the long-wavelength bands are assigned to the $^1T_{1g}$ ← $^1A_{1g}$ transition. The spectrum of $Co(ox)_3{}^{3-}$ has been reported with d–d bands at 16,500 and 23,800 cm^{-1}. From the Tanabe–Sugano diagrams,[11] B is calculated as 532 cm^{-1} and $10Dq$ is 17,600 cm^{-1} for this complex. From the literature,[12] an estimate of $10Dq$ for $Co(phen)_3{}^{3+}$ of 21,250 cm^{-1} leads to a predicted $10Dq$ value in $Co(ox)(phen)_2{}^+$ of 20,000 cm^{-1} compared with the observed value of 20,200 cm^{-1}. The satisfactory agreement here, using the simple average ligand field rule, may perhaps be fortuitous, though Figure 1 shows that there is better separation of the d–d band from the charge-transfer region than is found for the chromium complexes. The visible spectrum of $Co(ox)_2$-phen$^-$ could not be obtained owing to the low solubility of [Co(ox)(phen)$_2$][Co(ox)$_2$phen] and the decomposition that accompanied various metathesis attempts. A similar treatment to that given above has not been applied to the bipyridine complexes for which spectral data on the tris(bipyridine)cobalt(III) ions are lacking.

All of the optically active complexes described in this work are observed to racemize in neutral aqueous solution. (+)-Cr(ox)(bipy)$_2{}^+$ and (+)-Cr(ox)(phen)$_2{}^+$ racemize at very similar rates in water and are decomposed in 0.1 M alkali. In 1 M HCl at 25° Cr(ox)-(phen)$_2{}^+$ racemizes with a half-life of 385 min to be compared with a half-life of 14 min for Cr(ox)$_2$phen$^-$ under the same conditions. The corresponding cobalt-(III) complex, Co(ox)(phen)$_2{}^+$, racemizes very slowly in water (half-life is approximately 10 days at 40°), and the optical inactivation is accelerated by light and also by organic solvents. The last-mentioned cobalt complex does not racemize in 1 M hydrochloric acid. Detailed studies of the mechanisms of racemization and ligand exchange in these complexes will be published subsequently.

Circular Dichroism of Some Ethylenediaminetriacetate Complexes of Cobalt(III)[1]

BY CAROLYN W. VAN SAUN AND BODIE E. DOUGLAS

The preparation and resolution of the series of complexes Co(MEDTA)X$^-$ and Co(YOH)X$^-$ are reported, where MEDTA is the anion of N-methylethylenediamine-N,N′,N′-triacetic acid, YOH is the anion of N-hydroxyethylethylenediamine-N,N′,N′-triacetic acid, and X$^-$ is Br$^-$, Cl$^-$ or NO$_2{}^-$. The absorption spectra and circular dichroism (CD) curves for these complexes are compared with those for the related series of complexes Co(EDTA)X^{2-}. The CD splitting patterns are similar for complexes containing the same monodentate ligand, but significant variations are observed in the intensities of some CD bands, particularly for the NO$_2{}^-$ complexes. The great similarities of the CD curves for Co(MEDTA)X$^-$, Co-(YOH)X$^-$, and Co(EDTA)X^{2-} (X$^-$ = Br$^-$ or Cl$^-$) indicate that the free acetate group in Co(EDTA)X^{2-} does not make a significant contribution to the optical activity of the complex.

Introduction

Circular dichroism (CD) curves have been reported for cobalt(III) complexes containing EDTA acting as a hexadentate[2] or as a pentadentate[3] ligand. The pentadentate EDTA complexes studied previously have the general formula Co(EDTA)X^{2-}, where X$^-$ is Br$^-$, Cl$^-$, or NO$_2{}^-$. The circular dichroism splitting patterns for these complexes were used to relate their absolute configurations to those of Co(EDTA)$^-$. In the present work CD data were obtained for similar complexes with two related pentadentate ligands: N-hydroxyethylethylenediaminetriacetic acid (YOH) and N-methylethylenediaminetriacetic acid (MEDTA). The CD splitting patterns for these complexes are like those reported for the corresponding EDTA complexes so the assignments of configuration made previously hold for these cases also.

Significant variations were found in the intensities of some circular dichroism bands within series of corresponding complexes with differing pentadentate ligands. Such a variation allows the observation of a band in the CD curve of Co(EDTA)Cl^{2-} in 0.1 M hydrochloric acid which is completely hidden in the CD curves of the other chloro complexes. Also one CD peak in the curve for Co(MEDTA)NO$_2{}^-$ is observed as a shoulder in the curves of the other nitro complexes. These observations illustrate the importance of studying series of similar complexes when using CD data for obtaining stereochemical information.

