Table IV. Analytical Data (%)

	C		H		Co		Other		
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$Ph_3GeCo(CO)_3P(OPh)_3$	61.82	61.72	3.99	3.81	7.78	7.81			
$Ph_3SnCo(CO)_3P(OPh)_3$	58.31	58.38	3.76	3.78	7.34	7.30	14.78	14.56	(Sn)
$Ph_3PbCo(CO)_3P(OPh)_3$	52.53	52.61	3.39	3.52	6.61	6.68	23.23	22.82	(Pb)
$(CH_3)SnCo(CO)_3P(OPh)_3$	46.71	47.09	3.92	3.93	9.55	9.58	19.24	19.46	(Sn)
$Cl_3SnCo(CO)_3P(OPh)_3$	37.19	37.95	2.23	2.36	8.69	8.19	15.67	15.05	(Cl)
$Hg[Co(CO)_3P(OPh)_3]_2$	45.56	45.23	2.73	2.73	10.65	10.51	18.12	18.01	(Hg)
$Ph_3SnCo(CO)_3P(OCH_3)_3$	46.71	46.93	3.92	4.16	9.55	9.51	19.24	19.51	(Sn)
$Ph_3SnCo(CO)_3P(OC_2H_5)_3$	49.20	49.09	4.59	4.49	8.94	8.16	18.01	18.71	(Sn)
$Ph_3SnCo(CO)_3PPh_3$	62.02	61.99	4.00	3.99	7.80	7.80	15.72	15.36	(Sn)
$Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$	57.00	57.05	6.09	6.20	8.48	8.50	17.07	16.54	(Sn)
$Ph_3SnCo(CO)_2[P(OPh)_3]_2$	61.96	62.19	4.18	4.49	5.43	5.46	10.93	10.69	(Sn)
$Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$	43.79	44.32	4.66	4.70	8.26	8.33	16.64	16.78	(Sn)

30 min the yellow solution was filtered and added to 1.5 g (3.9 mmol) of $(C_6H_5)_3SnCl$ in 10 ml of THF. The mixture was stirred for 30 min and solvent removed under vacuum. The residue was washed with water and purified by recrystallization from methanol.

$(C_6H_5)_3SnCo(CO)_2[P(OC_6H_5)_3]_2$. In the glove box $ClCo(CO)_2[P(OC_6H_5)_3]_2$ was prepared according to the procedure of Hieber and Duchatsch.[12] A procedure of the same workers[13] was then employed to obtain a solution of 2.7 mmol of $NaCo(CO)_2[P(OC_6H_5)_3]_2$ in 125 ml of THF. To this was added 10 ml of THF containing 1.05 g (2.7 mmol) of $(C_6H_5)_3SnC$); the mixture was then stirred for 15 min. Solvent was removed under vacuum. The product was extracted with benzene. After filtration the desired product was precipitated as an off-white solid by addition of pentane.

$(C_6H_5)_3SnCo(CO)_2[P(OCH_3)_3]_2$. $CH_3Co(CO)_2[P(OCH_3)_3]_2$ was prepared using the procedure described by Heck.[14] In the glove box 4.9 g (12.1 mmol) of this material was dissolved in 10 ml of THF. A solution of 0.7 g (13 mmol) of $NaOCH_3$ in 15 ml of methanol was added and the mixture stirred for several hours. The solvent was removed under vacuum and the residue washed with pentane, filtered, and dried. It was stirred with 25 ml of THF and added to a solution of 4.8 g (12.2 mmol) of $(C_6H_5)_3SnCl$ in 20 ml of THF. The mixture was stirred 30 min and solvent removed under vacuum. The residue was stirred with methanol and filtered. The product was obtained as an off-white solid upon recrystallization from pentane.

Analytical data for all the compounds are presented in Table IV.

Registry No. $NaCo(CO)_3P(OC_6H_5)_3$, 32138-74-2; $(C_6H_5)_3GeCl$, 1626-24-0; $[Co(CO)_3P(OC_6H_5)_3]_2$, 21118-36-5; $SnCl_4$, 7646-78-8; $HgCl_2$, 7487-94-7; $NaCo(CO)_3P(C_6H_5)_3$, 33570-17-1; $(C_6H_5)_3SnCl$, 639-58-7; $NaCo(CO)_3P(n\text{-}C_4H_9)_3$, 29477-05-2; $NaCo(CO)_2[P(OC_6H_5)_3]_2$, 14564-38-6; $Ph_3GeCo(CO)_4$, 30406-47-4; $Ph_3SnCo(CO)_3P(OCH_3)_3$, 42989-50-4; $Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$, 42989-51-5; $Ph_3SnCo(CO)_3P(OPh)_3$, 42929-50-0; $Ph_3SnCo(CO)_2[P(OPh)_3]_2$, 42989-52-6; $Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$, 42989-53-7; $Ph_3GeCo(CO)_3P(OPh)_3$, 42989-54-8; $Ph_3PbCo(CO)_3P(OPh)_3$, 42989-55-9; $(CH_3)_3SnCo(CO)_3P(OPh)_3$, 42989-56-0; $Cl_3SnCo(CO)_3P(OPh)_3$, 42989-57-1; $Hg[Co(CO)_3P(OPh)_3]_2$, 42989-58-2; $Ph_3SnCo(CO)_3P(OC_2H_5)_3$, 42989-59-3; $Ph_3SnCo(CO)_3P(Ph)_3$, 36158-66-4.

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Circular Dichroism of Diamine-*uns-cis*-Trimethylenediamine-*N*,*N*′-diacetatocobalt(III) Complexes

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A series of cobalt(III) complexes containing trimethylenediamine-*N*,*N*′-diacetate anion (TMDDA) and ammonia, ethylenediamine (en), trimethylenediamine (tn), 2,2′-dipyridyl (dipy), or 1,10-phenanthroline (phen) in the remaining two coordination positions were prepared and their optical isomers resolved. From the absorption and circular dichroism (CD) spectra the complexes are concluded to be the uns-cis isomers. The absorption and CD spectra for newly resolved *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$ and newly prepared and resolved *uns-cis*-$[Co(EDDA)(tn)]^+$ are also reported. It was found that the central chelate ring size of EDDA and TMDDA and the ring size of bidentate ligands affect the shape of CD spectra in the same fashion.

