the unsubstituted EDDA complexes has been discussed previously.[3] If only coordinated atoms are considered, the complexes with ethylenediamine are of the type *trans*-[CoO$_2$N$_4$], while those with oxalate ion are *cis*-[CoN$_2$O$_4$]. Since in each case there is a weaker field along the unique axis than in the plane perpendicular to it, it is predicted that, of the two energy levels derived from $T_{1g}(O_h)$, the $E(D_{4h})$ level will lie lower in energy than the $A_2(D_{4h})$ level.[6] Thus the dominant, lowest energy CD band is assumed to be related to the A → E (D_{4h}) transition for all of the complexes. This band is positive for the isomers assigned the $\Lambda(C_3)$ configuration.

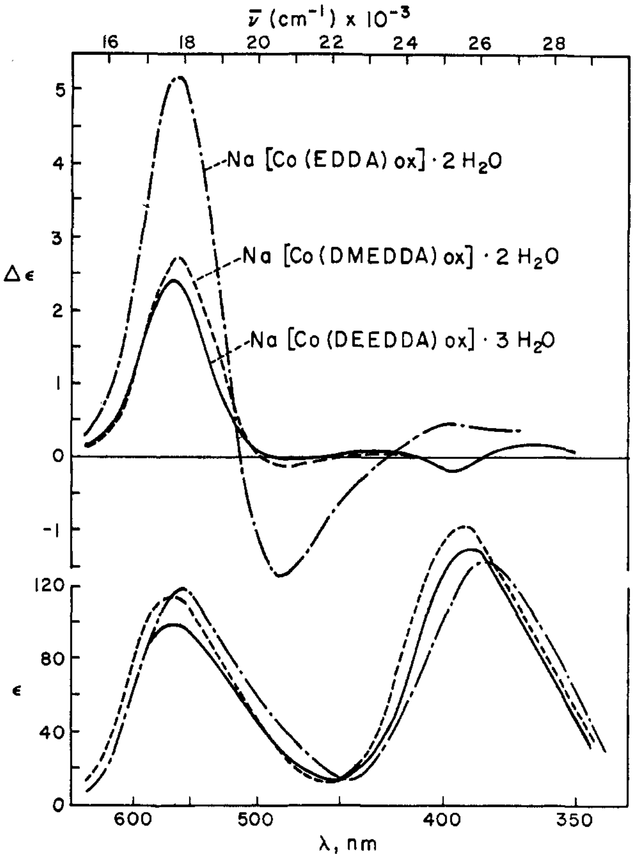

Figure 2.—Absorption and circular dichroism spectra of Na[Co(EDDA)ox]·2H$_2$O[3] and the corresponding complexes of *N,N'*-dimethyl- and *N,N'*-diethylethylenediamine-*N,N'*-diacetic acid.

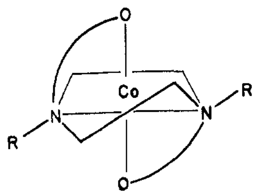

Figure 3.—The $\Lambda(C_3)$-*RR* configuration of *N,N'*-dialkyl-substituted EDDA in a complex of the type *trans*-[Co(RREDDA)-AA].

The vicinal effect due to the asymmetric nitrogens of the trans-coordinated EDDA has been approximated by subtracting the CD curves of the DEEDDA complexes from those of the corresponding EDDA complexes. The resulting difference curves (Figure 4) are quite similar for the ethylenediamine and for the oxalate series. While these curves give an approximation of the vicinal effect from the asymmetric nitrogens of EDDA, part of the observed differences might result from changes in ligand fields, positions of bands, and conformational effects when replacing EDDA with DEEDDA.

Because of the similarity of the CD curves for the DMEDDA and DEEDDA complexes, it is probable that the asymmetric nitrogens in the *N*-alkyl-substituted EDDA complexes make only a minor contribution to their optical activity. Such a small effect is reasonable because all the groups about the nitrogen are similar, differing only in the second or third atom from the nitrogen. The assumed unimportance of the asym-

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[6] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 106 ff.

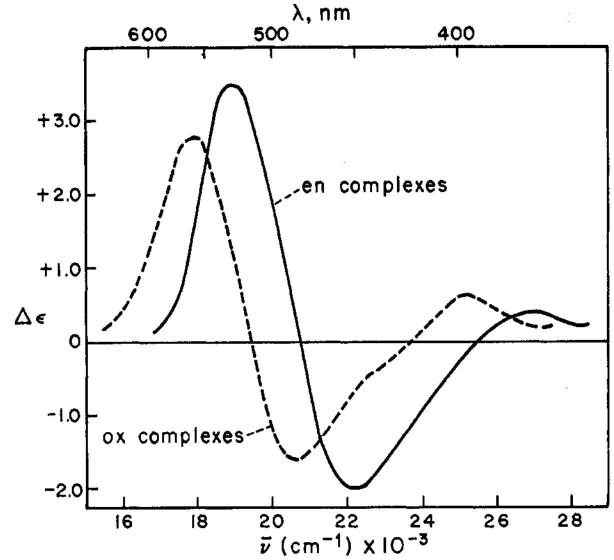

Figure 4.—Difference CD curves for $[Co(EDDA)en]NO_3 \cdot H_2O - [Co(DEEDDA)en]I \cdot H_2O$ (———) and $Na[Co(EDDA)ox] \cdot 2H_2O - Na[Co(DEEDDA)ox] \cdot 3H_2O$ (------).