For all of the complexes studied two relatively unstrained geometrical isomers are possible; the X group may be *trans* to either a nitrogen or an oxygen atom. The existence of at least two geometrical isomers has been invoked to interpret kinetic data for the bromo complexes with EDTA and YOH. Previous studies[3,4] and the present work with the optical isomers of these complexes, however, have found no evidence for geo-

(1) This work was supported by a research grant (GM 10829-09) from the Division of General Medical Studies, Public Health Service.
(2) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).
(3) R. A. Haines and B. E. Douglas, *ibid.*, **4**, 452 (1965).
(4) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

metrical isomerism. The least strained isomer should be the one with the X group *trans* to a nitrogen atom, so it is assumed that this was the isomer studied.

Theories of the origin of the optical activity of metal complexes[5,6] lead one to expect that decreasing strain in chelate systems should result in an accompanying decrease in the intensities of the CD peaks (more properly, the rotational strengths) for the d–d transitions. If this relationship holds, then when the strain of hexadentate EDTA complexes is relieved by the formation of pentadentate EDTA complexes, one would expect a significant decrease in CD peak intensities. Such a decrease is not observed.[2,3] From a consideration of the contributions of the five chelate rings in Co(EDTA)$^-$ to the net chirality,[7] it would also be expected that the removal of one chelate ring would decrease the CD intensities. The uncoordinated acetate chain might contribute to the net chirality, however, if there were a preferred conformation resulting, for example, from hydrogen bonding. The complexes reported here were studied to determine the significance of this possible contribution.

Experimental Section

Preparation of N-Methyl(ethylenediamine)-N,N′,N′-triacetic acid (MEDTA).—The method used by Dwyer and Garvan[8] for the preparation of 1,2-propylenediaminetetraacetic acid was used for the preparation of MEDTA. Monochloroacetic acid (94 g, 1 mol) in water (50 ml) was cooled in ice to 10° and a cold solution of sodium hydroxide (80 g, 2 mol) in water (170 ml) was added dropwise. The rate of addition was adjusted so that the temperature of the solution remained below 15°. N-Methylethylenediamine (16.7 g, 19.4 ml, 0.22 mol) was then added. The solution was left standing at room temperature for 6 days and then stored in the refrigerator. Since MEDTA could not be readily isolated in pure form from the reaction solution, cobalt(III) complexes with it were prepared directly from the solution. This procedure was justified by the spectra and analyses of the complexes obtained.

Preparation and Resolution of Sodium Nitro(N-methylethylenediaminetriacetato)cobaltate(III), Na[Co(MEDTA)NO₂].—The nitro complex of Co(III) with MEDTA was prepared by the method of Dwyer and Garvan[4] for the preparation of the corresponding complex with pentadentate EDTA. A portion of the MEDTA preparation solution (2.3×10^{-2} mol of MEDTA assuming a 100% yield) was acidified to pH 6 with concentrated hydrochloric acid. Nine grams of solid sodium cobaltinitrite (2.25×10^{-2} mol) was added and the mixture was heated to 50° with good stirring. The solution became red and NO₂ gas was evolved. After 0.5 hr at 50° the temperature was raised to 85° for 10 min. The solution was cooled and left overnight in the refrigerator. The red solid which separated was recrystallized from a minimum amount of water by addition of 95% ethanol followed by cooling in ice; yield 3.3 g, 38.5% based on Na₃[Co(NO₂)₆]. *Anal.* Calcd for Na[Co(C₉H₁₃N₂O₆)NO₂]: C, 28.96; H, 3.52; N, 11.26. Found: C, 28.75; H, 3.82; N, 11.22.

The silver salt of Co(MEDTA)NO₂$^-$ was used in the resolution procedure because of the high solubility of the diastereoisomers. Silver nitrate (1.2 g, 4.5×10^{-3} mol) and Na[Co(MEDTA)NO₂] (1.6 g, 4.3×10^{-3} mol) were dissolved in minimum amounts of hot water and then quickly combined with stirring. Ag[Co(MEDTA)NO₂] separated quantitatively. For the resolution Ag[Co(MEDTA)NO₂] (2.00 g, 4.3×10^{-3} mol)