Introduction

Circular dichroism (CD) studies[1-5] of Co(III) complexes with either ethylenediamine-*N*,*N*′-diacetate (EDDA) or the *N*,*N*′-dimethyl (DMEDDA) or *N*,*N*′-diethyl (DEEDDA) derivative coordinated in the s-cis geometry have been carried out extensively during the past several years. These s-cis complexes have been of interest because their CD spectra seem to depend primarily on the EDDA backbone[1,3,5] and the contribution from the asymmetric nitrogens.[4] The uns-cis isomers have been studied less extensively because of the difficulty in their isolation.[6] Legg[7] separated the four isomers of *uns-cis*-$[Co(EDDA)(S\text{-}pn)]^+$ by ion-exchange chromatography and *uns-cis*-$[Co(EDDA)dipy]^+$ has been resolved.[8] The preparation of *uns-cis*-EDDA

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cobalt complexes containing oxalate and malonate was reported.[9,10] Recently good yields of *uns-cis*-EDDA–Co complexes containing 1,10-phenanthroline, 2,2′-dipyridyl, ethylenediamine, or ammonia were reported.[11,12] It was of interest to study complexes of trimethylenediamine-*N,N*′-diacetic acid (H_2TMDDA) as an EDDA type ligand containing a larger diamine backbone. The *uns-cis*-TMDDA–Co complexes containing ammonia, ethylenediamine, trimethylenediamine, 2,2′-dipyridyl, or 1,10-phenanthroline in the remaining two coordination positions were prepared and their optical isomers resolved. For comparison, *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$ and *uns-cis*-$[Co(EDDA)(tn)]^+$ were prepared and resolved to determine the effects of changes in the diamine ligands.

Experimental Section

Preparation of Trimethylenediamine-*N,N*′-diacetic Acid Dihydrochloride, H_2TMDDA·2HCl. Chloroacetic acid (378 g, 4 mol) was dissolved in 500 ml of water and cooled in an ice bath. A cooled solution of NaOH (160 g. 4 mol) in 320 ml of water was added dropwise, the rate of addition being adjusted so that the temperature remained below 20°. Trimethylenediamine (148.2 g, 2 mol) was added to the above solution and then NaOH (160 g, 4 mol) in 320 ml of water was added little by little. The temperature was kept between 90 and 100° during this time (2 hr). Then the solution was neutralized with 560 ml of 6 *N* hydrochloric acid and concentrated to *ca.* 700 ml with a rotary evaporator. To this viscous slurry was added 600 ml of concentrated hydrochloric acid with stirring. A large amount of NaCl was separated by filtration. To the filtrate was added 600 ml of concentrated HCl, 600 ml of ethanol, and 600 ml of ether, and the resulting solution was cooled in an ice bath for *ca.* 4 hr. A white precipitate formed which was separated by filtration. The crude product was recrystallized from a water–ethanol (1:2) mixture; yield 36.8 g. *Anal.* Calcd for H_2TMDDA·2HCl = $C_7H_{16}N_2O_4Cl_2$: C, 31.95; H, 6.13; N, 10.65. Found: C, 31.88; H, 6.14; N, 10.61.

Preparation of Hydrogen Dichloro(trimethylenediamine-*N,N*′-diacetato)cobalt(III) Hemihydrate, H[Co(TMDDA)Cl_2]·0.5H_2O. Trimethylenediamine-*N,N*′-diacetic acid dihydrochloride (26 g), NaOH (12 g), and $CoCl_2·6H_2O$ (23 g) were dissolved in 380 ml of water. The solution was warmed in a water bath at *ca.* 80° for 3 hr. During this time 150 ml of 3% H_2O_2 and 4 g of NaOH in 20 ml of water were added little by little. The addition of NaOH was completed at an early stage of the oxidation. A purple complex precipitated gradually during the oxidation. After the solution was cooled in an ice bath, the insoluble purple complex was separated by filtration and washed with water, ethanol, and then ether. This solid complex was suspended in a small amount of water, 160 ml of concentrated hydrochloric acid was added, and the mixture was concentrated on a steam bath using an air stream. The green complex which crystallized gradually was filtered and washed with ethanol and then ether; yield 16.8 g. *Anal.* Calcd for $H[Co(C_7H_{12}N_2O_4)Cl_2]·0.5H_2O$: C, 25.63; H, 4.30; N, 8.54. Found: C, 25.93; H, 4.11; N, 8.25.

The crude complex was dissolved in a small amount of water, the solution was filtered, concentrated hydrochloric acid was added to the filtrate, and the mixture was warmed for a while. Deep green crystals used for elemental analyses were separated and washed with 6 *N* hydrochloric acid, ethanol, and then ether. The aquation of this complex is very fast in water.

Preparation and Resolution of *uns-cis*-Trimethylenediamine-*N,N*′-diacetato(ethylenediamine)cobalt(III) Chloride, *uns-cis*-[Co(TMDDA)(en)]Cl. Fifteen grams of the above dichloro complex in 1200 ml of water was warmed at *ca.* 65° for 25 min. The color changed from green to blue and finally violet. To the solution was added 300 ml of an aqueous solution containing 5.5 g of ethylenediamine, whereupon the color changed to light red at once. After the solution was cooled in an ice bath, a small amount of insoluble purple complex was filtered off. The filtrate was concentrated to 500 ml with a rotary evaporator, and a trace of insoluble purple complex was separated again. The filtrate was concentrated to near dryness with a rotary evaporator. The red complex was separated by filtration and washed with ethanol and then ether. The complex was recrystallized from an ethanol–water (1:1) mixture. Red rod-shaped crystals were separated and washed with ethanol and then ether; yield 7.6 g.

