$(Me_2dtc)_5$, 63866-82-0; $(NH_4)_2OsCl_6$, 12125-08-5; $K_2(NOsCl_5)$, 23209-29-2; $Fe(Et_2dtc)_3$, 13963-59-2.

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Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Circular Dichroism and Carbon-13 Nuclear Magnetic Resonance Studies of Some Phenyl-Substituted Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate Analogues

GARY G. HAWN, CHENG A. CHANG, and BODIE E. DOUGLAS*

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The cobalt(III) complexes containing the *l*-stilbenediamine-*N*,*N*,*N'*,*N'*-tetraacetate ion, $[Co(l\text{-sdta})]^-$, and the xylylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate ion, $[Co(xdta)]^-$, have been synthesized and characterized by circular dichroism and carbon-13 nuclear magnetic resonance spectroscopy. Both complexes are analogues of $[Co(edta)]^-$ (edta = ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate ion). The complex $[Co(l\text{-sdta})]^-$ contains a benzene ring bonded to each carbon of the ethylenediamine backbone, producing two asymmetric centers. The formation of the complex is stereoselective, yielding only one optical isomer. The complex $[Co(xdta)]^-$ has a benzene ring incorporated into the ethylenediamine backbone, producing a seven-membered ring when coordinated. Although studies indicated that the complex may be somewhat labile, resolution by fractional recrystallization after diastereoisomer formation was successful. The absorption, circular dichroism, ^1H NMR, and ^{13}C NMR spectra are reported and compared to those of other cobalt(III) sexidentate complexes. The phenyl groups appear to be the cause of some unusual behavior.

Introduction

The two model compounds $[Co(l\text{-sdta})]^-$ and $[Co(xdta)]^-$ (Figure 1) are related to $[Co(edta)]^-$, a complex which has been thoroughly investigated by absorption, circular dichroism (CD), and X-ray studies.[1,2] Van Saun and Douglas[3] reported a series of complexes where the strain in the chelate ring systems was varied, but the type of coordinated atoms was kept the same as for $[Co(edta)]^-$. The series included (1,3-propanediaminetetraacetato)cobaltate(III), $[Co(1,3\text{-pdta})]^-$, and [*cis*(*N*)-bis(iminodiacetato)]cobaltate(III), *cis*-$[Co(ida)_2]^-$, in which the backbone diamine ring was enlarged and eliminated, respectively. The complex (ethylenediaminetetrapropionato)cobaltate(III), $[Co(edtp)]^-$, in which both the "in-plane" (G) and "out-of-plane" (R) rings were enlarged, was also included. The intensities of the visible absorption bands are less for these model compounds, as would be predicted because of the decrease in ring strain. However, the CD spectra show an increase in net rotational strength for the less-strained model complexes, a result not expected from some theories of optical activity.[4,5]

The complex ions (1,2-propanediaminetetraacetato)cobaltate(III), $[Co(pdta)]^-$, and (*trans*-1,2-cyclohexanediaminetetraacetato)cobaltate(III), $[Co(cdta)]^-$, were prepared by Dwyer and Garvan.[6] These compounds are related to $[Co(edta)]^-$, containing one and two asymmetric centers, respectively, in the backbone. They found that the preparation of both complexes is stereospecific; that is, only one isomer forms when an optically active ligand is used to synthesize the complex. This was due to the fact that the methyl group in the pdta complex prefers an equatorial position and the cyclohexanediamine ring in the edta complex prefers one particular conformation. Brennen et al.[7] reported the CD spectra of $(-)_{546}$-$[Co\text{-}(+)\text{-pdta}]^-$ and $(-)_{546}$-$[Co\text{-}(+)\text{-cdta}]^-$. They found that the spectrum of the pdta complex was very similar to the spectrum of $[Co(edta)]^-$, whereas, the spectrum of the cdta complex, while similar to the other two, showed a high-energy peak in the $^1T_{1g}$ region with greater intensity. The authors concluded that the asymmetric carbon in the pdta complex has little effect on the CD spectra; on the other hand, there was a greater contribution from the cdta ligand on the CD spectra. Soma and Mizukami[8] prepared a cobalt(III) complex which contains *cis*-2-butene-1,4-diamine-*N*,*N*,*N'*,*N'*-tetraacetate. A seven-membered ring is formed upon coordination. The CD and ^1H NMR spectra were similar to those of analogous complexes.

The two model complexes $[Co(l\text{-sdta})]^-$ and $[Co(xdta)]^-$ were synthesized to study the effects of the benzene rings on the spectra. The polarizability theory of optical activity[9–14] indicates that phenyl groups, which possess a large and anisotropic polarizability, may exert a large influence on CD spectra. Also, it was of interest to investigate the stereospecificity of complex formation of $[Co(l\text{-sdta})]^-$.

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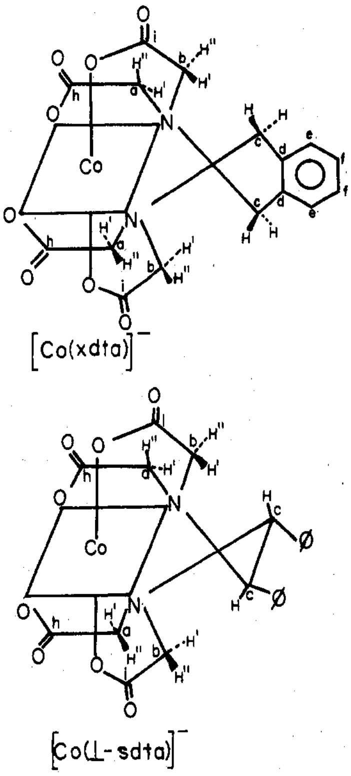

Figure 1. The [Co(xdta)]⁻ and [Co(*l*-sdta)]⁻ complexes with the same absolute configuration as that of $(-)_{546}$-[Co(edta)]⁻.

The ^{13}C NMR spectra of [Co(edta)]⁻ and several other related sexidentates have been reported.[15] The ^{13}C NMR of [Co(*l*-sdta)]⁻ and [Co(xdta)]⁻ are of interest for the study of the effects of the benzene rings and to verify that the complexes are sexidentate. The ^{1}H NMR spectra are also reported; the phenyl groups can produce either a shielding or a deshielding effect on the protons depending on where the protons are located relative to the phenyl groups. Assignments of peaks have been made by using both ^{1}H NMR and ^{13}C NMR.

Experimental Section

Two methods are used for the identification of optical isomers, the sign of rotation of plane-polarized light at a specific wavelength, e.g., $(+)_{589}$, and the sign of the low-energy CD peak in the $^1T_{1g}$ region, (+) or (−). Ethylenediamine-*N*-*N'*-diacetic acid was obtained from LaMont Laboratories, and *d*,*l*-isoamarine and most organic reagents were obtained from Aldrich Chemical Co. Elemental analyses were performed by Calgon Analytical Laboratories, Pittsburgh, PA, and Integral Microanalytical Laboratories Inc., Raleigh, NC.

Preparation and Resolution of *d*,*l*-1,1-Diamino-1,2-diphenylethane (*d*,*l*-Stilbenediamine), *d*,*l*-stien. Preparation and resolution procedures of Lifschitz and Bos[16] and Williams and Bailar[17] were modified as follows.

a. Preparation of *d*,*l*-*N*-Acetyl-*N'*-benzoylstilbenediamine. A mixture of 100 g (0.335 mol) of *d*,*l*-isomarine and 4 g (0.05 mol) of anhydrous sodium acetate was dissolved in 175 mL of acetic anhydride and heated at a gentle reflux for 3 h. The reaction mixture was cooled, acidified (300 mL of H_2O and 25 mL of concentrated HCl), heated on a steam bath for 2 h, and filtered. The melting point of the air-dried product was 251 °C, and the yield was quantitative.

b. Preparation of *d*,*l*-Stilbenediamine Dihydrobromide. A mixture of 113 g of *d*,*l*-*N*-acetyl-*N'*-benzoylstilbenediamine, 200 mL of glacial acetic acid, and 400 mL of HBr (45–47%) was refluxed for 24 h. The reaction mixture was cooled in an ice bath. The precipitate was filtered, washed with acetone and ether to remove benzoic acid, and air-dried. The yield was 60.3 g.

c. Preparation of *d*,*l*-Stilbenediamine. The dihydrobromide salt was dissolved in 250 mL of H_2O and made basic by the addition of saturated NaOH solution while keeping the temperature below 20 °C. After $^1/_2$ h of stirring, the precipitate was filtered and recrystallized from hot ligroin. The melting point was 82 °C, and 34 g of product was isolated, about a 50% yield based on *d*,*l*-isoamarine.

d. Preparation of *l*-Stilbenediamine *d*-Tartrate. A mixture of 31 g (0.146 mol) of *d*,*l*-stilbenediamine in 250 mL of hot ethanol and 21.4 g (0.146 mol) of *d*-tartaric acid in 150 mL of hot ethanol was stirred for 15 min, cooled, and filtered. The tartrate salt was recrystallized twice from 200 mL of warm water to which 150 mL of hot ethanol was added. The product gave $[\alpha]_D = -11°$ in water. The yield was 22.5 g or 85.1%. The *d*-stilbenediamine *d*-tartrate was obtained by evaporation of the filtrate and by fractional recrystallization, giving a constant $[\alpha]_D = +44°$ in water.

e. Preparation of *l*-Stilbenediamine. Ten grams of *l*-stilbenediamine *d*-tartrate dissolved in 100 mL of water was neutralized by addition of 4.0 g of KOH, keeping the temperature below 20 °C. The product was recrystallized from hot ligroin, giving $[\alpha]_D = -87°$ in ether and −108° in methanol. The yield was 4.2 g or 71.7%. The *d*-stilbenediamine was obtained in the same manner.

Preparation of *l*-Stilbenediamine-*N*,*N*,*N'*,*N'*-tetraacetic Acid, *l*-H_4sdta. This ligand has been synthesized previously;[18] however, attempts to repeat the synthesis yielded only a white syrupy product and not a crystalline material as reported. A mixture of 2.7 g (0.0127 mol) of *l*-stilbenediamine in 50 mL of methanol and 17.6 g (0.127 mol) of bromoacetic acid (previously neutralized below 10 °C) in 30 mL of water was stirred and heated at 40 °C. A 7 M NaOH solution was added intermittently to maintain the pH at 10–11. The methanol was removed by rotary evaporation, the solution was cooled, and the pH was adjusted to 1.0–1.5 to give a white syrupy mass.

Preparation of Potassium (*l*-Stilbenediaminetetraacetato)cobaltate(III) Tetrahydrate, K[Co(*l*-sdta)]·4H_2O. Since the ligand *l*-H_4sdta could not be isolated in crystalline form, the white syrupy material was used to prepare the complex. The complex was prepared on the basis of 100% yield of *l*-H_4sdta in the preceding preparation. The ligand was dissolved in 200 mL of H_2O by adding 2.03 g (0.0308 mol) of NaOH. A solution of 3.02 g (0.0127 mol) of $CoCl_2·6H_2O$ in 20 mL of H_2O was added and the solution was air oxidized for 24 h. The sodium salt could not be crystallized and crystals of the silver salt darkened after a few days even if kept in the dark. The complex was converted to its potassium salt by ion-exchange chromatography to give 2.2 g of purple crystals of K[Co(*l*-sdta)]·4H_2O.

Only one optical isomer should form and after two recrystallizations $\Delta\epsilon_{595} = +0.95$ did not change. It is possible that some racemization of *l*-H_4sdta could occur during its preparation, so the complex was resolved with $(+)_D$-[Co(en)$_2$ox]I·H_2O. For the resolution, 1.5 g (0.0025 mol) of Ag[Co(*l*-sdta)] and 1.1 g (0.0025 mol) of $(+)_D$-[Co(en)$_2$ox]I·H_2O were stirred at 60 °C for 15 min. The AgI was filtered and the solution was evaporated in a stream of air. Only the (+) isomer was found in any of the fractions. After combining fractions, two recrystallizations gave a fraction with a constant $\Delta\epsilon_{587} = +0.87$ (assuming an anhydrous 1:1 diastereoisomer, mol wt 766). The diastereoisomer was converted to K[Co(*l*-sdta)] by passing it through a Dowex 50W-X8 cation-exchange resin in the potassium form. After one recrystallization the $\Delta\epsilon_{595} = +0.95$ remained constant. Anal. Calcd for K[Co(*l*-sdta)]·4H_2O: C, 43.28; H, 4.59; N, 4.59. Found: C, 43.10; H, 4.05; N, 4.49.

Preparation of Dimethyl Iminodiacetate. The method used here is a modification of a process outlined in a U.S. patent.[19] Ninety-five grams (1.0 mol) of iminodiacetonitrile was dissolved in 750 mL of anhydrous methanol. A lecture bottle of HCl gas (312 g) was used to add the HCl at reflux over a period of 1 h. The mixture was refluxed for 3 h, cooled, and concentrated to one-third of its volume on a rotary evaporator. The remaining solid, which was a mixture of the hydrochloride salt of dimethyliminodiacetate and ammonium chloride, was filtered and air-dried. The hydrochloride salt was dissolved in water and then neutralized with $NaHCO_3$, and the ester was extracted with chloroform. The identity and purity of the product obtained by evaporation of $CHCl_3$ were confirmed by NMR. The yield was 48 g or 36%.

Preparation of α,α'-Diamino-*o*-xylene-*N*,*N*,*N'*,*N'*-tetraacetic Acid (Xylylenediaminetetraacetic Acid), H_4xdta. This ligand was prepared according to the method of Ando and Ueno[20] where α,α'-dibromo-*o*-xylene was condensed with dimethyl iminodiacetate followed by hydrolysis of the ester to yield the free acid.

Preparation and Resolution of Silver (Xylylenediaminetetraacetato)cobaltate(III) Hemihydrate, Ag[Co(xdta)]·0.5H_2O. A solution of 5.7 g (0.0155 mol) of H_4xdta, which was neutralized with 2.5 g (0.062 mol) of NaOH, and 3.7 g (0.0155 mol) of $CoCl_2·6H_2O$ was air oxidized for 48 h in the presence of activated charcoal. After the

Table I. Circular Dichroism and Absorption Data for $[Co(l\text{-sdta})]^-$ and $[Co(xdta)]^-$

compd[a]	absorption		CD	
	$10^{-3}\bar{\nu}$, cm^{-1}	ϵ	$10^{-3}\bar{\nu}$, cm^{-1}	$\Delta\epsilon$
(+)-$Ag[Co(xdta)]\cdot 0.5H_2O$	16.61	158	15.87	+6.43
			17.86	−6.32
	25.00	201	22.73	+0.83
			25.77	+1.80
(+)-$K[Co(l\text{-sdta})]\cdot 4H_2O$	18.42	295	16.81	+0.95
			18.80	−2.57
	26.18	219	24.10	+0.43
			27.78	+0.42

[a] The optical isomers are designated (+), the sign of the low-energy CD band in the $^1T_{1g}$ region.

charcoal was filtered off, the solution was evaporated to dryness. Attempts to form crystals of the sodium salt failed, so the silver salt was obtained as blue crystals. The yield was 6.7 g or 80.0%.