and ($-$)₅₄₆-[Co(en)₂(ox)]Br (1.5 g, 4.3×10^{-3} mol) were combined in 12 ml of water at 65° and stirred for 5 min. The silver bromide was removed and washed with 3 ml of warm water. The filtrate was placed in the refrigerator and fractions of the red diastereoisomers were continuously removed as small portions were formed. The CD of the various fractions was measured at the 520-mμ maximum. Fractions with nearly identical Δε values at 520 mμ were combined and fractionally recrystallized from minimum amounts of warm water. After several fractional recrystallizations and recombinations of similar fractions, fractions of diastereoisomers with maximum (-2.8) and minimum (-1.9) values of Δε₅₂₀ were obtained. These fractions were separately ground with three times their weight of sodium iodide in a few drops of water. The resolving agent was removed as the insoluble iodide salt and the optical isomers of Na[Co(MEDTA)-NO₂] were recovered from the filtrates by addition of 95% ethanol. The fractions of diastereoisomer with Δε₅₂₀ = -2.8 gave the isomer of Na[Co(MEDTA)NO₂] with Δε₅₁₇ = -0.4, while fractions of diastereoisomer with Δε₅₂₀ = -1.9 gave the isomer with Δε₅₁₇ = $+0.4$. Under the conditions used, the order of solubilities of the various fractions of diastereoisomer had no reproducible relationship to the intensities of their CD at 520 mμ.

Since the intensities of the major CD bands for Na[Co(MEDTA)NO₂] were only about one-third those for the corresponding pentadentate EDTA complex,[3] the above resolution procedure was repeated using ($+$)₅₄₆-*cis*-[Co(en)₂(NO₂)₂]Br as the resolving agent. The final CD values were the same as those obtained in the [Co(en)₂(ox)]Br resolution. It was also found that recrystallization of partially resolved samples of Na[Co(MEDTA)NO₂] increased their optical activity, but only to Δε = ±0.4 at 517 mμ.

Preparation and Resolution of Sodium Bromo(N-methylethylenediaminetriacetato)cobaltate(III), Na[Co(MEDTA)Br].—Schwarzenbach's method[9] for the preparation of the corresponding pentadentate EDTA complex was used to prepare Na[Co(MEDTA)Br]. A portion of the solution from the MEDTA preparation (3.9×10^{-2} mol of MEDTA assuming 100% yield) was acidified to pH 4 with concentrated hydrochloric acid and placed in a glass-stoppered flask. Solid cobalt(II) chloride hexahydrate (6 g, 2.5×10^{-2} mol) was added, and the resulting solution was cooled to 0°. Bromine (2 ml) in glacial acetic acid (5 ml) was added, and the mixture was left stirring in an ice bath for about 21 hr. At the end of this time the green solution was placed in an evaporating dish under a slow stream of air in the hood and left stirring until it became blue (0.25–1 hr). The solution was then cooled in ice and 95% ethanol (300 ml) was slowly added with stirring. After 20 min a crude blue solid was removed; it was recrystallized from a minimum amount of cold water by adding 95% ethanol and cooling in ice; yield 6.5 g, 63% based on CoCl₂·6H₂O. *Anal.* Calcd for Na[Co(C₉H₁₃N₂O₆)Br]: C, 26.55; H, 3.23; N, 6.88; Br, 19.63. Found: C, 26.63; H, 3.43; N, 7.05; Br, 19.35.

The resolution of Na[Co(MEDTA)Br] was accomplished with ($+$)₅₄₆-Co(en)₂(ox)$^+$. ($+$)₅₄₆-[Co(en)₂(ox)]Br (1.3 g, 3.7×10^{-3} mol) and silver acetate (0.6 g, 3.6×10^{-3} mol) were combined in 40 ml of water at 70° and the mixture was stirred for about 10 min. Silver bromide was removed and washed with warm water (10 ml). The filtrate was warmed to 55° and solid racemic Na[Co(MEDTA)Br] (3 g, 7.4×10^{-3} mol) was added with rapid stirring. The purple diastereoisomer ($+$)₅₄₆-Co(en)₂(ox)–($-$)₅₄₆-Co(MEDTA)Br began to separate at once. The mixture was cooled slowly to room temperature. The diastereoisomer was removed, washed with a few milliliters of cold water, 95% ethanol, and ether, and air dried; yield 1.8 g.

Three grams of sodium perchlorate was added to the filtrate and the solution was left in ice for 15 min. The excess resolving agent which precipitated was removed and Na[($+$)₅₄₆-Co(MEDTA)Br] was fractionally precipitated from the filtrate by addition of 95% ethanol. The first fraction (1.1 g) was nearly racemic (Δε =

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

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

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

(8) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959).

(9) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

−0.3 at 574 mμ); for the second fraction, Δε = −1.4 at 574 mμ.

The diastereoisomer was ground with sodium perchlorate (4.5 g) in a few milliliters of water. After removal of the resolving agent, 95% ethanol was added to the filtrate to precipitate Na[(−)₅₄₆-Co(MEDTA)Br] (1.2 g, Δε = +1.2 at 574 mμ). One recrystallization from a minimum amount of cold water gave fractions with Δε = +1.4 at 574 mμ. Further recrystallization of these fractions did not increase their optical activity.

Preparation and Resolution of Potassium Chloro(N-methylethylenediaminetriacetato)cobaltate(III) Monohydrate, K-[Co(MEDTA)Cl]·H₂O.—K[Co(MEDTA)Br] (3 g, 0.7 × 10⁻² mol) was combined with silver acetate (1.2 g, 0.72 × 10⁻² mol) in 50 ml of water. The mixture was stirred at 70° in a water bath for 15 min. Silver bromide was removed. A concentrated aqueous potassium chloride solution was added dropwise to the purple filtrate until no more silver chloride precipitated. The silver chloride was removed and the filtrate was evaporated to a thick syrup on a steam bath. Concentrated hydrochloric acid (2 ml) was added with stirring and the mixture was evaporated to dryness. The resulting blue mass was cooled and water (10–15 ml) was added while the solid was scraped from the sides of the dish. The solid was precipitated by addition of methanol (50 ml). The crude solid was recrystallized by dissolving in a minimum amount of cold water, adding about 1.5 volumes of ethanol, and cooling in ice; yield 1 g. *Anal.* Calcd for K[Co-(C₉H₁₃N₂O₆)Cl]·H₂O: C, 27.20; H, 3.78; N, 7.06; Cl, 8.95. Found: C, 27.72; H, 3.89; N, 7.14; Cl, 9.06.

Racemic K[Co(MEDTA)Cl]·H₂O was resolved by a procedure identical with that used for Na[Co(MEDTA)Br] except that potassium iodide was used in place of sodium perchlorate. For the two resolved isomers Δε was ±1.5 at 570 mμ.

Preparation and Resolution of Sodium Nitro(N-hydroxyethylethylenediaminetriacetato)cobaltate(III) Monohydrate, Na[Co-(YOH)NO₂]·H₂O.—Na[Co(YOH)NO₂]·H₂O was prepared and resolved by Brushmiller's method[10] using [(+)₅₄₆-cis-Co(en)₂-(NO₂)₂]I as the resolving agent. The optical isomers (Δε = ±0.82 at 520 mμ) obtained had higher optical activity than Brushmiller's samples.

Resolution of Potassium Bromo(N-hydroxyethylethylenediaminetriacetato)cobaltate(III), K[Co(YOH)Br].—K[Co-(YOH)Br] was prepared by the method of Morris and Busch[11] using potassium hydroxide in place of sodium hydroxide. The complex was resolved with [(+)₅₄₆-Co(en)₂(ox)]Br. [(+)₅₄₆-Co(en)₂(ox)]Br (0.6 g, 1.75 × 10⁻³ mol) and silver acetate (0.28 g, 1.7 × 10⁻³ mol) were stirred together in water (10 ml) at 50° for 10 min. Silver bromide was removed and washed with hot water (15 ml). The filtrate was combined with a solution of K[Co(YOH)Br] (1.67 g, 3.5 × 10⁻³ mol) in water (10 ml). The purple diastereoisomer (+)₅₄₆-Co(en)₂(ox)-(−)₅₄₆-Co(YOH)Br began to separate immediately. The mixture was quickly cooled to 25° and then filtered; yield 1.1 g. Ethanol was added to the filtrate to precipitate partially resolved K[(+)₅₄₆-Co(YOH)-Br] (0.7 g).

The diastereoisomer was ground with 2 g of potassium iodide in water (5 ml). The resolving agent was removed and the K[(−)₅₄₆-Co(YOH)Br] was recovered from the filtrate by addition of ethanol. The optical isomers were fractionally recrystallized from cold water by addition of ethanol. Fractions with similar Δε values at 578 mμ were combined and recrystallized until the high, constant values of Δε = ±1.4 at 578 mμ were reached.

Resolution of Potassium Chloro(hydroxyethylethylenediaminetriacetato)cobaltate(III) Sesquihydrate, K[Co(YOH)Cl]·1.5H₂O.—K[Co(YOH)Cl]·1.5H₂O was made by the method of Morris and Busch[11] substituting potassium hydroxide for sodium hydroxide. The potassium salt of the complex is not hygroscopic so it can be handled and stored in air. The complex was re-

solved by the same procedure as that used for K[Co(YOH)Br] above. At 570 mμ the resolved isomers gave Δε = ±1.5.

Complexes with Pentadentate EDTA.—The chloro and bromo complexes with pentadentate EDTA were prepared and resolved by the methods of Dwyer and Garvan.[4]

Spectra.—The absorption spectra were measured on a Cary Model 14 recording spectrophotometer and the CD curves were recorded with a Roussel–Jouan Dichrograph using a Sylvania Sun Gun light source. The optical isomers are identified by the sign of optical rotation at a specified wavelength, *e.g.*, (+)₅₄₆.

Results

In the course of the present work an error was found in the CD data reported[3] for K₂[(+)₅₄₆-Co(EDTA)Cl]·3H₂O. Contrary to the data reported previously, a small positive component of the CD curve at 15,450 cm⁻¹ is not observed for the complex ion in its basic form (*i.e.*, the divalent anion) dissolved in water. The CD curve reported[3] is a composite of data for the complex dissolved in water (λ below 600 mμ) and for the complex dissolved in hydrochloric acid (600–800 mμ). This confusion resulted from the fact that the two portions of the curve were determined independently. This positive component is also observed when K₂-[(+)₅₄₆-Co(EDTA)Cl]·3H₂O is dissolved in a solution containing any one of a variety of other electrolytes such as LiCl, NaCl, KNO₃, or BaBr₂. An example of the variation observed is given in Figure 1. The new peak is most pronounced in 0.1 *M* hydrochloric acid solution and more pronounced in a BaBr₂ solution than in solutions containing the monovalent cations in the same concentration. A similar change is observed in the CD curve of Na₂[(+)₅₄₆-Co(EDTA)Br]·4H₂O in 0.1 *M* hydrochloric acid solution.
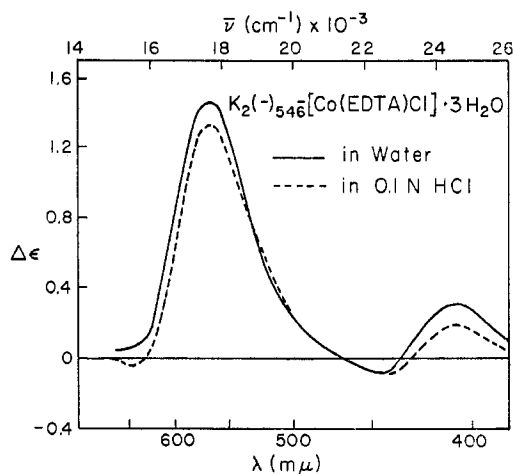
Figure 1.—Circular dichroism *vs.* wave number for K₂[(−)₅₄₆-Co(EDTA)Cl]·3H₂O in water (———) and in 0.1 *N* hydrochloric acid (− − − −).

Table I contains a summary of the absorption and circular dichroism data for the compounds resolved in this study and also data for the related complexes of EDTA reported[2,3] previously. The CD bands in the region of the low-energy absorption band are numbered to indicate corresponding bands for the various complexes with respect to those of Co(EDTA)⁻. The CD

(10) J. G. Brushmiller, Ph.D. Thesis, University of Pittsburgh, Pittsburgh, Pa, 1962.

(11) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

Table I

Absorption and Circular Dichroism Data for Cobalt(III) Pentadentate EDTA-Type Complexes

Compound	Absorption		Circular dichroism		CD band no.[b]
	Cm⁻¹	ε	Cm⁻¹	Δε	
K[(+)₅₄₆-Co(EDTA)]·2H₂O²	18,600	347	17,300	−1.51	I
			19,830	+0.76	II
			(21,750)	(+0.26)[a]	III
	26,650	246	24,050	−0.29	
			27,900	−0.33	
K₂[(−)₅₄₆-Co(EDTA)Cl]·3H₂O	17,100	220	15,500	−0.05	I
in 0.1 M HCl			17,700	+1.33	II
	24,750	190	22,800	−0.10	
			24,400	+0.20	
K₂[(−)₅₄₆-Co(EDTA)Cl]·3H₂O³	17,100	250	17,700	+1.48	II
	24,750	221	22,350	−0.07	
			24,650	+0.30	
K[(−)₅₄₆-Co(YOH)Cl]·1.5H₂O	17,100	278	17,600	+1.45	II
	24,800	251	22,500	−0.03	
			24,600	+0.31	
K[(−)₅₄₆-Co(MEDTA)Cl]·H₂O	17,300	210	17,500	+1.50	II
	24,800	188	22,400	−0.04	
			24,600	+0.14	
Na₂[(−)₅₄₆-Co(EDTA)Br]·4H₂O³	17,050	293	17,500	+1.44	II
	25,050	282	22,100	−0.08	
			24,300	+0.27	
Na[(−)₅₄₆-Co(YOH)Br]	17,000	241	17,350	+1.41	II
	25,000 sh	243	22,200	−0.05	
			24,100	+0.28	
Na[(−)₅₄₆-Co(MEDTA)Br]	17,100	215	17,420	+1.38	II
	24,900	216	22,300	−0.04	
			24,100	+0.18	
Na₂[(+)₅₄₆-Co(EDTA)NO₂]·3H₂O³	17,100 sh	116	17,150	−1.01	I
	20,050	236	19,450	+1.13	II
			21,750 sh	+0.32	III
	29,400	3410	24,450	−0.25	
Na[(+)₅₄₆-Co(YOH)NO₂]·H₂O	17,100 sh	110	17,300	−0.69	I
	20,200	232	19,200	+0.82	II
			21,800 sh	+0.35	III
	29,200	3470	24,200	−0.26	
Na[(+)₅₄₆-Co(MEDTA)NO₂]	17,100 sh	90	17,400	−0.33	I
	20,300	182	19,300	+0.40	II
			21,800	+0.32	III
	29,400	3100	24,600	−0.21	

[a] From Gaussian analysis. [b] Numbers denote corresponding CD bands with respect to those of K[Co(EDTA)].

and absorption curves for the chloro and bromo complexes with the three pentadentate ligands are all very similar (Figures 2 and 3). The intense absorption below 400 mμ is characteristic of the bromo complexes, not of the YOH complexes. Unlike the pentadentate EDTA complexes, however, the chloro and bromo complexes with YOH and MEDTA do not show a change in their CD curves in the 15,400-cm⁻¹ region in the presence of acid or other cations.

The absorption curve for the nitro complexes is shown in Figure 4. The shape and position of the bands are nearly the same for all three complexes, but the intensities of the maxima for the MEDTA complex are about 20% lower than those for the other two complexes. The CD curves (Figure 5) also have similar shapes and positions of bands, but the two bands of lowest energy show marked variations in intensity through the series. The CD curves are nearly the same for the nitro complexes in hydrochloric acid solution, except for Na₂[Co(EDTA)NO₂] for which there are some variations in peak heights.

Discussion

Three CD peaks³ are apparent in the region of the low-energy absorption band for (−)₅₄₆-Co(EDTA)-NO₂²⁻, giving a curve very similar to that² of (−)₅₄₆-Co(EDTA)⁻ so that these two complexes were assigned the same configurations.³ The CD curves for the opposite isomers of (+)₅₄₆-Co(YOH)NO₂⁻ and (+)₅₄₆-Co(MEDTA)NO₂⁻, shown in Figure 5 along with that of (+)₅₄₆-Co(EDTA)NO₂²⁻, are obviously those of complexes of the same configuration. The (+)₅₄₆-Co-(EDTA)Cl²⁻ and (+)₅₄₆-Co(EDTA)Br²⁻ ions were assigned the same configurations as (−)₅₄₆-Co(EDTA)-NO₂²⁻ and (−)₅₄₆-Co(EDTA)⁻ on the basis of the similar sign patterns of their CD curves.³ It has been shown that the conversion (+)₅₄₆-Co(EDTA)X²⁻ → (−)₅₄₆-Co(EDTA)⁻ + X⁻ (X⁻ = Cl⁻ or Br⁻) proceeds with no loss of optical activity.⁴ Hence, the chirality of the pentadentate portion of the EDTA ligand must be unchanged in the conversion. The CD data reported here, Figures 1–3 and Table I, make it
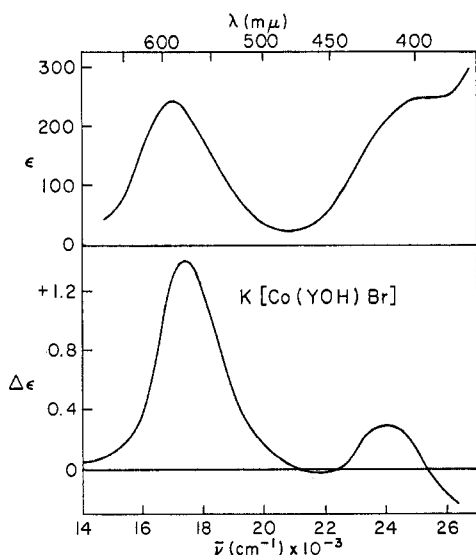
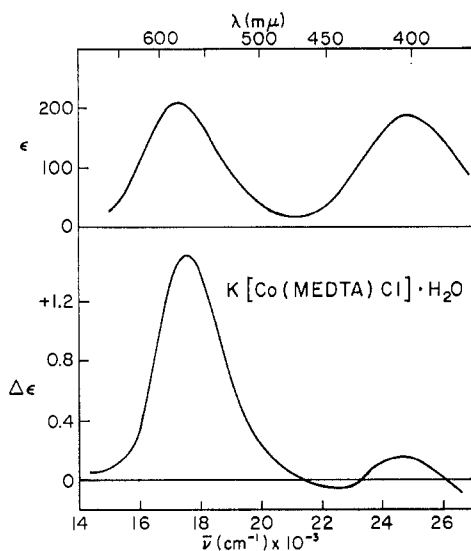Figure 2.—Circular dichroism and molar absorptivity *vs.* wave number for $K[(-)_{546}\text{-}Co(YOH)Br]$.

