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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, hydrogen positional parameters, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Macrotricyclic Hexaamine Cage Complexes of Cobalt(III): Synthesis, Characterization, and Properties

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Syntheses of the sexidentate ligand 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn) and chiral [Co(taetacn)]$^{3+}$ are described along with the chiral macrotricyclic cage derivatives [Co(nosartacn)]$^{3+}$ (nosartacn = 9-nitro-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane), [Co(amsartacn)]$^{3+}$ (amsartacn = 9-amino-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane), and [Co(azasartacn)]$^{3+}$ (azasartacn = 1,4,7,9,11,14,19-heptaazatricyclo[7.7.4.2^{4,14}]docosane). Their absolute configurations have also been assigned. Electrochemical studies showed reversibility of the Co(III)/Co(II) redox couple for the cage complexes, which are kinetically inert and optically stable in both oxidation states. The visible, rotatory dispersion, and circular dichroism spectra of the Co(III) oxidation states are reported. The kinetics of the electron self-exchange reactions of Co(II)/Co(III)-cage couples were studied to establish if the ready access along the molecular C_3 axis assisted the electron exchange. The rates for the Δ-[Co(amsartacnH)]$^{3+}$/Λ-[Co(amsartacnH)]$^{4+}$ couple ($k = 0.04$ M^{-1}·s^{-1}, 25 °C, $\mu = 0.2$ M) and the Δ-[Co(amsartacn)]$^{2+}$/Λ-[Co(amsartacn)]$^{3+}$ couple ($k = 0.09$ M^{-1}·s^{-1}) are not very different from those of related cage systems in which access along the C_3 axis is barred by the ligands.

Introduction

In a recent publication the facile condensation of NH_3 and CH_2O with [Co(en)$_3$]$^{3+}$ to give the [Co(sepulchrate)]$^{3+}$ cage molecule was reported.[2] The synthesis basically involved the construction of a trimethylaminetriyl cap on the trigonal facial arrangement of three primary amine groups of each of the coordinated ethylenediamine ligands in the precursor complex. By inference, this strategy should be generally applicable for building caps on similar facial arrangements of coordinated primary amines in other metal ion complexes, provided their stereochemistry is not prohibitive. This applicability has been demonstrated in one case by the synthesis, from [Co(sen)]$^{3+}$, of the [Co(azamesar)]$^{3+}$ cage complex in which the metal center, as in [Co(sepulchrate)]$^{3+}$, is encapsulated by a macrobicyclic ligand structure.[2] This paper reports the syntheses, by analogous routes, of some novel macrotricyclic (hexaamine)cobalt(III) cage complexes derived from the (1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane)cobalt(III) ion (ligand abbreviated "taetacn") (**1**) (Chart I). For practical reasons the cage ligands and their complexes described here have been given shorthand names: [Co(nosartacn)]$^{3+}$ (**2**), [Co(amsartacn)]$^{3+}$ (**3**) (the protonated form of **3** is named [Co(amsartacnH)]$^{4+}$ (**3$^+$**)), [Co(azasartacn)]$^{3+}$ (**4**). The systematic ligand names appear in the abstract.

Experimental Section

Absorption and circular dichroism (CD) spectra were recorded with a Cary 14 spectrophotometer and a Cary 61 CD instrument, respectively. The calibration standard for CD measurements was [(+)$_{589}$-[Co(en)$_3$]Cl$_3$]$_2$·NaCl·6H$_2$O (0.5 mM, in H$_2$O, $\epsilon_l - \epsilon_r = +1.80$ M^{-1}·cm^{-1}/Co in the maximum at 490 nm). All listed values of molar absorptivity (ϵ) and molar CD ($\Delta\epsilon = \epsilon_l - \epsilon_r$) are in units of M^{-1}·cm^{-1}. Optical rotations and rotatory dispersion spectra were measured with a Perkin-Elmer P22 spectropolarimeter (±0.002°) in 1-dm quartz cells. All listed values of specific ($[\alpha]_\lambda$) and molecular ($[M]_\lambda$) rotations are at 25.0 ± 0.1 °C in units of deg·mL·g^{-1}·dm^{-1} and deg·M^{-1}·m^{-1}, respectively. NMR spectra were recorded with JEOL 100-MHz Minimar (^{1}H) and JNM-FX 60-MHz Fourier transform (^{13}C) spectrometers at 30 and 25 °C, respectively, using Me$_4$Si in CDCl$_3$ as an internal standard for ^{1}H spectra and 1,4-dioxane in D$_2$O for ^{13}C spectra. Chemical shifts (positive downfield) are given relative to these standards.