For the resolution, 6.7 g (0.0124 mol) of $Ag[Co(xdta)]\cdot O.5H_2O$ and 5.1 g (0.0124 mol) of $(+)_D$-$[Co(en)_2ox]I\cdot H_2O$ were stirred in 100 mL of water at 60 °C for 15 min. The AgI was filtered and the solution was evaporated in a stream of air. The solubilities of the two diastereoisomers were very similar, so many recrystallizations had to be made to purify them. Also, it appears that racemization of the diastereoisomer occurred, because the $\Delta\epsilon$ value of a solution decreased a few percent each day. A much larger amount of the (+) isomer was obtained because of racemization of the more soluble (−) isomer on standing; a constant $\Delta\epsilon$ of the expected magnitude for the (−) isomer could not be obtained. The (+) isomer was recrystallized six times, with $\Delta\epsilon_{630}$ varying from +7.66 to +8.41 (assuming an anhydrous 1:1 diastereoisomer, mol wt 790). The diastereoisomer was converted to the potassium salt by ion exchange, but crystals could not be obtained, so the silver salt was formed. The $\Delta\epsilon$ dropped drastically from approximately +8.0 for the diastereoisomer to +2.0 for the enantiomer. After five recrystallizations, a constant $\Delta\epsilon_{630}$ = +6.45 was reached. Anal. Calcd for $Ag[Co(xdta)]\cdot O.5H_2O$: C, 35.56; H, 3.15; N, 5.18. Found: C, 35.57; H, 3.14; N, 5.19.

Spectral Measurements. The visible absorption spectra were recorded on a Cary recording spectrophotometer Model 14 using a tungsten lamp. The spectra were measured in 1-cm quartz cells at room temperature in either methanol or water. Sample concentrations were in the range of 10^{-3} M.

The CD spectra were recorded on a Cary Model 61 CD spectropolarimeter using a xenon arc source. Spectra were measured in 1-cm quartz cells in either aqueous or methanol solutions with concentrations in the range of 10^{-3}–10^{-4} M (absorbance values were less than 1.0 for all CD measurements).

Proton magnetic resonance spectra were recorded on a Varian Associates A-60D Analytical NMR spectrometer using DSS (sodium 3-(trimethylsilyl)-1-propanesulfonate) as the internal reference in D_2O. Carbon-13 nuclear magnetic resonance spectra were recorded on a JEOL, Inc., JNM-FX60 Fourier transform NMR spectrometer operating at approximately 15 MHz in the ^{13}C mode. Most spectra were recorded in the broad-band random-noise ^1H-decoupling mode, with the field frequency ratio stabilized by locking to the sample solvent, D_2O. Samples were placed in 8–10-mm coaxial tubes with benzene as the external standard in the outer coaxial tube (δ 128.7 downfield from Me_4Si, tetramethylsilane).

Results and Discussion

The complexes $[Co(l\text{-sdta})]^-$ and $[Co(xdta)]^-$ which contain phenyl substituents are analogues of $[Co(edta)]^-$. Although their absorption, CD, ^1H NMR, and ^{13}C NMR spectra are similar to those of $[Co(edta)]^-$ and other cobalt(III) sexidentates, there are some significant differences.

Absorption and Circular Dichroism Spectra. The absorption and CD spectra of $[Co(edta)]^-$ and related compounds are shown in Figure 2. The absorption and CD spectra of $[Co(l\text{-sdta})]^-$ and $[Co(xdta)]^-$ are shown in Figure 3 with the corresponding data listed in Table I.

The absorption and CD spectra of $[Co(l\text{-sdta})]^-$ are similar to the spectra of the previously described less-strained model compounds of $[Co(edta)]^-$ (Figure 2). The absorption maxima are shifted toward the red and the intensities are less than for $[Co(edta)]^-$. Also, the high-energy peak in the $^1T_{1g}$ region of the CD spectrum is more intense than the low-energy peak.

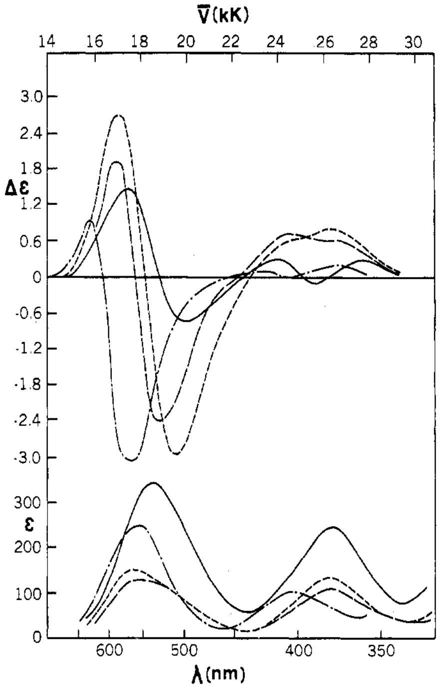

Figure 2. Absorption and circular dichroism spectra of $[Co(edta)]^-$ (—), $[Co(1,3\text{-pdta})]^-$ (- - -), $[Co(edtp)]^-$ (–·–), and *cis*-$[Co(ida)_2]^-$ (···).[3]

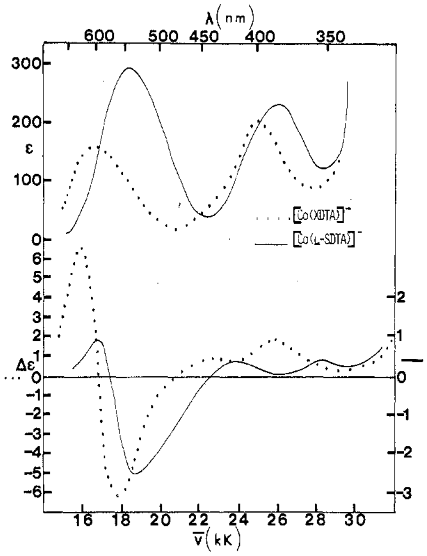

Figure 3. Absorption and circular dichroism spectra of $[Co(l\text{-sdta})]^-$ and $[Co(xdta)]^-$.

Van Suan and Douglas[3] have shown that the isomers of the three less-strained model compounds which have a positive rotational strength for the lowest energy CD band are related to $(-)_{546}$-$[Co(edta)]^-$ (Figure 1) in absolute configuration. Therefore, $[Co(l\text{-sdta})]^-$ which also has a low-energy positive CD band is assigned the same absolute configuration. Just as pdta coordinates stereospecifically, *l*-sdta also coordinates stereospecifically because the two benzene rings prefer equatorial positions. Since *l*-stilbenediamine (*l*-stien) has the (*S,S*) absolute configuration,[21] only one isomer forms, the same isomer as predicted from the CD study.

The CD spectrum of $[Co(l\text{-sdta})]^-$ is more similar to those of the less-strained model compounds than to that for $[Co(edta)]^-$, but there is no enlargement of rings in $[Co(l\text{-sdta})]^-$.

The presence of phenyl groups in the backbone may weaken the structure of the complex. While [Co(*l*-sdta)]$^-$ appears to be stable to acid and base in both aqueous and alcohol solutions, some degradation of the complex was noted after heating at 60 °C for several hours in a 2.0 M acidic solution.

The maximum $\Delta\epsilon$ values for [Co(*l*-sdta)]$^-$ were obtained by repeated recrystallizations. Although only one isomer forms upon coordination and optically pure *l*-stien was used as starting material for the preparation of *l*-sdta, it was possible that some racemization of *l*-sdta could have occurred during its preparation because of the basic environment. Because of the possibility of some racemization occurring, [Co(*l*-sdta)]$^-$ was resolved with [Co(en)$_2$ox]$^+$ (see Experimental Section). Many different fractions of the diastereoisomer were obtained and recrystallized but in no case was any of the opposite isomer found. Conversion of the diastereoisomer to the potassium salt gave the enantiomer with the same $\Delta\epsilon$ as before resolution. We have assumed the resolution to be successful and the $\Delta\epsilon$ values reported to be the maximum values. The amount of racemization of *l*-sdta during its preparation appears to be minimal and fractional recrystallization of [Co(*l*-sdta)]$^-$ removed any trace amounts of [Co(*d*-sdta)]$^-$ which may have formed.

The other [Co(edta)]$^-$ analogue prepared in this study, [Co(xdta)]$^-$, exhibited a marked difference from any previously prepared edta model compound. The absorption and CD spectra along with the corresponding data are seen in Figure 3 and Table I. Unlike other *cis*-N_2O_4 sexidentates, which are always red-violet or purple, [Co(xdta)]$^-$ is blue. The color of the complex suggested initially that cobalt is in the +2 oxidation state and not +3 or that the complex is quinquedentate with a water molecule or chloride ion occupying the sixth coordination site. The visible absorption spectrum shows two maxima which is indicative of Co^{3+} and not Co^{2+}. The ^{13}C NMR spectrum, which will be discussed later, confirms that the complex is sexidentate.

The complex [Co(xdta)]$^-$ contains a seven-membered ring in its backbone so the strain would be expected to be less than for [Co(edta)]$^-$. A model of [Co(xdta)]$^-$ shows that the seven-membered ring is locked into a fairly rigid conformation because of the benzene ring, but there appears to be much less strain in the G rings than for [Co(edta)]$^-$. Actually, the absorption and CD spectra of [Co(xdta)]$^-$ are similar in some respects to the spectra of the less-strained model compounds. The visible absorption maxima are shifted to lower energy, indicating that xdta is a weaker field ligand, and the intensities are much weaker than for [Co(edta)]$^-$. The CD spectrum of [Co(xdta)]$^-$ has two bands of opposite sign in the $^1T_{1g}$ region but unlike the bands for [Co(edta)]$^-$ or the model compounds, they are of approximately equal intensity.

The most significant feature of the CD spectrum of [Co(xdta)]$^-$ is the unusually large $\Delta\epsilon$ values. The values are more than twice as large as any $\Delta\epsilon$ value in the d–d absorption region for any of the less-strained model compounds and 4 times greater than the maximum $\Delta\epsilon$ value for [Co(edta)]$^-$. The first absorption band is unsymmetrical with a shoulder on the higher energy side, indicating greater splitting of the components than for [Co(edta)]$^-$. An increase in splitting would reduce the extent of mutual cancellation of the two components and enhance their intensities. The complex was resolved into its optical isomers with [Co(en)$_2$ox]$^+$ (see Experimental Section). Although a constant $\Delta\epsilon$ value was reached, there were some difficulties encountered during the resolution procedure. The diastereoisomers appeared to be in an equilibrium which favored the (+) isomer. Much more of the (+) isomer was isolated and it was never possible to attain a maximum $\Delta\epsilon$ value for the (−) fraction of diastereoisomer. In fact, mixtures of (−) fractions often yielded (+) fractions after recrystallization. Also, even though the (+) fraction of the diastereoisomer was recrystallized to a fairly constant $\Delta\epsilon$ value of approximately +8.0, this value decreased several percent each day on standing. When the diastereoisomer was converted to the potassium salt via ion-exchange chromatography, the $\Delta\epsilon$ value decreased drastically, to about +2.0. The potassium salt could not be recrystallized, yielding only a glassy substance, but the complex could be isolated in crystalline form as the silver salt. Fortunately, the optical purity of Ag[Co(xdta)] was increased by fractional recrystallization to a constant $\Delta\epsilon$ value of +6.43. In the same manner that the less-strained model compounds are related to the absolute configuration of $(-)_{546}$-[Co(edta)]$^-$ because the low-energy peaks in the CD spectra are positive,[3] the absolute configuration for the (+) isomer of [Co(xdta)]$^-$ is assigned the same as for $(-)_{546}$-[Co(edta)]$^-$.

Table II. ^1H NMR Chemical Shifts for Glycinate Protons in Cobalt(III) Aminocarboxylates[a]

	R rings (out-of-plane)		G rings (in-plane)	
	H_b'	H_b''	H_a'	H_a''
[Co(edta)]$^-$ [b]	3.94	3.81	3.89	3.57
[Co(cdta)]$^-$ [b]	4.23	3.37	3.83	3.54
[Co(xdta)]$^-$	3.29		3.85	3.07
[Co(*l*-sdta)]$^-$	3.09	4.03	4.37	3.40

[a] Chemical shifts in ppm relative to DSS. [b] Data are taken from ref 24.

While these two novel complexes, [Co(*l*-(sdta)]$^-$ and [Co(xdta)]$^-$, exhibit many features which are similar to other previously studied *cis*-N_2O_4 sexidentates, some unusual behavior has been noted. However, unpredictable behavior with complexes containing *l*-stien has been noted before. The complex [Co(*l*-stien)$_3$]$^{3+}$ gives a CD spectrum which differs significantly in magnitude from other analogous tris(alkyl-substituted-1,2-diamine)cobalt(III) complexes.[22] Phenyl groups have a large and anisotropic polarizability and some theoretical models[9–13,21] predict that such groups may produce unpredictable CD spectra. The substitution of phenyl groups into the edta analogues studied in this work seems to support these theories.

Proton Magnetic Resonance. The proton NMR spectra of both [Co(*l*-sdta)]$^-$ and [Co(xdta)]$^-$ are of interest since the ring current of a phenyl group can produce either shielding or deshielding effects on the protons depending on where the protons are located relative to the phenyl group. Table II lists the assigned ^1H NMR chemical shifts for glycinate protons in [Co(xdta)]$^-$ and [Co(*l*-sdta)]$^-$ together with their model complexes [Co(edta)]$^-$ and [Co(cdta)]$^-$. The spectrum of [Co(xdta)]$^-$ shows one AB quartet centered at 3.46 ppm with a coupling constant of 15.7 Hz and two singlets at 3.29 and 3.85 ppm, respectively. There are three kinds of methylene protons: "in-plane" (G) and "out-of-plane" (R) glycinate rings and the benzyl backbone. Another singlet at 7.36 ppm in the spectrum clearly indicates the phenyl-ring protons. From framework molecular model studies, it is seen that the R-ring methylene protons are located very closely on top of the phenyl-ring plane. Therefore it is very likely that the ring current would shield the R-ring methylene protons. The benzyl methylene protons are nearly in the same plane as the phenyl ring and would be predicted to be deshielded.[23] Assuming other factors affecting the chemical shifts are small, we assign the singlet at 3.85 ppm to the benzyl methylene proton resonance, the AB quartet to the G-ring methylene proton resonance, and the singlet at 3.29 ppm to the R-ring methylene proton resonance. These assignments were checked by measuring the 250-MHz ^1H NMR spectrum. In the 250-MHz spectrum the singlet at 3.89 ppm and the AB quartet are maintained; however, the singlet at 3.29 ppm is split to a quartet. Computer analysis of the spectrum indicates that this new quartet has a coupling constant of 17.28 Hz while the other is 15.66 Hz. This finding is consistent with the known R- and G-ring methylene proton geminal coupling constants of 18 and 16 Hz, respectively. The low-field doublet of the G-ring AB pattern is assigned to the proton H_a' resonance (on carbon a; see Figure 1). The high-field one is then assigned to the H_a'' proton resonance. This assignment is made by analogy with [Co(cdta)]$^-$ and [Co(edta)]$^-$.[24] The H_a'' protons are more shielded than the corresponding ones in the model complexes, probably due to the ring-current effect and minor conformational change causing different anisotropic shielding by C–N bonds.[25]

The ^{1}H NMR spectrum of [Co(*l*-sdta)]$^-$ shows one singlet at 7.43 ppm, one singlet at 5.56 ppm, and two AB pattern quartets centered at 3.89 and 3.56 ppm, respectively. The two singlets are assigned to the phenyl-ring protons and *l*-stilbenediamine backbone protons, respectively, due to their characteristic chemical shifts and relative peak intensities. The quartet centered at 3.89 ppm has a corresponding coupling constant of 16 Hz (G ring), while the coupling constant of the other quartet is 19 Hz (R ring).