For the resolution, 1.5 g of *uns-cis*-[Co(TMDDA)(en)]Cl was dissolved in 10 ml of water. To it was added 0.80 g of silver *d*-tartrate and 0.33 g of *d*-tartaric acid, and the suspension was warmed at *ca.* 75° for 10 min with stirring. Silver chloride was filtered and washed with 5 ml of warm water. The filtrate and washings were combined and concentrated to *ca.* 11 ml in a warm water bath. About 0.7 g of soft silky pink crystals were separated with $\Delta\epsilon_{500} = +1.30$, assuming a 1:1 diastereomer, mol wt 456.3. One recrystalization of this isomer from a minimum amount of ethanol–water (1:1) mixture gave the same $\Delta\epsilon$ value. After the filtrate was cooled in a refrigerator overnight, *ca.* 0.2 g of diastereomer with a smaller positive $\Delta\epsilon$ value was separated by filtration. Addition of ethanol to the filtrate and cooling resulted in precipitation of the other diastereomer (0.6 g) with $\Delta\epsilon_{500} = -1.23$. The diastereomer with $\Delta\epsilon_{500} = +1.30$ was dissolved in a small amount of water and passed through an anion-exchange column (Dowex 1-X8, chloride form). This solution was concentrated to dryness under an air stream. The solid was dissolved in a small amount of water. The solution was filtered, ethanol was added to the filtrate, and it was cooled in an ice bath. Silky light red crystals were separated by filtration and washed with ethanol and then ether; $\Delta\epsilon_{500} = +1.48$. Recrystallization by addition of ethanol was repeated, but there was no improvement of optical activity; yield 0.15 g. The diastereomer with $\Delta\epsilon_{500} = -1.23$ was treated by the same procedure as above. Silky light red crystals were separated with $\Delta\epsilon_{500} = -1.48$. Further recrystallization did not increase the CD intensity; yield 0.08 g. *Anal.* Calcd for $[Co(C_7H_{12}N_2O_4)(C_2H_8N_2)]Cl·1.5H_2O$: C, 29.24; H, 6.27; N, 15.16. Found: C, 29.26; H, 6.28; N, 14.96.

Preparation and Resolution of *uns-cis*-Trimethylenediamine-*N,N*′-diacetato(trimethylenediamine)cobalt(III) Chloride, *uns-cis*-[Co(TMDDA)(tn)]Cl. The complex was prepared as for the ethylenediamine complex using 7.0 g of trimethylenediamine to yield 7.9 g of purple-red crystals. The resolution was also similar, starting with 4.0 g of *uns-cis*-[Co(TMDDA)(tn)]Cl to give 2.5 g of diastereomer ($\Delta\epsilon_{496} = -1.52$, assuming a 1:1 diastereomer, mol wt 470.3). The diastereomer was recrystallized from water by addition of ethanol ($\Delta\epsilon_{496} = -1.67$). The filtrate became gummy when ethanol was added, so 0.93 g of KI was added and the mixture was cooled. A mixture of a white substance and complex was filtered. As the filtrate was concentrated under an air stream, light red needle-shaped crystals appeared. The crystals (1.0 g) were separated by filtration and washed with ethanol and then ether; $\Delta\epsilon_{496} = +1.68$ (assuming anhydrous iodide, mol wt 448.2). The diastereomer with $\Delta\epsilon_{496} = -1.67$ was dissolved in a small amount of water and passed through an anion (Cl^-)-exchange column. The eluate was evaporated under an air stream. The solid was dissolved in a small amount of water, and the solution was filtered and then cooled after ethanol was added. Purple-red crystals were separated by filtration and washed with ethanol and then ether. One more recrystallization was enough to reach a constant $\Delta\epsilon_{496} = -1.94$; yield 0.35 g. The iodide of the opposite enantiomer ($\Delta\epsilon_{496} = +1.68$) was converted to the chloride and isolated as above; $\Delta\epsilon_{496} = +1.94$; yield 0.65 g. *Anal.* Calcd for $[Co(C_7H_{12}N_2O_4)(C_3H_{10}N_2)]Cl·H_2O$: C, 32.05; H, 6.46; N, 14.96; Cl, 9.46. Found: C, 32.10; H, 6.48; N, 15.04; Cl, 9.58.

Preparation and Resolution of *uns-cis*-Trimethylenediamine-*N,N*′-diacetato(diammine)cobalt(III)Chloride, *uns-cis*-[Co(TMDDA)-$(NH_3)_2$]Cl. Fifteen grams of the dichloro complex in 150 ml of water was warmed for 15 min at 65°. To it was added 30 ml of 12 *N* ammonia and 3 g of activated charcoal and the solution was warmed (65–70°) for 1.5 hr in a water bath with stirring. The activated charcoal and a small amount of insoluble purple complex were filtered. The filtrate was concentrated under an air stream to *ca.* 50 ml as silky light red crystals appeared gradually. The crystals were separated by filtration and recrystallized from water; yield 5.9 g.

For the resolution, 3.6 g of *uns-cis*-$[Co(TMDDA)(NH_3)_2]$Cl was dissolved in 85 ml of water. To the solution were added 2.06 g of silver *d*-tartrate and 0.85 g of *d*-tartaric acid. The suspension was heated at 75° and stirred for 10 min. Silver chloride was filtered off and washed with 6 ml of warm water. The filtrate and washings were combined and evaporated to dryness with a rotary evaporator. The diastereomers were dissolved in 75 ml of hot water and kept in a refrigerator for a few days. Red rectangular crystals were separated

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and washed with ethanol and then ether. One recrystallization did not change the CD intensity ($\Delta\epsilon_{486} = -1.23$, assuming 1:1 diastereomer, mol wt 430.3). The diastereomer (1.6 g) was dissolved in 275 ml of water and passed through an anion-exchange (Cl^-) column. The eluate was evaporated under an air stream. The solid was dissolved in 15 ml of water, then 10 ml of ethanol was added to it, and this solution was cooled in an ice bath. Flaky red crystals (1.1 g) were separated and washed with ethanol and then ether. These were recrystallized again from 10 ml of water by addition of 7 ml of ethanol without change in CD intensity, $\Delta\epsilon_{486} = -1.28$; yield 0.83 g. *Anal.* Calcd for $[Co(C_7H_{12}N_2O_4)(H_6N_2)]Cl \cdot 2H_2O$: C, 23.84; H, 6.29; N, 15.89. Found: C, 24.10; H, 6.43; N, 16.41. The opposite enantiomer was not obtained optically pure.

Preparation and Resolution of *uns-cis*-Trimethylenediamine-*N,N'*-diacetato(2,2'-dipyridyl)cobalt(III) Chloride, *uns-cis*-[Co(TMDDA)(dipy)]Cl. Twelve grams of the dichloro complex in 120 ml of water was warmed for 15 min (65–70°). Then 11.8 g of 2,2'-dipyridyl in 150 ml of ethanol–water (1:1) mixture was added to it. The solution was warmed (65–70°) for 15 min more. During this time the color gradually changed to light red. After the solution was cooled to room temperature, it was shaken well with 200 ml of ether in a separatory funnel in order to extract excess 2,2'-dipyridyl. This procedure was repeated twice. The solution containing the product was concentrated under an air stream to near dryness. The light red complex was separated by filtration and recrystallized from an ethanol–water (1:1) mixture; yield 6.2 g.

For the resolution, 4.0 g of *uns-cis*-[Co(TMDDA)(dipy)]Cl was dissolved in 20 ml of water. To the solution were added 1.66 g of silver *d*-tartrate and 0.68 g of *d*-tartaric acid and the suspension was warmed at 70° for 10 min with stirring. Silver chloride was removed as before. Forty milliliters of ethanol was added to the combined filtrate and washings, and this solution was cooled in an ice bath. A pink precipitate, which appeared gradually, was separated by filtration and washed with ethanol and then ether. The diastereomer was recrystallized twice from water by addition of ethanol. One recrystallization was enough to reach constant CD intensity; $\Delta\epsilon_{509} = -2.07$ (assuming a 1:1 diastereomer, mol wt 552.4). The diastereomer (0.66 g) was dissolved in 10 ml of water and passed through an anion-exchange column (Dowex 1-X8, iodide form). The eluate was evaporated to dryness under an air stream. The solid obtained was dissolved in 15 ml of an ethanol–water (1:1) mixture and 5 ml of ether was added to it. When the solution was cooled in an ice bath, brownish orange needle crystals appeared. The crystals were filtered and washed with ethanol and then ether; yield 0.25 g; $\Delta\epsilon_{509} = -2.58$. *Anal.* Calcd for $[Co(C_7H_{12}N_2O_4)(C_{10}H_8N_2)]I$: C, 38.51; H, 3.80; N, 10.57. Found: C, 38.33; H, 3.80; N, 10.61. The opposite enantiomer was not obtained optically pure.

Preparation and Resolution of *uns-cis*-Trimethylenediamine-*N,N'*-diacetato(1,10-phenanthroline)cobalt(III) Iodide, *uns-cis*-[Co(TMDDA)(phen)]I. Fifteen grams of the dichloro complex in 500 ml of water was warmed (60–65°) for 20 min. To it was added 18.6 g of 1,10-phenanthroline in 300 ml of an ethanol–water (1:1) mixture. The color turned from violet to light red. The insoluble purple complex was removed as before. The filtrate was concentrated to *ca.* 120 ml with a rotary evaporator. To the filtrate was added 10 g of KI. All at once a brownish orange precipitate appeared. This was separated by filtration and washed with ethanol and then ether. The crude complex was recrystallized from an ethanol–water (1:1) mixture; yield 6.7 g.

For the resolution, solid Ag[(–)$_{546}$-Co(EDTA)][4] (2.0 g) and *uns-cis*-[Co(TMDDA)(phen)]I (2.4 g) were stirred in 15 ml of water for 15 min at room temperature. Silver iodide was removed and washed with 5 ml of water. The filtrate and washings were combined and concentrated to dryness with a rotary evaporator. The diastereomers were dissolved in a small amount of water. Methanol was added and the solution was cooled to produce fine light red crystals. The diastereomer was separated in four fractions. Each was washed with a small amount of methanol and then ether. All four fractions had the same CD intensity, $\Delta\epsilon_{566} = +2.05$ (assuming 1:1 diastereomer, mol wt 774.5). The diastereomer (1.5 g) was dissolved in a small amount of water and passed through an anion-exchange (Cl^-) column. To the eluate was added 0.32 g of KI to precipitate the active complex as the iodide. The complex iodide was separated and washed with a small amount of methanol and then ether; yield 0.86 g. Recrystallization of the active complex from an ethanol–water (1:1) mixture by addition of ether yielded soft silky bright red crystals. Two recrystallizations did not change the CD intensity; $\Delta\epsilon_{518} = +2.89$. *Anal.* Calcd for $[Co(C_7H_{12}N_2O_4)(C_{12}H_8N_2)]I \cdot H_2O$: C, 39.88; H, 3.88; N, 9.79. Found: C, 40.06; H, 4.03; N, 9.40. The opposite enantiomer was not obtained optically pure.