Figure 3.—Circular dichroism and molar absorptivity *vs.* wave number for $K[(-)_{546}\text{-}Co(MEDTA)Cl]\cdot H_2O$.

clear that the $(-)_{546}$-chloro and -bromo complexes with YOH and MEDTA have the same configuration as $(-)_{546}\text{-}Co(EDTA)Cl^{2-}$, since their CD curves have the same form throughout.

In the region of the low-energy absorption band, one sees only one CD peak with a shoulder of the same sign at higher frequency for the chloro and bromo complexes (Figures 2 and 3). These are considered to correspond to CD bands II and III of $Co(EDTA)^-$. A new peak (I), with sign opposite that of the major peak (II), is observed for $Co(EDTA)Cl^{2-}$ in the presence of acid or other electrolytes (see Results section and Figure 1). This new peak indicates that there should be three peaks in this region as observed for $Co(EDTA)NO_2{}^{2-}$ and, with the aid of Gaussian analysis, $Co(EDTA)^-$. Presumably this weak peak is obscured by the much more intense neighboring peak (II) in the absence of added electrolytes. The appearance of the third peak upon addition of electrolytes for
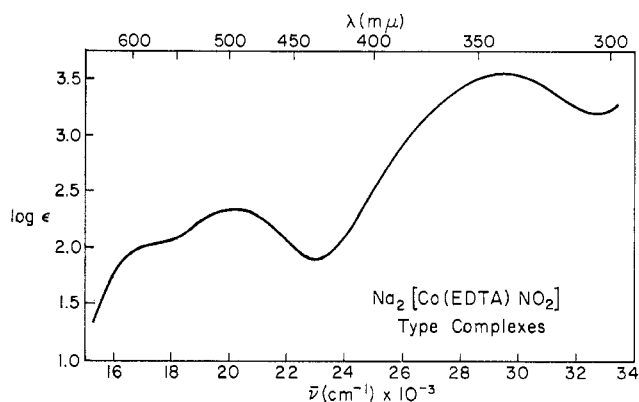

Figure 4.—Log (molar absorptivity) *vs.* wave number for the nitro complexes with EDTA, MEDTA, or YOH.
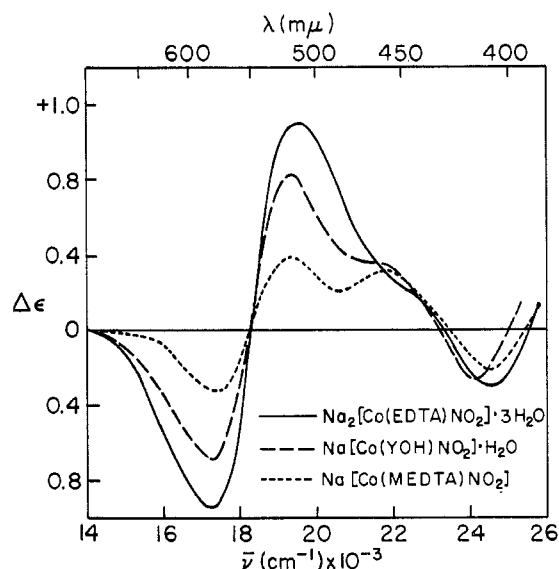

Figure 5.—Circular dichroism *vs.* wave number for the $(+)_{546}$ isomers of the nitro complexes with the various pentadentate ligands.

$Co(EDTA)Cl^{2-}$ gives the same sign pattern, $+$, $-$, $-$ or $-$, $+$, $+$, as for the corresponding isomers of $Co(EDTA)^-$ with the same configuration. The association of a cation with the free carboxylate group or the enhanced association with the doubly negative anionic complex presumably alters the electrostatic environment of the cobalt(III) in such a way that the weak band (I) is no longer hidden by the dominant peak of opposite sign (II). The shape of curves of this type involving overlapping bands of opposite sign is very sensitive to slight changes in the position or intensity of either band. Shapes of CD curves are known to be affected greatly by added electrolytes.[12,13] Since the nitro complexes (Figure 5) show three CD bands in the region of the low-energy absorption band, there are no hidden CD bands and no changes in the general appearance of the curve are observed for $Na_2[Co(EDTA)\text{-}NO_2]$ in acid solution.

The intensities of the first two low-energy CD bands

(12) H. L. Smith and B. E. Douglas, *J. Am. Chem. Soc.*, **86**, 3385 (1964); *Inorg. Chem.*, **5**, 784 (1966).

(13) S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 339 (1964); R. Larsson, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, A, 301 (1966).

of the bromo and chloro complexes are notably different from those of the corresponding bands for Co(EDTA)⁻. The intensity of the second CD band is approximately twice that for Co(EDTA)⁻ while the intensity of the first band approaches zero for the pentadentate complexes. These changes may be due in part to the very low symmetry of the pentadentate complexes. If approximate C_s symmetry is assumed, one might expect transitions polarized perpendicular to the plane containing the halide ion to have quite different rotational strengths from those polarized parallel to this plane. Another factor which probably contributes to this change in intensities is the decrease in strain in the EDTA chelate system. For complexes similar to Co(EDTA)⁻ in which the strain of the chelate system has been reduced by enlarging or eliminating the five-membered diamine ring, the intensity of the second CD band is increased more than is that of the lowest energy band.[14]

The CD curves of the bromo and chloro complexes do not vary significantly with the pentadentate ligand used, indicating the relative unimportance of the acetate or hydroxyethyl side chain. By contrast the CD curves for the nitro complexes change markedly as the pentadentate ligand is varied (Figure 5). Possibly the sensitivity of the CD spectra of the nitro complexes to the nature of the pentadentate ligand is due to the π-bonding ability of the nitro group. The π-bonding of the nitro group could be affected by hydrogen bonding to the hydroxyethyl chain or through water to the ace-

tate chain. The electronegativity of the variable portion of the pentadentate ligand cannot explain the observations since the order $-CH_2CH_2OH > -CH_3 > -CH_2COO^-$ is not consistent with the trend of the change in the CD curves. The coordinated nitrogens to which these groups are attached are asymmetric but it is unlikely that this factor would cause variation within the nitro series but not within the series of halide complexes. Thus, although steric and electrical properties of the pentadentate ligands apparently affect the interaction of the nitro group with the metal ion, the exact reason for the changes observed is not now known.

Since the total areas of CD bands in the low-energy region are comparable for Co(EDTA)⁻, Co(EDTA)X²⁻, Co(MEDTA)X, and Co(YOH)X⁻ (X⁻ = Cl⁻ or Br⁻), coordination of the fourth acetate group must make little contribution to the total rotational strength of Co(EDTA)⁻. The small contribution found is contrary to predictions that increasing the number of chelate rings or the strain in a chelate complex should increase its rotational strength. Also the uncoordinated acetate group in Co(EDTA)X²⁻ (X⁻ = Cl⁻ or Br⁻) apparently makes no significant contribution to the optical activity; this group would be expected to contribute significantly to the optical activity only if it is in a preferred conformation.

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CONTRIBUTION FROM THE ISTITUTO CHIMICO "G. CIAMICIAN" DELL'UNIVERSITA, CENTRO NAZIONALE DI CHIMICA DELLE RADIAZIONI E DEI RADIOELEMENTI, SEZIONE III, BOLOGNA, ITALY, AND ISTITUTO CHIMICO DELL' UNIVERSITA, CENTRO NAZIONALE DI CHIMICA DEI COMPOSTI DI COORDINAZIONE ED ELEMENTO ORGANICI, FERRARA, ITALY

Photochemical Reactions of Nitropentaamminecobalt(III) Ion

BY V. BALZANI, R. BALLARDINI, N. SABBATINI, AND L. MOGGI

The photochemical behavior of $Co(NH_3)_5NO_2^{2+}$ has been investigated in aqueous solution and in the solid state. Excitations have been performed by radiations at 254, 313, 365, and 442 mμ, corresponding to charge-transfer and ligand-field bands of the complex. The nature of the photoreactions has been established by spectrophotometric measurements in the uv, visible, and ir spectral regions and by chemical analyses of some of the reaction products. In aqueous solution at all of the wavelengths of irradiation, the oxidation–reduction decomposition involving the NO_2^- ligand and the nitro → nitrito linkage isomerization occur simultaneously. In the solid state the nitro → nitrito isomerization occurs at all of the wavelengths of irradiation, accompanied at 254 mμ by a minor oxidation–reduction decomposition. For aqueous solutions the quantum yields of the two photoreactions have been determined. They decrease with decreasing energy of the exciting radiations, but their ratio is almost wavelength independent. The mechanisms of the photoreactions are discussed, and it is proposed that the same photoreactive excited state is involved, independent of the wavelength of irradiation. On the basis of the data obtained, it is also concluded that, even in solution, the linkage photoisomerization must occur through an intramolecular mechanism.

Transition metal complexes may undergo three principal types of photoreactions: (1) photoxidation–reduction reactions, involving changes in oxidation number of metal and/or ligand(s); (2) photosubstitution reac-

tions (generally, photoaquations), involving changes in the composition of the coordination shell; (3) photoisomerization reactions, involving changes in the coordination arrangement of the ligands.