The assignments of the four doublets constituting the two quartets of the [Co(*l*-sdta)]$^-$ spectrum are more difficult than for the [Co(xdta)]$^-$ spectrum. The benzyl backbone of [Co(xdta)]$^-$ forms a seven-membered chelate ring with a fixed conformation. The conformation of the stilbenediamine backbone of [Co(*l*-sdta)]$^-$ is also fixed, but the phenyl groups can rotate partially. A time-average spectrum is expected for the phenyl groups. There are two doublets constituting the R-ring proton AB pattern centered at 3.09 and 4.03 ppm. The doublet at 3.09 ppm is assigned to the H_b' proton which is located within the shielding range of the benzene rings. The other one at 4.03 ppm is then assigned to H_b'' (see Figure 1). Similar assignments are made for the G-ring AB pattern for the doublets centered at 3.40 ppm.

Carbon-13 Magnetic Resonance. The noise-decoupled ^{13}C NMR spectra of both [Co(xdta)]$^-$ and [Co(*l*-sdta)$^-$ are very simple indicating the complexes are sexidentate. In the spectrum of [Co(xdta)]$^-$, the three peaks farthest upfield are assigned to the three sets of methylene carbons. The detailed assignments have been made by both selective-decoupling (double-resonance) and acid-catalyzed deuteration techniques. The selective-decoupling technique is applied by irradiating the sample at a constant frequency corresponding to the resonance of a certain type of proton while the ^{13}C NMR spectrum is accumulating.[26] Only the carbon resonance which has its protons irradiated at their ^{1}H NMR frequency should remain as a singlet with great intensity. By irradiating separately at the proton resonance ranges 3.29, 3.46, and 3.85 ppm, we could assign the ^{13}C peaks at 60.20, 64.58, and 65.39 ppm to the resonances of the benzyl methylene, G-ring methylene, and R-ring methylene carbons, respectively. The acid-catalyzed deuteration experiment was also performed to ensure the assignment of R-ring methylene carbon resonance. Blackmer and Vickrey have shown that by deuterium exchange the peak for the carbon which has had the hydrogen replaced by deuterium will decrease in intensity or vanish due to the loss of the nuclear Overhauser effect.[15] Their studies on the ^{13}C NMR spectra of [Co(edta)]$^-$, [Co(cdta)]$^-$, and [Co(pdta)]$^-$ confirm that the less-strained R ring undergoes deuterium exchange while the more-strained G ring does not. This result is consistent with earlier findings based on a study of ^{1}H NMR spectra of the same compounds.[27] The deuterium exchange reaction performed on [Co(xdta)]$^-$ shows that the peak at 65.39 ppm loses its spectral intensity although minor decomposition occurs. Thus the experiment confirms the assignment of the R-ring methylene carbon resonance. The chemical shift order of R-ring and G-ring methylene carbon resonances indicates that [Co(xdta)]$^-$ is more similar in overall structural arrangement to [Co(edta)]$^-$ than to related complexes containing[28,29] six-membered backbones.

Table III. ^{13}C NMR Chemical Shifts of Some Cobalt(III) Aminocarboxylates[a]

	methylene			carbonyl		
	G	R	back-bone	G	R	benzene
[Co(edta)]$^-$ [b]	65.8	66.0	64.0	182.4	183	
[Co(cdta)]$^-$ [c]	65.1	59.3	73.3, 26.8, 23.8	183.1	183.7	
[Co(xdta)]$^-$	64.58	65.39	60.2	180.32	181.61	130.48, 131.78, 133.57
[Co(*l*-sdta)]$^-$	66.99	60.03	77.08	182.59	183.57	130.32, 131.13 132.11, 133.24

[a] Chemical shifts are corrected using benzene carbon of 128.7 ppm relative to Me_4Si as an external standard. [b] Data are taken from ref 31. [c] Data are taken from ref 32.

The three peaks in the benzene carbon chemical shift range are easily assigned to the three kinds of benzyl-ring carbons. The middle one at 131.78 ppm is assigned to the d carbon resonance since in an off-resonance spectrum it remains as a singlet indicating that no protons are attached to these carbons. The other two peaks at 130.48 and 133.57 ppm are assigned to the f and e carbons on the basis of the intuitive fact that the f carbon resonance should be close to that of pure benzene since they are farthest removed from the coordination center. The carbonyl carbon resonances at 180.32 and 181.61 ppm are assigned, respectively, to the G-ring and R-ring carbonyl carbons as for [Co(edta)]$^-$ and [Co(cdta)]$^-$.[15,31,32]

The assignments of the ^{13}C NMR spectrum of [Co(*l*-sdta)]$^-$ have been made similarly. The peak at 60.03 ppm disappeared after a deuterium exchange reaction. The peak at 77.08 ppm is assigned to the methine carbons because the partially decoupled (off-resonance decoupled) spectrum showed that this peak was split into a doublet while the peaks at 60.03 and 66.99 ppm were split into triplets.

The aromatic carbons are assigned to the four peaks in the region 130–133 ppm on the basis of the intensities of the peaks. While the two weaker peaks probably represent carbons d and g and the two larger peaks result from e and f, the order within each set is not known for certain. The two downfield peaks at 182.59 and 183.57 ppm are assigned to the in-plane and out-of-plane carbonyl peaks according to the chemical shift order observed for those of [Co(edta)]$^-$, [Co(cdta)]$^-$, and other model complexes. The ring current of benzene seems to have little effect on carbon resonances in either complex, if there is any.

In [Co(*l*-sdta)]$^-$, the R-ring methylene carbon resonance is upfield from that of the G-ring methylene carbon. This is an indication of a steric compression shift of R-ring methylene carbon resonance since, upon complexation of *l*-sdta, the backbone phenyl groups stereospecifically interact with R-ring methylene protons and it is well-known that this kind of steric interaction shifts the corresponding carbon resonance upfield.[33] If we assume the chelate structure is similar to that of [Co(edta)]$^-$, the degree of steric interactions may be revealed by the chemical shift separation of the R-ring and G-ring methylene carbon resonances. The greater the interaction, the greater the upfield shift of the R-ring methylene carbon resonance and the larger the chemical shift separation of R-ring and G-ring methylene carbon resonances.[34] This separation observed is the least (0.2 ppm) for [Co(edta)]$^-$ but it increases through $[Co(cdta)]^-$ (5.8 ppm) to $[Co(\textit{l}\text{-}sdta)]^-$ (6.9 ppm). In terms of the size of the backbone substituents, it is easy to rationalize that $[Co(\textit{l}\text{-}sdta)]^-$ would have the largest chemical shift separation between R-ring and G-ring methylene carbons. Table III lists the ^{13}C NMR chemical shifts and their assignments for $[Co(xdta)]^-$ and $[Co(\textit{l}\text{-}sdta)]^-$ together with those for model complexes $[Co(edta)]^-$ and $[Co(cdta)]^-$.

Registry No. Ag[Co(xdta)], 69596-90-3; K[Co(*l*-sdta)], 69596-91-4; *l*-stilbenediamine *d*-tartrate, 29841-69-8; *l*-stilbenediamine *d*-tartrate, 69576-66-5; *d,l*-stilbenediamine, 16635-95-3; *d,l*-stilbenediamine dihydrobromide, 69576-64-3; *d,l*-*N*-acetyl-*N'*-benzoylstilbenediamine, 69576-65-4; *d,l*-isoamarine, 33722-46-2; dimethyl aminodiacetate, 6096-81-7; iminodiacetonitrile, 628-87-5.

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Contribution from the Department of Chemistry, Faculty of Science,
Tohoku University, Aoba, Aramaki, Sendai 980, Japan

Stoichiometric, Kinetic, and Mechanistic Investigations of the Reactions of O-Bonded (Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)pentaamminecobalt(III) Complex and Its Related Complexes with Hexaaquachromium(II) Ions

HIROSHI OGINO,* KEIICHI TSUKAHARA, and NOBUYUKI TANAKA[†]

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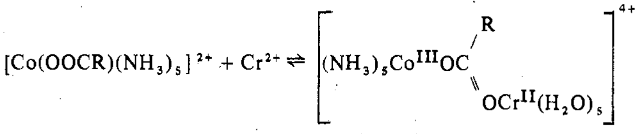
The products of the reactions of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, and $[Co(edta)]^-$ with $[Cr(H_2O)_6]^{2+}$ in acid solutions were separated with the aid of SP-Sephadex column chromatography and identified from the chromatographic behavior, visible absorption spectra, and chemical analyses of chromium and/or cobalt ions. Three chromium(III) complexes were newly characterized as the reaction products: $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co(H_nedta)Cr(H_2O)_5]^{(n+2)+}$, and $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$. From the determination of the quantitative product distribution, stoichiometry of the reactions was established. Then, kinetic measurements were made for these reactions. On the basis of these results, the mechanisms of the reactions are discussed.

Introduction

Many studies on the electron-transfer reactions of cobalt(III) complexes with hexaaquachromium(II) ions (Cr^{2+}) have been carried out. Through the characterization of the chromium(III) complexes produced in these reactions, attempts to infer the structures of the precursor and/or activated complexes have also been made. These studies provide not only the information on the mechanisms of the electron-transfer reactions but also, sometimes, an elegant way for the preparation of novel chromium(III) complexes.

In the chromium(II) reductions of (carboxylato)pentaamminecobalt(III) complexes ($[Co(OOCR)(NH_3)_5]^{2+}$), Cr^{2+} is believed to attack the carbonyl oxygen to form a precursor complex I.[1]



$$[Co(OOCR)(NH_3)_5]^{2+} + Cr^{2+} \rightleftharpoons \left[(NH_3)_5Co^{III}OC\overset{R}{\diagup}{=}OCr^{II}(H_2O)_5\right]^{4+}$$

I

$$\rightarrow Co^{2+} + [Cr(OOCR)(H_2O)_5]^{2+} + 5NH_4^+ \quad (1)$$

The rate constants of reaction 1 lie in the range of 10^{-3}–10 $M^{-1}\ s^{-1}$.[2] However, if the $RCOO^-$ ligand contains such an appropriate functional group that the ligand can serve to chelate Cr^{2+}, it is known that the electron-transfer reaction is accelerated.[3]

It was found, in this work, that the reactions of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, and $[Co(edta)]^-$ with Cr^{2+} ions in acid solutions gave various chromium(III) products.[4]

[†] Presently working at the Department of Chemistry, Faculty of Science, Shimane University, Nishikawatsucho, Matsue 690, Japan.

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