Preparation and Resolution of *uns-cis*-Ethylenediamine-*N,N'*-diacetato(diammine)cobalt(III) Perchlorate, *uns-cis*-[Co(EDDA)(NH$_3$)$_2$]ClO$_4$. The preparation of this complex was carried out by a modified procedure of Kuroda's method.[11,12] To 30 ml of aqueous solution of *s-cis*-[Co(EDDA)(H$_2$O)$_2$]ClO$_4$[11] (5.0 g) was added 10 ml of 3 *N* ammonia. The blue solution containing a precipitate was immersed in an oil bath (100–110°). Gradually the solution became reddish. Concentration was continued to near dryness with stirring. Ten milliliters of 3 *N* ammonia was added again and heating was continued to near dryness. This was repeated once more after the addition of 10 ml of 3 *N* ammonia. When the tarry substance was cooled for a while, the whole solidified. The substance was dissolved in 20 ml of hot water. Some of the s-cis isomer which remained undissolved was removed by filtration. As the filtrate was concentrated under an air stream, red needle-shaped crystals appeared gradually. The complex (1.6 g) was separated and washed with ethanol and then ether. The preparation of the uns-cis isomer on a large scale did not lead to a good yield, the small-scale preparation was repeated several times to get enough of the complex for optical resolution. The complex was recrystallized from hot water.

For the resolution, 4.0 g of *uns-cis*-[Co(EDDA)(NH$_3$)$_2$]ClO$_4$ was converted to the chloride salt using an anion-exchange column and then to the hydrogen tartrate diastereomer as above. The filtrate and washings from the removal of AgCl were combined and evaporated in a rotary evaporator to dryness. The diastereomers were dissolved in 20 ml of water and 3 ml of ethanol was added. The solution was kept in a refrigerator. The pink diastereomer (*ca.* 2.5 g) was separated by filtration from the gelatinous solution and washed with ethanol and then ether. Three recrystallizations from water by addition of ethanol were necessary to reach a constant CD intensity, $\Delta\epsilon_{483} = +1.78$ (assuming a 1:1 diastereomer, mol wt 416.2). The diastereomer was dissolved in a small amount of water and passed through an anion-exchange (Cl^-) column. The eluate was concentrated under an air stream to dryness. The solid was recrystallized from water by addition of ethanol. Red needle-shaped crystals were separated and washed with ethanol and then ether. One more recrystallization did not change the CD intensity; $\Delta\epsilon_{483} = +1.87$; yield 0.16 g. *Anal.* Calcd for $[Co(C_6H_{10}N_2O_4)(H_6N_2)]Cl \cdot 1.5H_2O$: C, 21.86; H, 5.81; N, 17.00. Found: C, 21.70; H, 5.46; N, 17.18. The opposite enantiomer was not obtained optically pure.

Preparation and Resolution of *uns-cis*-Ethylenediamine-*N,N'*-diacetato(trimethylenediamine)cobalt(III) Perchlorate, *uns-cis*-[Co(EDDA)(tn)]ClO$_4$. To 30 ml of aqueous solution of *s-cis*-[Co(EDDA)(H$_2$O)$_2$]ClO$_4$ (5.0 g) was added 0.5 g of trimethylenediamine in 10 ml of water. The blue solution containing a precipitate was immersed in an oil bath (100–110°). Gradually the solution became reddish. Heating in an oil bath was continued for 40 min. Then an additional 0.5 g of trimethylenediamine in 10 ml of water was added. Heating was continued for 10 min more. During this time light red crystals began to appear. After the solution was cooled in an ice bath, the crystals (uns-cis isomer) were separated and washed with ethanol and then ether; yield 2.5 g. The filtrate was concentrated under an air stream. A purple-red complex appeared gradually, and this was identified as the s-cis isomer by its electronic absorption spectrum. The above preparation was repeated two times in order to get enough of the uns-cis isomer. The complex was recrystallized from hot water to give fairly large deep red crystals.

The resolution was carried out as for the ammonia complex. The combined filtrate and washings were concentrated, methanol was added, and the solution was kept in a refrigerator. A small amount of inactive complex was separated by filtration. More methanol was added again to the filtrate and it was kept in a refrigerator. Light red silky crystals (0.71 g) were separated and washed with methanol and then ether. The diastereomer was recrystallized twice from water by addition of methanol. One recrystallization was enough to reach constant CD intensity; $\Delta\epsilon_{490} = -1.50$ (assuming 1:1 diastereomer, mol wt 456.3). The diastereomer was dissolved in a small amount of water and passed through an anion (I^-)-exchange column. The eluate was concentrated to 3 ml and then to 13 ml of ethanol was added and kept in a refrigerator. The deep red crystals obtained were recrystallized from water by addition of ethanol; yield 0.13 g; $\Delta\epsilon_{490} = -2.00$. The filtrate, after the separation of the above diastereomer, was concentrated to get rid of methanol and diluted with water. The solution was passed through an anion (I^-)-exchange column. The eluate was concentrated, ethanol was added, and the solution was kept in a refrigerator. After the inactive complex (0.16 g) was separated, more ethanol was added to the filtrate and it was returned to a refrigerator. The active complex (0.22 g) was separated and recrystallization from water by addition of ethanol was carried out twice; yield 0.03 g; $\Delta\epsilon_{490} = +2.00$. *Anal.* Calcd for $[Co(C_6H_{10}N_2O_4)(C_3H_{10}N_2)]I \cdot 1.5H_2O$: C, 23.44; H, 5.03; N, 12.15. Found: C, 23.72; H, 4.63; N, 11.77.

Spectra. The absorption spectra were recorded on a Cary 14 spectrophotometer at room temperature using a tungsten source. The CD spectra were recorded on a Roussel-Jouan Dichrograph using a tungsten source.

Analyses. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz.

Results and Discussion

The preparation of the EDDA-Co^{III} complexes containing diammine and trimethylenediamine was carried out in an oil bath (100-110°) on Kuroda's assumption[11,12] that the coordination mode of EDDA depends on the temperature and uns-cis isomers need a higher temperature. The CD and absorption spectra for the complexes *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$ and *uns-cis*-$[Co(EDDA)(tn)]^+$ are shown in Figure 1. The intensities of the absorption bands for the complexes are much larger than for the corresponding s-cis isomers. This fact reflects the lower symmetry of the uns-cis isomers. It is well known experimentally[8,13,14] and theoretically[15,16] that the *trans*(O)-$[Co(N_4O_2)]$ type complexes exhibit large splitting of the first absorption band, while for the *cis*(O)-$[Co(N_4O_2)]$ type complexes this band is nearly symmetrical because of the smaller splitting. The first absorption bands for the complexes shown are nearly symmetrical. Therefore they are all uns-cis isomers. If only coordinated atoms are considered, these complexes have holohedrized tetragonal symmetry. Under tetragonal (D_{4h}) symmetry the $T_{1g}(O_h)$ level is split into A_2 and E levels. In the present complexes (Figure 2) there is a stronger field along the unique axis (N-N) than in the plane perpendicular to it. Therefore it is predicted that the $A_2(D_{4h})$ level lies lower in energy than the $E(D_{4h})$ level, opposite to that of *s-cis*-$[Co(EDDA)en]^+$ and *s-cis*-$[Co(EDDA)(NH_3)_2]^+$ where the weaker field is along the unique (O-O) axis.[1,6] The CD spectrum of *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$ shows two bands of opposite sign in the first absorption band region. The more intense peak, $E(D_{4h})$, is at higher energy than A_2, opposite[5] to the order for *s-cis*-$[Co(EDDA)(NH_3)_2]^+$. The CD spectrum of *uns-cis*-$[Co(EDDA)(tn)]^+$ shows a very small A_2 band and the E band is unsymmetrical, being steeper on the lower energy side. The very small negative band at 17.3 kK was checked with a very concentrated sample for both enantiomers. Therefore there is no doubt about its existence. Thus the negative $A_2(D_{4h})$ component diminishes in intensity from the diammine complex to the trimethylenediamine complex and it completely disappears for the corresponding ethylenediamine complex.[17] These changes in the CD spectra of *uns-cis*-EDDA complexes are in contrast with those of *s-cis*-EDDA complexes for which the splitting (E and A_2) within the first absorption band is greater. For the s-cis isomers, there are always two CD peaks which show remarkable insensitivity to changes in the nature of the bidentate ligands.

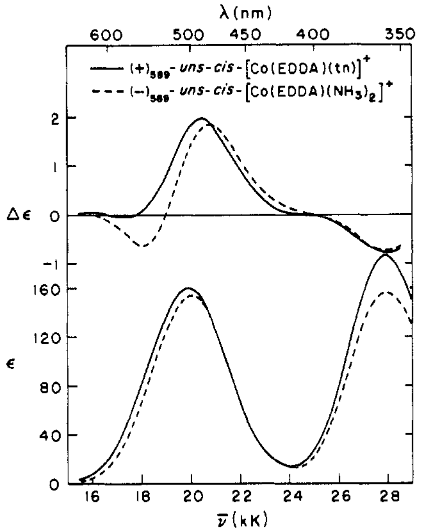

Figure 1. Absorption and CD spectra for *uns-cis*-$[Co(EDDA)(tn)]^+$ and *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$.

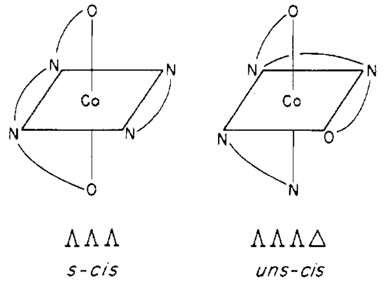

Figure 2. Chirality of s-cis and uns-cis isomers of the [Co(EDDA)-(en)]$^+$ type.

Although the intensities of the absorption bands are significantly greater for the less symmetrical *uns-cis*-[Co-(EDDA)(diamine)]$^+$ complexes than for the corresponding s-cis isomers, the CD intensities are more than twice as great for the s-cis isomers. On the basis of the ring-pairing approach[18] or the IUPAC system[19] for designating absolute configurations, any combination of the two glycinate rings and the diamine ring (en or tn) define the same chirality for the s-cis isomers, as is shown in Figure 2. In the case of the uns-cis isomers this is still true, but the en or tn ring in combination with the en backbone of EDDA defines the *opposite* chirality. This is consistent with the lower CD peak intensities, but also the smaller splitting (A_2 and E) for uns-cis isomers would result in greater mutual cancellation. Also the two asymmetric N atoms must have the same absolute configuration for s-cis isomers, but they are not necessarily the same for uns-cis isomers. The net rotational strength for the uns-cis isomers, which allows complete cancellation of the weaker peak, decreases slightly in the order en[17] > tn > $(NH_3)_2$.

Spectral assignments of *s-cis*-$[Co(EDDA)L_2]$ complexes have been made using effective tetragonal symmetry,[1,4,6,8] but absolute configurations have been made by relating the C_2 symmetry of the complexes[1,3] to $[Co(en)_3]^{3+}$ as a known reference. These assignments have been confirmed by the assignment of the absolute configuration of Δ-*s-cis*-[Co-

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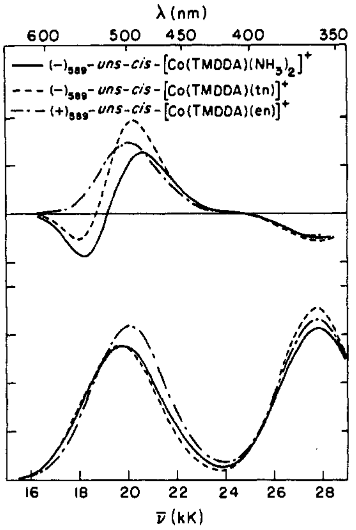

Figure 3. Absorption and CD spectra for *uns-cis*-[Co(TMDDA)-(diamine)]$^+$ complex ions.

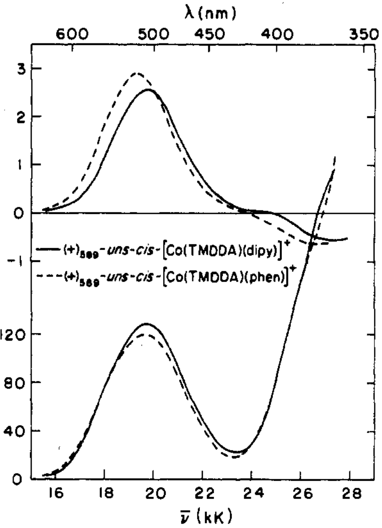

Figure 4. Absorption and CD spectra of *uns-cis*-[Co(TMDDA)-(dipy)]$^+$ and *uns-cis*-[Co(TMDDA)(phen)]$^+$.

(LL-EDDP)(en)]$^+$ from nmr studies.[20] These studies[20] also included Δ-*uns-cis*-[Co(LL-EDDP)(en)]$^+$ which has a negative major CD peak in the first absorption band region. On this basis, the complexes with positive major CD peaks shown in Figure 1 can be assigned confidently the ΛΛΛΔ configuration.[19] The same assignments result for the s-cis and uns-cis isomers if one uses the sign of the net rotational strength in the $T_{1g}(O_h)$ band region as proposed by Richardson[21,22] and as related to $[Co(en)_3]^{3+}$. The use of the sign of the net rotational strength is equivalent to the use of the sign of the major CD peak when this is dominant. The uns-cis isomers lack C_2 symmetry (Figure 2) and any C_2-D_3 correlation is tenuous.

For the preparation of the TMDDA-Co^{III} complexes containing diamines, $H[Co(TMDDA)Cl_2]\cdot 0.5H_2O$ was used as a starting material. Kuroda and Watanabe used *s-cis*-$[Co(EDDA)(Cl)(H_2O)]\cdot H_2O$ or *s-cis*-$[Co(EDDA)(H_2O)_2]ClO_4$ as starting materials for the preparation of a variety of EDDA-Co^{III} complexes.[11,12] It is to be noted that the TMDDA-Co^{III} complexes prefer the uns-cis configuration, while the EDDA-Co^{III} complexes prefer the s-cis configuration. Size of the diamine chelate ring seems to have a profound effect on the distribution of geometrical isomers.

The CD and absorption spectra for the complexes *uns-cis*-$[Co(TMDDA)(NH_3)_2]^+$, *uns-cis*-[Co(TMDDA)(tn)]$^+$, and *uns-cis*-[Co(TMDDA)(en)]$^+$ are shown in Figure 3. The first absorption band of each of these complexes is nearly symmetrical, as expected for uns-cis isomers. Although the presence of two components cannot be recognized in the absorption spectra, they are well resolved in the CD spectra of uns-cis-$[Co(TMDDA)(NH_3)_2]^+$ and *uns-cis*-[Co(TMDDA)(tn)]$^+$. These two complexes show two CD peaks of opposite sign in the first absorption band region. As for the *uns-cis*-$[Co(EDDA)L_2]^+$ complex ions (Figure 1), these peaks can be assigned as A_2 (lower energy) and E, using effective D_{4h} symmetry. *uns-cis*-[Co(TMDDA)(en)]$^+$ shows, however, only one CD band in the first absorption band region. Also in this case the CD band maximum and the absorption band maximum are at the same position, indicating very small splitting of the T_{1g} band. In the CD spectra of the three complexes, the A_2 component is reduced gradually in the order from the diammine complex to the trimethylenediamine complex and it completely disappears for the ethylenediamine complex. This is the same trend observed for the *uns-cis*-EDDA complexes. This corresponds to going from no chelate ring for the diammine to a trimethylenediamine chelate ring and then to a more strained ethylenediamine chelate ring. The net rotatory strength (T_{1g}, O_h) is decreased in the order of ethylenediamine, trimethylenediamine, and diammine complexes.

The comparison of CD and absorption spectra between *uns-cis*-$[Co(TMDDA)(NH_3)_2]^+$ and *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$ and also between *uns-cis*-[Co(TMDDA)(tn)]$^+$ and *uns-cis*-[Co(EDDA)(tn)]$^+$ can be seen from Figures 1 and 3 and Table I. Both of the EDDA complexes have much higher intensities than the TMDDA complexes in both d–d absorption bands. This might be expected from the greater rigidity of the EDDA framework, since the molar absorptivities are significantly greater for [Co(EDTA)]$^-$ in comparison to less rigid model compounds.[23] The difference in the central ring size also produces changes in the shape of CD spectra. In the more rigid EDDA complexes, the intensity of the A_2 component is reduced from that of the less rigid TMDDA complexes. The net rotational strength is greater for the more rigid EDDA complexes. The changes in the rigidity of the central ring of EDDA and TMDDA and the rigidity of bidentate ligands affect the intensity of the A_2 component in the same way. It is interesting to note that these two chelate rings (or octahedral edges spanned in the case of the diammine complex) form the Δ chiral pair of Figure 2, of opposite chirality to the other three chiral pairs. There is no pair of opposite chirality in the case of the s-cis isomers and the CD spectra are relatively unchanged by changes in the bidentate ligand.

The CD and absorption spectra for the complexes *uns-cis*-[Co(TMDDA)(dipy)]$^+$ and *uns-cis*-[Co(TMDDA)(phen)]$^+$ are shown in Figure 4. The first absorption band in each case is nearly symmetrical, indicating that they are also uns-cis isomers. The second absorption band occurs as a shoulder on an intense charge-transfer band in both complex-

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Table I. Absorption and Circular Dichroism Data for Cobalt(III) Complexes Containing TMDDA or EDDA

	Absorption		CD	
Compd	kK	ϵ	kK	$\Delta\epsilon$
(+)$_{589}$-*uns-cis*-[Co(TMDDA)(en)]Cl·1.5H$_2$O	20.04	127	20.00	+1.48
	27.78	132	27.55	−0.48
(+)$_{589}$-*uns-cis*-[Co(TMDDA)(tn)]Cl·H$_2$O	19.69	112	18.02	+0.53
			20.16	−1.94
	27.70	142	27.78	+0.56
(+)$_{589}$-*uns-cis*-[Co(TMDDA)(NH$_3$)$_2$]Cl·2H$_2$O	19.76	112	18.22	+0.89
			20.58	−1.28
	27.78	126	27.78	+0.48
(−)$_{589}$-*uns-cis*-[Co(TMDDA)(dipy)]I	19.72	128	19.65	−2.58
	26.67 sh	218	27.03	+0.54
(+)$_{589}$-*uns-cis*-[Co(TMDDA)(phen)]I·H$_2$O	19.69	120	19.31	+2.89
	25.64 sh	135	26.60	−0.63
(−)$_{589}$-*uns-cis*-[Co(EDDA)(NH$_3$)$_2$]Cl·1.5H$_2$O	20.04	154	18.05	−0.64
			20.70	+1.87
	27.93	157	27.93	−0.72
(−)$_{589}$-*uns-cis*-[Co(EDDA)(tn)]I·1.5H$_2$O	19.90	160	17.30	+0.029
			20.41	−2.00
	27.93	187	28.09	+0.77

es. The CD spectra of the two complexes show only one band in the first absorption band region as is the case for the corresponding ethylenediamine complex. Close examination of the CD spectrum of the phenanthroline complex plotted on graph paper shows, however, deformation of the band on the higher energy side. Furthermore the CD band maximum is shifted to lower energy by *ca.* 0.4 kK from the first absorption maximum. These facts suggest that there is a small component of the same sign as that of the main component on the higher energy side. In the type of chromophore, *cis*-[Co(N$_4$O$_2$)], the A$_2$(D_{4h}) component should exist on the lower energy side of the E(D_{4h}) component. Therefore the small component at the higher energy side might arise from the splitting of E(D_{4h}). The actual symmetry of the complex is C_1.

The TMDDA complexes shown in Figures 3 and 4 with net positive rotational strengths in the T$_{1g}$ absorption band region can be assigned the ΛΛΛΔ configuration[19] (Figure 2) as in the case of the *uns-cis*-EDDA complexes above.

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Registry No. H$_2$TMDDA·2HCl, 7597-26-4; H[Co(TMDDA)-Cl$_2$], 43200-14-2; (+)-*uns-cis*-[Co(TMDDA)(en)]Cl, 43156-67-8; (−)-*uns-cis*-[Co(TMDDA)(en)]Cl, 43156-68-9; (−)-*uns-cis*-[Co(TMDDA)-(tn)]Cl, 43200-15-3; (+)-*uns-cis*-[Co(TMDDA)(tn)]Cl, 43156-69-0; (+)-*uns-cis*-[Co(TMDDA)(NH$_3$)$_2$]Cl, 43200-16-4; (−)-*uns-cis*-[Co-(TMDDA)(dipy)]Cl, 43200-17-5; (+)-*uns-cis*-[Co(TMDDA)(phen)]I, 43200-18-6; (−)-*uns-cis*-[Co(EDDA)(NH$_3$)$_2$]Cl, 43156-70-3; (+)-*uns-cis*-[Co(EDDA)(tn)]I, 43200-19-7; (−)-*uns-cis*-[Co(EDDA)(tn)]I, 43200-20-0; (−)-*uns-cis*-[Co(TMDDA)(NH$_3$)$_2$]$^+$, 43200-21-1; (+)-*uns-cis*-[Co(TMDDA)(dipy)]$^+$, 43156-71-4.

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Preparation and Spectral Studies of Some Acidopentacyanorhodate(III) and -iridate(III) Complexes

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Complexes of the type [M(CN)$_5$X]$^{n-}$ [M = Rh(III), Ir(III); X = Cl$^-$, Br$^-$, I$^-$, OH$^-$, NCCH$_3$] are readily prepared by thermal anation reactions of [M(CN)$_5$H$_2$O]$^{2-}$, the aquo complexes being formed by uv irradiation of acidic solutions of [M(CN)$_6$]$^{3-}$. The K$^+$ and Co(NH$_3$)$_6$$^{3+}$ salts of several of the [M(CN)$_5$X]$^{n-}$ complexes have been isolated and their ir spectra have been recorded and assigned. The uv spectra of all [M(CN)$_5$X]$^{n-}$ and [M(CN)$_6$]$^{3-}$ complexes have been measured in aqueous solution. The lowest energy electronic absorption band in the [Rh(CN)$_5$X]$^{n-}$ complexes is assigned to the ligand field transition $^1A_1 \rightarrow {}^1E^a$, whereas in [Ir(CN)$_5$X]$^{n-}$ both $^1A_1 \rightarrow {}^3E^a$ and $^1A_1 \rightarrow {}^1E^a$ absorptions are observed. The position of the $^1A_1 \rightarrow {}^1E^a$ transition establishes the order of decreasing ligand field strength of X as NCCH$_3$ > OH$^-$ > H$_2$O > Cl$^-$ > Br$^-$ > I$^-$ for both Rh(III) and Ir(III) complexes. Halide-to-metal charge-transfer bands are observed for [M(CN)$_5$X]$^{n-}$ complexes with X = Br$^-$ and I$^-$.

In view of the large number of [Co(CN)$_5$X]$^{n-}$ complexes, it is surprising that the only pentacyanorhodate(III) and -iridate(III) derivatives reported to date have been [Rh(CN)$_5$C$_2$F$_4$H]$^{3-}$,(1) [Rh(CN)$_5$NO$_2$]$^{3-}$,(1) [Rh(CN)$_5$COCH$_3$]$^{3-}$,(2) [Rh(CN)$_5$H]$^{3-}$,(2) and [Ir(CN)$_5$H]$^{3-}$.(3) Utilizing the photolability of the parent [M(CN)$_6$]$^{3-}$ species, we have been able

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