metric nitrogens in the *N*-alkyl complexes is supported by the similarity of the CD curves of these complexes and of C_2-*cis*(*N*)-$[Co(ox)(gly)_2]^-$[7] and C_2-*cis*(*N*)-$[Co(en)(gly)_2]^+$.[8] The latter complexes differ from EDDA complexes in that they lack the puckered backbone ring and asymmetric nitrogens of the tetradentate ligand. Studies are currently underway to evaluate the effect of the backbone ring conformation on the CD spectra of these complexes. On the basis of the work reported here, however, it is likely that the *N*-alkyl-substituted EDDA and the bis-glycinato complexes show similar CD patterns because similar chelate rings are the dominant source of asymmetry in each.

Previous studies[9,10] of complexes with asymmetric nitrogens have concentrated on cases with no chirality due to the distribution of chelate rings. For such cases it is generally recognized that the asymmetric nitrogens are a major, if not dominant, factor for determining rotational strengths. The results of the present study show that such nitrogens may make a contribution to the asymmetry of a complex with importance comparable to that from the distribution of chelate rings. The contributions of the nitrogens are small for the DMEDDA and DEEDDA ligands where the three R groups on nitrogen are alkyls or substituted alkyls. The contribution is large, however, for EDDA where one R group is hydrogen. Because the effect of an asymmetric donor nitrogen seems to depend upon the effective symmetry of the cobalt(III) chromophore,[8] such atoms will provide useful information for both experimental and theoretical work with circular dichroism. They may prove important for clarifying previously unexplained changes in CD curves for certain series of compounds.[11,12] Conversely, they may be valuable for gaining information about structure of complexes from their CD curves.

[7] N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.* **9**, 719 (1970).

[8] N. Matsuoka, J. Hidaka, and Y. Shimura, presented at 18th Symposium on Coordination Chemistry, Sendai, Japan, Sept 1969.

[9] Much of the work has been recently reviewed: (a) S. F. Mason, *J. Chem. Soc. A*, 667 (1971); (b) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, pp 196–209.

[10] S. Larsen, K. J. Watson, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 847 (1968).

[11] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968).

[12] G. R. Brubaker and D. P. Schaefer, *ibid.*, **10**, 970 (1971).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Kinetics and Mechanism of the Reaction of Dicobalt Octacarbonyl with Alkynes

BY PAUL C. ELLGEN

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The kinetics of the reaction of dicobalt octacarbonyl with alkynes to give hexacarbonyl-μ-alkyne-dicobalt complexes have been reexamined. In contrast to the previous interpretation that the substitution reaction proceeds by attack of alkyne on a "reactive form" of dicobalt octacarbonyl, the present study proves that this reaction involves dissociation of carbon monoxide to give dicobalt heptacarbonyl, which rapidly adds alkynes.

Introduction

Shortly after the discovery that dicobalt octacarbonyl reacts with alkynes[1,2] to give hexacarbonyl-μ-alkyne-dicobalt complexes (eq 1), Tirpak and coworkers[3,4] studied the rate of this reaction in toluene solution and at atmospheric pressure by monitoring the volume of carbon monoxide evolved as a function of time. The rate of CO evolution was found to exhibit a complex dependence on the reagent concentrations. While the reaction rate was sensitive to the concentrations of both reagents, the dependence on the concentration of the alkyne was somewhat weaker than the dependence on dicobalt octacarbonyl concentration. Additionally, evidence for the occurrence of an acetylenic dicobalt heptacarbonyl intermediate was adduced. An elegant analysis resulted in the conclusion that the kinetic data were consistent with the mechanism shown in eq 2 (with $\kappa_{-2} = 0$), where B represents a postulated

$$Co_2(CO)_8 + RC_2R' \longrightarrow Co_2(CO)_6RC_2R' + 2CO \qquad (1)$$

$$Co_2(CO)_8 \underset{\kappa_{-1}}{\overset{\kappa_1}{\rightleftharpoons}} B \qquad (2a)$$

[1] H. W. Sternberg, *et al.*, *J. Amer. Chem. Soc.*, **76**, 1457 (1954).

[2] H. Greenfield, *et al.*, *ibid.*, **78**, 120 (1956).

[3] M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **80**, 4265 (1958).

[4] M. R. Tirpak, C. A. Hollingsworth, and J. H. Wotiz, *J. Org. Chem.*, **25**, 687 (1960).