Polarograms and cyclic voltammograms were recorded on a PAR electrochemistry system, Model 170, with a conventional three-electrode *iR*-compensated configuration. For studies in water, 0.1 M NaClO$_4$ was used as the supporting electrolyte and a saturated calomel electrode was used as the reference electrode. In acetone and acetonitrile, 0.1 M (CH$_3$)$_4$N(O$_3$SCF$_3$)[3] (TMAT) was used as the supporting electrolyte and Ag/AgCl (0.1 M LiCl in acetone) as the reference electrode. A low-porosity salt bridge of the relevant medium separated the reference electrode from the working compartment. A platinum-wire auxiliary electrode was used on all occasions. The working electrode was a dropping mercury electrode or, for the cyclic voltammograms, a hanging mercury drop electrode. Prior to recording of a polarogram or voltammogram, solutions were thoroughly degassed via a standard purge tube with argon saturated with the solvent used. Results were obtained at ambient temperature, 22 [illegible] 2 °C.

The concentration acid dissociation constant, K_a, was determined by standard procedures[4] in CO$_2$-free 1.00 M NaClO$_4$ under N$_2$ at 25.00 ± 0.05 °C with a Radiometer (Copenhagen) PHM 26 pH meter with a G202B glass electrode and a K4112 saturated calomel reference electrode connected via a 1.6 M NH$_4$NO$_3$, 0.2 M NaNO$_3$ salt bridge. The instrument was calibrated with hydrogen phthalate (0.05 M, pH 4.00, 25 °C) and borate (0.01 M, pH 9.18, 25 °C) buffers. A standard 1.00 mM HCl (Volucon), 1.00 M NaClO$_4$ solution gave pH 3.00, and pH = −log [H$^+$] was therefore assumed in the region $2.8 < \text{pH} < 5.0$. All SP-Sephadex C-25 ion-exchange columns used for separations and resolutions were prewashed with the eluant to be used. Complexes were sorbed on the columns by mixing a suspension of the complex in water (10 mL) with an equal volume of resin and carefully placing the resulting suspension evenly at the top of the column before eluting. Dimensions given for Sephadex columns are

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[2] Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016–6025; **1977**, *99*, 3181. Bakac, A.; Espenson, J.; Creaser, I. I.; Sargeson, A. M. *Ibid.*, in press.

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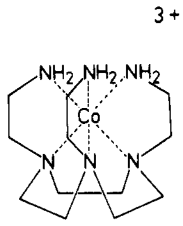
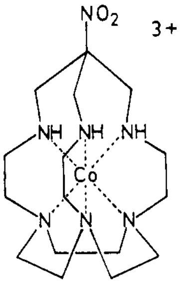
Chart I



1



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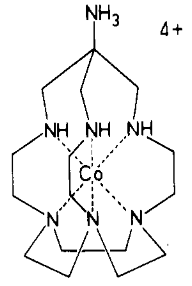

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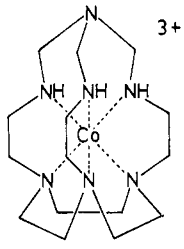

4

for the Na^+ form washed with water. Unless stated, the size of Bio-Rad AG 50W-X2 cation-exchange resin (200–400 mesh) columns used was 2.5 × 5 cm (H^+ form). All evaporations were performed at reduced pressure (~20 torr) in a Büchi rotary evaporator using a water aspirator and water bath (40 °C).

All chemicals were analytical grade. Commercial HO_3SCF_3 (3M Co.) was distilled before use. NaO_3SCF_3 was prepared from NaOH and HO_3SCF_3.[5] $(N(CH_3)_4)OOCCH_3$ was prepared from aqueous $(N(CH_3)_4)OH$ and CH_3COOH.

Phthalimidoacetaldehyde. Crude phthalimidoacetaldehyde hydrate[6] (0.65 mol) was dehydrated by azeotropic removal of water with benzene (0.6 L). On concentration of the resulting solution to 150 mL followed by cooling to 0 °C the aldehyde separated as colorless crystals. These were collected, washed with ice-cold benzene, and dried in a stream of air (yield 76 g). ^1H NMR ($CDCl_3$): δ_{Me_4Si} 9.60 (s, 1 H, aldehyde), 7.9 (m, 4 H, phenyl), 4.55 (s, 2 H, methylene).

1,4,7-Tris(2-aminoethyl)-1,4,7-triazacyclononane Hexahydrobromide (taetacn·6HBr). To a stirred slurry of finely ground 1,4,7-triazacyclononane trihydrobromide[7] (18.6 g, 50.0 mmol) and 3-Å molecular sieves (15 g) in dry acetonitrile (400 mL) was added phthalimidoacetaldehyde (38 g, 0.20 mol) followed by anhydrous tetramethylammonium acetate (0.5 g) and sodium cyanoborohydride (9.4 g, 0.15 mol). The reaction vessel was closed off with a $CaCl_2$-filled tube and the mixture left to stir for 15 h at room temperature. After removal of molecular sieves by decantation followed by concentration to one-tenth its original volume the milky suspension was mixed with a solution of $LiOH{\cdot}H_2O$ (21 g, 0.50 mol) in water (60 mL) and extracted with chloroform (4 × 100 mL). The combined chloroform extracts were extracted with aqueous 2 M LiOH (100 mL) and then dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness, leaving a yellowish oil of crude 1,4,7-tris(2-phthalimidoethyl)-1,4,7-triazacyclononane. ^1H NMR ($CDCl_3$): δ_{Me_4Si} 7.8 (m, ~4 H, phenyl), 3.6 (t, ~2 H, methylene), 2.6 (m, ~6 H, methylenes). The oil was treated with a mixture of 48% aqueous HBr (100 mL) and glacial acetic acid (100 mL) and the resulting mixture refluxed for 15 h. After evaporation to dryness the solid residue was treated with 1 M HBr (100 mL) and the undissolved residue of phthalic acid removed by filtration. The filtrate was evaporated to dryness and redissolved in hot 48% HBr (75 mL). On gradual addition of glacial acetic acid (200 mL) to the stirred and ice-cooled solution the crude amine hexahydrobromide precipitated, which was collected, washed thoroughly with ethanol and ether, and finally dried over P_4O_{10} at 15 torr (yield 20 g).

$\Lambda(+)_{487}$- and $\Delta(-)_{487}$-[Co(taetacn)]($ClO_4)_3$. A mixture of crude taetacn·6HBr (7.4 g), $CoCl_2{\cdot}6H_2O$ (2.6 g), NaOH (2.0 g), and activated charcoal (1 g, "Norit A") in water (150 mL) was aerated for 5 h. After filtration the dark brown solution was sorbed on a column (4.5 × 8.0 cm) of H^+ form AG 50W-X2 resin. The column was washed with 1 M HCl (1 L), whereby residual Co^{2+} and a red band were eluted. The main orange-colored band was eluted with 4 M HCl. The eluate was evaporated and the residue dissolved in hot water (10 mL). The complex was crystallized by addition of $NaClO_4{\cdot}H_2O$ (6.3 g) and cooling to 0 °C. The collected product was recrystallized from a boiling solution of $NaClO_4{\cdot}H_2O$ (1.5 g) in water (16 mL) to yield orange-red crystals (4.6 g), which were washed with methanol and ether, and dried in air. Anal. Calcd for $[Co(C_{12}H_{30}N_6)](ClO_4)_3$: Co, 9.57; C, 23.41; H, 4.91; N, 13.65; Cl, 17.27. Found: Co, 9.3; C, 23.3; H, 4.9; N, 13.5; Cl, 17.3.

Racemic perchlorate salt (2.6 g in batches of no more than 0.6 g) was resolved on a column of SP-Sephadex C-25 (5.5 × 80 cm) with use of 0.2 M disodium $(+)_{589}$-tartrate as eluant. Two equal yellow bands corresponding to each enantiomer separated. The collected eluates of the first band were sorbed on a column of AG 50W-X2 resin and washed with 1 M HCl (0.5 L) to elute Na^+. The complex was eluted with 4 M HCl and evaporated to dryness, and the solid residue (in 3.0 mL of H_2O) was recrystallized by addition of $NaClO_4{\cdot}H_2O$ (1.3 g) followed by methanol (2 mL). The orange crystals (1.3 g) were collected, washed with methanol, and dried in air. The product was recrystallized from a boiling aqueous solution (12 mL) of $NaClO_4{\cdot}H_2O$ (0.7 g) to yield large orange-brown crystals (1.2 g), which were treated as before and dried in vacuo over P_4O_{10} for 20 h. Anal. Found ($\Lambda(+)_{487}$ isomer): Co, 9.5; C, 23.3; H, 5.4; N, 13.3; Cl, 17.4. Specific rotations (0.03%, in H_2O): $[\alpha]_{487}$, +1160; $[\alpha]_{425}$, −676; $[\alpha]_{385}$, −570.

The combined eluates of the second band were treated in the same manner to give the same yield. Anal. Found ($\Delta(-)_{487}$ isomer): Co, 9.4; C, 23.7; H, 5.2; N, 13.6; Cl, 17.2. Specific rotations (0.03%, in H_2O): $[\alpha]_{487}$, −1150; $[\alpha]_{425}$, +678; $[\alpha]_{385}$, +567. Visible–UV (λ_{max} (nm), ϵ_{max}): 480, 242; 347, 198; 236, 18.6 × 10^3. CD (λ_{max} (nm), $\Delta\epsilon_{max}$): 513, +1.14; 458, −2.40; 348, +1.01.

$\Lambda(+)_{490}$- and $\Delta(-)_{490}$-[Co(nosartacn)]$_2(S_2O_6)_3$. To a stirred mixture of [Co(taetacn)]($ClO_4)_3$ (1.2 g), nitromethane (1.2 g), and water (20 mL) was added 37% (w/w) formaldehyde solution (4.9 g) followed rapidly by Na_2CO_3 (0.5 g). The resulting solution turned dark brown almost instantaneously. After 5 min the reaction mixture was cautiously acidified with glacial acetic acid (2.5 mL), diluted to 500 mL with water, and sorbed on a column of SP-Sephadex C-25 (6 × 25 cm). Eluting with 0.2 M K_2SO_4 solution revealed three bands. The eluate of the major (second, red-brown) band was sorbed on a column of H^+-form AG 50W-X2 resin and the column washed with 1 M HCl (0.5 L) to elute K^+. The complex was eluted with 4 M HCl and the eluate evaporated to dryness, leaving a crystalline solid, which was triturated with ethanol, collected, washed with methanol, and dried in air; yield of crude complex chloride 0.7 g. This was recrystallized from a mixture of water (2 mL) and ethanol (3 mL), yielding fine yellow-orange crystals (0.6 g), which were isolated by the same procedure as above. Anal. Calcd for $[Co(C_{16}H_{33}N_7O_2)]Cl_3{\cdot}2H_2O$: Co, 10.58; C, 34.51; H, 6.70; N, 17.61; Cl, 19.10. Found: Co, 10.8; C, 34.3; H, 6.4; N, 17.4; Cl, 18.9.

The racemic chloride dihydrate salt (0.31 g) was resolved on a column of SP-Sephadex C-25 resin (5 × 75 cm) with use of 0.15 M disodium bis($(+)_{589}$-tartrato)diantimonate ($Na_2[Sb_2((+)_{589}\text{-tart})_2]$) as the eluant. Two equal bands separated. The eluate of the first band was sorbed on a column of Na^+-form AG 50W-X2 resin and the column washed with water (0.1 L) followed by 1 M HCl (0.5 L). The complex was eluted with 4 M HCl and the eluate evaporated to dryness. The solid residue was taken up in the minimal amount of hot water, and after addition of $Li_2S_2O_6$ (0.3 g) followed by ethanol (20 mL), crystallization of the dithionate salt was induced by scratching with a glass rod. The collected product (0.20 g) was recrystallized from a mixture of water (5 mL) and ethanol (1 mL), yielding large orange prisms (0.15 g), which were washed with ethanol and ether. Anal. Calcd for $\Lambda(+)_{490}$-$[Co(C_{16}H_{33}N_7O_2)]_2(S_2O_6)_3{\cdot}8H_2O$: Co, 8.11; C, 26.45; H, 5.69; N, 13.49; S, 13.24. Found: Co, 8.2; C, 26.6; H, 5.5; N, 13.5; S, 13.0. Specific rotations (0.02%, in H_2O): $[\alpha]_{540}$, −900; $[\alpha]_{490}$, +3350.

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The eluate of the second band was treated identically to give an identical yield of the $\Delta(-)_{490}$ enantiomer. Anal. Found: Co, 8.2; C, 26.7; H, 5.6; N, 13.5; S, 13.2. Specific rotations (0.02%, in H_2O): $[\alpha]_{540}$, +910; $[\alpha]_{490}$, −3340. Visible–UV (λ_{max} (nm), ϵ_{max}): 488, 328; 350, 267; 248, 20.1 × 10^3. CD (λ_{max} (nm), $\Delta\epsilon_{max}$): 513, +5.31; 461, −4.42; 348, +2.74.

The optically pure enantiomers were also obtained directly from the optically active salts of $[Co(taetacn)](ClO_3)_4$ by employing the same procedure as described above for the preparation of racemic $[Co(nosartacn)]Cl_3\cdot 2H_2O$, but with the final products isolated as the dithionate salts; $\Lambda(+)_{487}$-$[Co(taetacn)](ClO_4)_3$ thus yielded Λ-$(+)_{490}$-$[Co(nosartacn)]_2(S_2O_6)_3\cdot 8H_2O$.

$\Lambda(+)_{492}$- and $\Delta(-)_{492}$-[Co(amsartacnH)]$(O_3SCF_3)_4$. A solution of $[Co(nosartacn)]Cl_3\cdot 2H_2O$ (0.40 g) in water (30 mL) was deoxygenated with a stream of N_2 gas. To the stirred solution was added Zn dust (0.3 g) followed by concentrated aqueous HCl (4 mL). The mixture was stirred for 5 h with a continuous N_2 flow. The solution was filtered and hydrogen peroxide (32%, 5 mL) added to the filtrate, which was subsequently heated on the steam bath for 10 min. The resulting orange solution was sorbed on a column of H^+-form AG 50W-X2 resin, which was then washed with 1 M HCl (0.1 L) to elute Zn^{2+}. The orange band was eluted with 4 M HCl and the eluate evaporated to complete dryness, leaving a solid residue, which was treated with anhydrous HO_3SCF_3 (3 mL). When all solid had dissolved and gas evolution (HCl) had ceased, ether (0.1 L) was carefully added to precipitate the complex, which was collected, washed with ether, and recrystallized from a mixture of water (2 mL), NaO_3SCF_3 (0.5 g), and HO_3SCF_3 (1 mL), yielding regular orange crystals (0.66 g). These were collected, washed with ethanol/ether (1/4, v/v) and ether, and dried over P_4O_{10} at 0.1 torr. Anal. