S20 characteristics (RCA 7265) was used. The Valvo photomultiplier tube was cooled with the vapor boiled off from a container with liquid nitrogen. The photocurrent was fed to the input of a galvanometer amplifier with dark-current compensation. The output of the amplifier was connected to an electronic paper chart potentiometer which allowed the spectra to be recorded automatically.

The results of the luminescence measurements are seen in Figures 10–16. Above, the luminescence spectra of the two components are given; below, the spectra of the respective double complex salts are shown. The luminescence intensity is given in arbitrary units and plotted *vs.* wave numbers. Comparing the emission of the double salts with that of pure $K_3[Cr(CN)_6]$ the observed differences in luminescence intensity are not seen from the figures. The relation of the phosphorescence intensity of the double salts to the intensity of $K_3[Cr(CN)_6]$ is given in Table I, column 4. This relation was obtained from the current of the photomultiplier taken for the band in the phosphorescence spectra, which has the greatest intensity. The values in column 4 are related to the emission of solid $K_3[Cr(CN)_6]$, whose intensity is set at unity. The first value for a given compound was obtained taking into account only the intensity of the lamp (the intensity distribution of the lamp has been measured using a bolometer which was calibrated by means of a standard light source) and the transmission of the BG 38 filter at the wavelength of the exciting light. The second value in addition includes corrections for the absorption coefficients of $K_3[Cr(CN)_6]$ and of the double complex salts taken from the absorption spectra of $K_3[Cr(CN)_6]$ and from the respective superposition curves. The oxygen-coordinated compounds $[Cr(ur)_6]Cl_3 \cdot H_2O$, $[Cr(atp)_6](ClO_4)_3$, and $[Cr(imid)_6](ClO_4)_3 \cdot 2H_2O$ exhibit both types of emission phosphorescence and fluorescence (dotted curves in Figures 11 and 12). The first compound at 77°K yields only phosphorescence; on raising the temperature, the broad-band fluorescence is seen; the more intense it is, the higher the temperature.

Lifetimes.[13]—Reported lifetimes (Table II) were measured by the following single-pulse method. The sample located in a cuvette within a transparent quartz dewar was excited by means of a giant-pulse ruby laser equipped with a second harmonic generator (347 mμ). The luminescence was detected by a Valvo 56 CVP photomultiplier (S1) after passing filters to eliminate laser radiation and a 0.25-m Jarrell–Ash Ebert monochromator. The photomultiplier and the voltage divider were cooled with the vapor boiled off from a liquid nitrogen reservoir. The resulting signal of the anode current was displayed on a Siemens oscilloscope, Oscillar M 214. Decay curves where photographed using a Polaroid camera equipped with high-speed film of Type 410. In Q-switch operation the excitation pulse had a half-width of ~20 nsec and about 2-MW average power. To prove simple exponential decays, the results were plotted on linear logarithmic paper. Lifetimes have been evaluated from these plots using the usual procedure.

Acknowledgments.—We are indebted to H. U. Zander for measuring the lifetimes and to A. D. Kirk for stimulating discussions. The work was sponsored in part by the Deutsche Forschungsgemeinschaft and in part by NATO Grant No. 213.

[13] H. U. Zander, Thesis, Frankfurt am Main, 1969.

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Circular Dichroism of Some Less Strained Model Compounds for the Ethylenediaminetetraacetatocobaltate(III) Ion[1]

BY CAROLYN W. VAN SAUN AND BODIE E. DOUGLAS

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A series of model compounds for $Co(EDTA)^-$ have been prepared and resolved. This series includes the following complex ions: 1,3-propanediaminetetraacetatocobaltate(III), $Co(1,3\text{-}PDTA)^-$, *cis*-bis(iminodiacetato)cobaltate(III), *cis*-$Co(IDA)_2^-$, and ethylenediaminetetrapropionatocobaltate(III), $Co(EDTP)^-$. All of these complex ions have the same effective crystal field and general arrangement of chelate rings as $Co(EDTA)^-$, but they have less strained chelate ring systems. The intensities of the visible absorption bands for these compounds are lower than those for $Co(EDTA)^-$, but the net intensities of their CD bands are greater. The observed increase in rotational strength when the strain of the chelate ring system was decreased contradicts predictions of theoretical studies of optical activity of coordination complexes.

Introduction

Theoretical treatments of the optical activity of coordination compounds have thus far proved inadequate for explaining the circular dichroism (CD) spectra of these systems. The use of CD for obtaining structural information is based on empirical correlations, the theoretical bases for which are generally not understood. The present work was undertaken to determine the influence of various structural changes in the ligand on the rotational strengths of the d–d transitions of cobalt(III) in a series of complexes. Such information is vitally needed to guide future theoretical studies of the optical activity of coordination complexes.

The complexes prepared in this work are all related to the ethylenediaminetetraacetatocobaltate(III) ion, $Co(EDTA)^-$. An X-ray structure determination has been done for this complex ion.[2] The complex contains five chelate rings with the cobalt(III) bonded to the two nitrogen atoms of the ethylenediamine and to one oxygen atom from each of the four carboxylate groups. Structural parameters such as bond lengths and angles show notable departures from regular octahedral

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[1] This work was supported in part by a research grant (GM-10829) from the Division of General Medical Studies, Public Health Service. Presented, in part, at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

coordination and imply that the chelate ring system is strained, particularly in the case of the two amino acid chelate rings in the same plane. The deviations from normal bond angles indicate that the strain in the system could be relieved by enlarging or removing some of the chelate rings.

The chelating ligands used for preparing the series of complexes reported here were chosen so that the arrangement of chelate rings and the nature of the coordinated atoms would be the same as in $Co(EDTA)^-$, but so that the strain in the chelate ring system would be less. In the complex ions 1,3-propanediaminetetraacetatocobaltate(III), $Co(1,3\text{-}PDTA)^-$, and *cis*-N-bis(iminodiacetato)cobaltate(III), *cis*-$Co(IDA)_2^-$, the diamine ring of $Co(EDTA)^-$ has been enlarged and eliminated, respectively. In the ethylenediaminetetrapropionatocobaltate(III) ion, $Co(EDTP)^-$, the glycinate rings of $Co(EDTA)^-$ have each been enlarged by one atom. Comparison of the CD spectra of these complexes with that of $Co(EDTA)^-$ should show the effect of strain in the chelate system on the rotational strength of the d–d transitions.

Experimental Section

Optical isomers are identified either by (+) or (−), the sign of the longest wavelength CD band, or by the sign of the optical rotation at a specified wavelength, *e.g.*, $(+)_{546}$.

Preparation of 1,3-Propanediamine-N,N,N′,N′-tetraacetic Acid, 1,3-PDTA.—The procedure used by Dwyer and Garvan[3] for the synthesis of 1,2-propanediaminetetraacetic acid was used to prepare 1,3-PDTA. 1,3-Propanediamine was substituted for 1,2-propanediamine. After the solution had stood for 6 days, it was used directly for the preparation of the cobalt(III) complex.

Preparation and Resolution of Sodium 1,3-Propanediaminetetraacetatocobaltate(III) Trihydrate, $Na[Co(1,3\text{-}PDTA)]\cdot 3H_2O$.—To a portion of the solution from the preparation of 1,3-PDTA calculated to contain 0.05 mol of 1,3-PDTA (assuming 100% yield) was added $CoCl_2\cdot 6H_2O$ (12 g, 0.05 mol). The resulting solution was heated almost to boiling and 3% H_2O_2 (50 ml) was added dropwise with stirring. The solution was cooled in ice for 1 hr. The purple product was collected, washed with 95% ethanol and acetone, and air dried. About 200 ml of 95% ethanol was added to the filtrate which was then cooled overnight in the refrigerator. More purple product was collected; total yield, 9 g. *Anal.* Calcd for $Na[Co(C_{11}H_{14}N_2O_8)]\cdot 3H_2O$: C, 30.20; H, 4.57; N, 6.40. Found: C, 30.08; H, 4.65; N, 6.59.

For the resolution, $(+)_{546}$-$[Co(en)_2ox]I$ (4.0 g, 0.01 mol) and silver acetate (1.6 g, 0.01 mol) were stirred for several minutes in 15 ml of warm water. The AgI was removed. Racemic $Na[Co(1,3\text{-}PDTA)]\cdot 3H_2O$ (4.2 g, 0.01 mol) in water (15 ml) was added to the filtrate. The resulting solution was cooled in ice for 45 min, after which the diastereoisomer containing (−)-$Co(1,3\text{-}PDTA)^-$ was removed (2.7 g). The diastereoisomer was ground with NaI (2 g) in 25 ml of water. The $(+)_{546}$-$[Co(en)_2ox]I$ was removed and 95% ethanol was added to the filtrate. After this solution had cooled in ice for 30 min, the (−) isomer was removed, washed with 95% ethanol and acetone, and air dried; yield, 1.2 g, with $\Delta\epsilon = -1.9$ at 590 mμ.

The filtrate from the diastereoisomer was treated with NaI (2 g) and cooled in ice for a few minutes. Excess $(+)_{546}$-$[Co(en)_2ox]I$ was removed and the filtrate was cooled in ice for 1 hr. Partially resolved (+)-$Na[Co(1,3\text{-}PDTA)]$ (2.2 g) was removed. Two fractional recrystallizations from warm water gave resolved fractions of this isomer; yield, 0.9 g, with $\Delta\epsilon = +1.9$ at 590 mμ.

Preparation and Resolution of Potassium *cis*-Bis(iminodiacetato)cobaltate(III) Sesquihydrate, *cis*-$K[Co(IDA)_2]\cdot 1.5H_2O$.—This complex was prepared by a method similar to that used by Hidaka, *et al.*[4] Disodium iminodiacetate monohydrate (10 g) was dissolved in water (25 ml); potassium acetate (7.5 g) and $CoCl_2\cdot 6H_2O$ (6 g) were added. The solution was cooled in ice and 15% H_2O_2 (20 ml) was added. After the mixture had been stirred for 20 min, purple crystals were removed (5.8 g). A second fraction of product (1.9 g) was removed after the filtrate was left in the refrigerator for 2 days. After this material had been recrystallized once from warm water, no golden-brown crystals of the *trans*-N isomer could be detected when the sample was examined with a magnifying glass. *Anal.* Calcd for $K[Co(C_4H_5NO_4)_2]\cdot 1.5\ H_2O$: C, 24.81; H, 3.36; N, 7.25. Found: C, 25.02; H, 3.42; N, 7.43.

For the resolution $(-)_{546}$-$[Co(en)_2ox]I$ (8.4 g, 0.022 mol) and silver acetate (3.6 g) were stirred in water (20 ml) at 65°. After several minutes the AgI was removed and washed with 20 ml of water. The wash was added to the filtrate. Solid racemic *cis*-$K[Co(IDA)_2]\cdot 1.5H_2O$ (4.8 g, 0.016 mol) was added to the filtrate at 65°. After the solution had cooled in ice for 90 min, the diastereoisomer with (−)-*cis*-$Co(IDA)_2^-$ was removed (4.1 g). After 4 hr, the other diastereoisomer was removed (3.4 g). These diastereoisomers were fractionally recrystallized from warm water. Yields of resolved diastereoisomer were 2 g with $\Delta\epsilon = -2.3$ at 590 mμ and 0.8 g with $\Delta\epsilon = +2.2$ at 590 mμ. These fractions were separately treated with 1.5 times their weight of KI in a few milliliters of water. The resolving agent was removed and the isomers of *cis*-$K[Co(IDA)_2]$ were precipitated from the filtrate by slowly adding 95% ethanol and cooling in ice. The yields were 0.8 g with $\Delta\epsilon = -2.7$ at 585 mμ and 0.25 g with $\Delta\epsilon = +2.7$. When excess resolving agent was not used in this resolution procedure, racemic *cis*-$K[Co(IDA)_2]$ separated instead of the diastereoisomers.

Preparation of Ethylenediamine-N,N,N′,N′-tetrapropionic Acid, EDTP.—This ligand was prepared by the method which Dwyer and Garvan[3] used for the preparation of 1,2-propanediaminetetraacetic acid. The reagents used were 3-chloropropionic acid (142 g, 1.3 mol), NaOH (87 g, 2.2 mol), and ethylenediamine (14 ml, 0.23 mol). After 6 days some gum had settled to the bottom of the beaker. The supernatant liquid was decanted, cooled in ice, and acidified to pH 2 by gradual addition of concentrated HCl (90 ml). A ball of white gum was removed. The filtrate was evaporated under a stream of air at room temperature to a volume of about 150 ml. White solid (90 g) was removed. This material did not melt below 250°. The filtrate was evaporated to 40 ml, and a white powder was removed (4.8 g, mp 190–195°). About 15 ml of concentrated HCl was added to the filtrate which was cooled in ice. More white powder was removed (7.5 g, mp 190–193°). The white powder was recrystallized once from hot water by cooling in ice. This material was not analyzed, but analysis of the cobalt(III) complex gave the carbon to nitrogen ratio expected for EDTP.

Preparation and Resolution of Potassium Ethylenediamine-N,N,N′,N′-tetrapropionatocobaltate(III) Octahydrate, $K[Co(EDTP)]\cdot 8H_2O$. — Ethylenediamine-N,N,N′,N′-tetrapropionic acid (3.5 g, 0.01 mol) was dissolved in 10 ml of hot water containing potassium acetate (4 g, 0.04 mol). To this solution was added $CoCl_2\cdot 6H_2O$ (2.4 g, 0.01 mol), and the resulting solution was heated quickly to 90°. Eight milliliters of 3% H_2O_2 was gradually added. After 5 min, the purple solution was cooled and evaporated under a stream of air at room temperature to a volume of 15 ml. After the solution had stood in the refrigerator overnight, purple crystals were collected (1.7 g). The filtrate was evaporated to 10 ml, and after 1–2 weeks in the refrigerator, more purple crystals were removed (1.3 g). The purple solid was recrystallized from warm water by cooling in ice. *Anal.* Calcd for $K[Co(C_{14}H_{20}N_2O_8)]\cdot 8H_2O$: C, 28.66; H, 6.19; N, 4.78; C/N, 6.00. Found: C, 29.21; H, 6.30; N, 4.90;

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(3) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959). This ligand was isolated recently by J. A. Weyh and R. A. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

(4) J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **35**, 567 (1962).

C/N, 5.96. The air-dried crystals of K[Co(EDTP)]·$8H_2O$ lost 7 mol of water per mole (21% weight loss) when dried in a vacuum oven at 55° for 24 hr. About 75% of this weight loss was regained when the dried crystals were left standing in air for several days.

For the resolution $(+)_{546}$-[Co(en)$_2$ox]I (3.5 g, 0.009 mol) and silver acetate (1.4 g, 0.0085 mol) were stirred together in 10 ml of warm water for several minutes. The AgI was removed and washed with 10 ml of water. The filtrate was warmed to 60°, and solid K[Co(EDTP)]·$8H_2O$ (3.9 g, 0.0066 mol) was added with stirring. The resulting solution was evaporated under a stream of air at room temperature to 15 ml. Resolving agent which had separated was removed (0.4 g). The filtrate was left in the refrigerator for 4 hr. A fraction of purple diastereoisomer (1.1 g) was removed. The filtrate was evaporated to 10 ml and returned to the refrigerator. After 4 days another fraction of diastereoisomer (1.1 g) was removed. These two fractions were combined and recrystallized twice from warm water. Fractions with $\Delta\epsilon = -2.6$ at 570 mμ (assuming anhydrous 1:1 diastereoisomer, MW = 670) were obtained. If $(-)_{546}$-Co(en)$_2$ox$^+$ was used in place of the $(+)_{546}$ isomer, the diastereoisomer with $\Delta\epsilon = -2.6$ at 570 mμ was obtained. Since optically active Co(EDTP)$^-$ would not crystallize readily as the K$^+$ or Na$^+$ salt, CD data were taken for solutions of the complex. These solutions of the resolved complex were obtained from solutions of the resolved diastereoisomers by removal of the resolving agent with excess sodium perchlorate. The concentrations of Co(EDTP)$^-$ in these solutions were determined from their visible absorption spectra.

Spectra.—Visible absorption spectra were measured on a Cary Model 14 recording spectrophotometer using a tungsten lamp. The CD curves were recorded with a Roussel-Jouan Dichrograph using a Sylvania Sun Gun light source. Spectra were measured at room temperature.

Analyses.—Elemental analyses were performed by Alfred Bernhardt, Elbach, West Germany, and by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Results and Discussion

The circular dichroism and absorption spectra of Co(1,3-PDTA)$^-$, *cis*-Co(IDA)$_2^-$, and Co(EDTP)$^-$ are shown in Figure 1 along with those of Co(EDTA)$^-$. All of the curves have the same general shape, but they differ markedly in intensity. These data are summarized in Table I. The visible spectra for Co(1,3-PDTA)$^-$ and *cis*-Co(IDA)$_2^-$ agree well with those reported previously.[4-6] A resolution of Co(1,3-PDTA)$^-$ has been reported recently,[7] but CD data were not given.

The decrease in intensity of the visible absorption bands of the model compounds relative to Co(EDTA)$^-$ is consistent with the expected decrease in the strain in their chelate ring systems. The vibronic mechanism is generally assumed to account for most of the intensity of these bands, and this mechanism would be expected to be less effective as the rigidity or strain of the ring system is decreased. It is also possible that the strain in the EDTA chelate system makes the symmetry of Co(EDTA)$^-$ lower than that of the model complexes, so the d–d transitions of the former may be more intense for this reason. The maxima of the lower energy absorption bands are shifted toward the red and are more skewed for the model compounds than for Co(EDTA)$^-$.

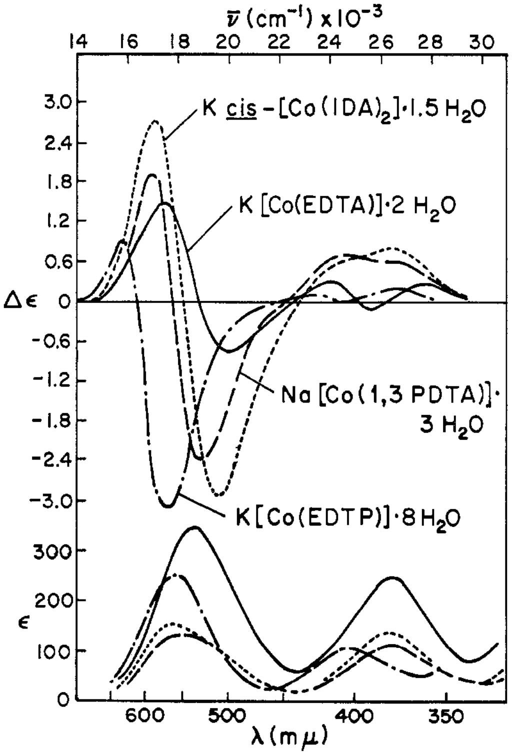

Figure 1.—CD and absorption spectra for $(-)_{546}$-K[Co(EDTA)]·$2H_2O$ and corresponding isomers of Co(1,3-PDTA)$^-$, *cis*-Co(IDA)$_2^-$, and Co(EDTP)$^-$.

These changes could reflect an increased splitting of the levels derived from T_{1g} (O_h), but they could also be due to the vibronic origin of the band intensities.

Although the CD bands in the region of the low-energy absorption band are assumed to arise from transitions from the ground-state to levels derived from T_{1g} (O_h), the energy differences between the maxima of these CD bands are not a reliable guide to the relative splittings between these levels for a series of compounds. This unreliability is due to the fact that the observed CD bands result from the partial cancelation of two (or more) bands of opposite sign. The separation between band maxima is thus very sensitive not only to the separation between the maxima of the canceling bands but also to their half-widths and relative intensities. The CD curves for Co(1,3-PDTA)$^-$ and *cis*-Co(IDA)$_2^-$ are sufficiently similar so that the observed separation between the first two CD maxima which are in the order *cis*-Co(IDA)$_2^-$ > Co(1,3-PDTA)$^-$ probably reflects a similar change in the separations between the maxima of the canceling bands. Since the lower energy visible absorption bands for these compounds are also increasingly skewed in the order *cis*-Co(IDA)$_2^-$ > Co(1,3-PDTA)$^-$, this change may well reflect the amount of splitting of the T_{1g} (O_h) level in the C_2 symmetry of the complex. The CD curves for Co(EDTA)$^-$ and Co(EDTP)$^-$ differ too much in the relative intensities and possibly half-widths of these bands to make such a comparison meaningful.

The lowest energy CD band for $(-)_{546}$-Co(EDTA)$^-$ has a positive rotational strength and has generally been

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(5) N. Tanaka and H. Ogino, *Bull. Chem. Soc. Japan*, **37**, 877 (1964).

(6) M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, *ibid.*, **35**, 75 (1962).

(7) H. Ogino, Y. Takahashi, and N. Tanaka, presented at the 18th Symposium on Coordination Chemistry, Kyoto, Japan, Oct 1968.

TABLE I

ABSORPTION AND CD DATA FOR COBALT(III) HEXADENTATE EDTA TYPE OF COMPLEXES

Compound[a]	Absorption: Peak position, cm^{-1}	Absorption: ϵ	Circular dichroism: Peak position, cm^{-1}	Circular dichroism: $\Delta\epsilon$
$K[Co(EDTA)]\cdot 2H_2O$	18,600	347	17,100	+1.50
			19,800	−0.69
	26,650	246	23,800	+0.28
			25,600	−0.09
			27,600	+0.29
$Na[Co(1,3\text{-}PDTA)]\cdot 3H_2O$	18,200	131	17,000	+1.91
			19,000	−2.41
	26,400	115	24,600	+0.69
$K[Co(IDA)_2]\cdot 1.5H_2O$	17,800	152	17,100	+2.72
			19,600	−2.94
	26,300	135	26,300	+0.79
$K[Co(EDTP)]\cdot 8H_2O$	18,000	253	15,800	+0.88
			17,600	−3.28
	24,800	110	23,300	+0.09
			26,300	+0.18

[a] Data are for isomers for which the rotational strength of the lowest energy CD band is positive.

assigned to the A → A transition.[8,9] This assignment is consistent with both the ring-pairing[10] and octant sign[9] methods of assigning absolute configurations and is also consistent with the empirical observation that the A → A band is usually the dominant one in the region of the lower energy absorption band.[11] The absolute configuration of $(-)_{546}$-Co(EDTA)$^-$ is shown in Figure 2.

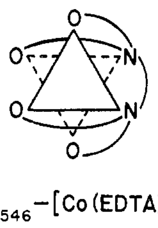

Figure 2.—Absolute configuration of $(-)_{546}$-Co(EDTA)$^-$.

Since by the ring-pairing method[10] the diamine ring makes no contribution to the net chirality of these complexes, the isomers of the three model complexes with the configuration shown in Figure 2 would also have a low-energy A → A transition with positive rotational strength. Because these compounds have the same effective crystal field as Co(EDTA)$^-$ and their CD curves show the same general shape and sign pattern, the lowest energy CD band for each of these compounds is also assigned to the A → A transition. Thus the isomers of the three model complex ions which have a positive rotational strength for the lowest energy CD band are assigned the same absolute configuration as $(-)_{546}$-Co(EDTA)$^-$ (Figure 2). All of these isomers give the less soluble diastereoisomer with $(+)_{546}$-Co(en)$_2$ox$^+$, so this assignment of absolute configuration is also compatible with the solubility rule.[12] This rule states that isomers of similar compounds with the same absolute configuration should form the less soluble diastereoisomer with a given resolving agent.

The two most notable differences between the CD spectra of Co(EDTA)$^-$ and the model compounds are the reversal of the relative intensities of the first two CD bands and the greater net rotational strengths of the model compounds. For Co(EDTA)$^-$ the lowest energy CD band is the dominant one in the region of the low-energy absorption band, but for the model compounds the second CD band has the greater relative intensity. Since the lowest energy CD band is assigned to the A → A transition for all of the compounds, the model complexes are exceptions to the empirical rule[11] that the A → A transition gives the dominant CD band in the region of the low-energy absorption band.

The observed increase in the net rotational strength of the visible transitions of the model compounds relative to Co(EDTA)$^-$ contradicts predictions of the theories of optical activity proposed by Piper[13] and by Liehr.[14] These theories predict that optical activity should be greater the more the ligand atoms are distorted from octahedral positions or the greater the misalignment of metal–ligand bonding orbitals. It seems quite certain, however, that the ligands of the model compounds give more nearly octahedral arrangements of coordinating atoms than does EDTA. Scale molecular models indicate that all of the model complex ions should have rather unstrained ring systems. This prediction is supported by failure of attempts to prepare complexes in which 1,3-PDTA functions as a pentadentate ligand. With EDTA, which forms a strained hexadentate complex ion, pentadentate complexes of the type Co(EDTA)X^{2-} are quite readily formed.

It should be mentioned that since the CD curves being discussed are the resultant of overlapping bands of opposite sign, an apparent increase in net rotational strength could result from increased separation between the maxima of the overlapping bands. The spectra indicate that a slightly increased splitting between these bands is probable for the *cis*-Co(IDA)$_2^-$ and Co(1,3-

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(8) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

(9) C. J. Hawkins and E. Larsen, *Acta Chem. Scand*, **19**, 1970 (1965).

(10) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

(11) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(12) A. Werner, *Chem. Ber.*, **45**, 1229 (1912).

(13) A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

(14) A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).

PDTA)$^-$ ions, but it is doubtful if this increased splitting is great enough to account for the observed increase in net rotational strength. For Co(EDTP)$^-$, the splitting of the T_{1g} (O_h) level appears to be less than that for Co(EDTA)$^-$. The fact that this compound also shows a marked increase in net rotational strength when compared with that of Co(EDTA)$^-$ supports the contention that the net rotational strengths of the d–d transitions of the model complexes are higher than those for the corresponding transitions of Co(EDTA)$^-$.

It is interesting to note that the results of this study, *i.e.*, that an increase in the rotational strength of the d–d transitions accompanies a decrease in strain in systems such as Co(EDTA)$^-$, are compatible with the results for two other compounds studied earlier by Douglas and Haines.[8] The species Co(en)(ox)$_2^-$ and Co(en)(mal)$_2^-$ also have larger net rotational strengths for the d–d transitions than does Co(EDTA)$^-$. Co(en)(mal)$_2^-$, for which the distortion of the coordinating atoms from octahedral positions might be expected to be the least, has the largest net rotational strength for these transitions. There are also three closely spaced CD peaks of alternating signs in the first-band region, a situation ideally suited for reduced intensities from maximum cancelation. This correlation between the results for the model compounds studied previously and those studied in the present work may be strictly fortuitous, however, since the previously studied model compounds differ from Co(EDTA)$^-$ not only in the strain of the ligand system, but also in arrangement of chelate rings and the nature of coordinated atoms. Either of these latter two changes could be responsible for the observed differences in rotational strengths for these compounds and Co(EDTA)$^-$.

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Contribution from the Evans Chemical Laboratory,
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Nickel(II) Complexes of the New Macrocyclic Ligands *meso*- and *rac*-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene

By JACK LEE KARN and DARYLE H. BUSCH

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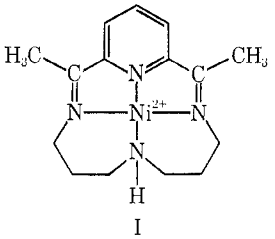
Hydrogenation under mild conditions of the macrocyclic complex 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II), abbreviated Ni(CR)$^{2+}$, yields two new isomeric complexes. The process hydrogenates the two azomethine linkages and produces two asymmetric carbon centers. The observed isomerism is due to the resulting *meso* and racemic ligand forms. Stereochemical considerations and derivatives have permitted identification of the more abundant (~10:1) red isomer as the *meso* structure. The *meso* form folds to admit the donors of bidentate ligands onto pairs of adjacent coordination sites, *e.g.*, oxalate or ethylenediamine. A variety of derivatives Ni(CRH)X$_2\cdot x$H$_2$O [X = Cl, Br, I, ClO$_4$, BF$_4$, NO$_2$, NCS, N$_3$, or 0.5C$_2$O$_4$] have been prepared and characterized.

Introduction

The condensation of 2,6-diacetylpyridine with 3,3′-diaminodipropylamine in the presence of nickel(II) produces the macrocyclic complex cation 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II), hereafter referred to as Ni(CR)$^{2+}$, structure I.



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This complex was first prepared as the perchlorate salt by Curry during an investigation of the reaction of linear polyamines with diacetylpyridine in the presence of metal ions.[1,2] The preparations of Ni(CR)(ZnCl$_4$) and Cu(CR)(ZnCl$_4$) were also reported by Rich and Stucky.[3]

Ni(CR)$^{2+}$ is a diamagnetic, planar complex with unhindered axial sites, and derivatives with coordinating anions comprise a series of paramagnetic, tetragonal complexes. The characterization and spectral and magnetic properties of a number of these complexes have been reported earlier.[4] The present communication concerns the reduction of the azomethine linkages of Ni(CR)$^{2+}$ and the characterization of the ligands produced by this reduction and their nickel(II) complexes.

Experimental Section

Materials.—2,6-Diacetylpyridine was obtained from Aldrich Chemical Co., and 3,3′-diaminodipropylamine was obtained from Matheson Coleman and Bell Chemical Co. and used without further purification. Platinum oxide catalyst was obtained from Matheson Coleman and Bell Chemical Co. All other chemicals were the usual reagent grade materials.

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[1] J. D. Curry, Ph.D. Thesis, The Ohio State University, 1964.

[2] J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964).

[3] R. L. Rich and G. L. Stucky, *Inorg. Nucl. Chem. Letters*, **1**, 85 (1965).

[4] J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966).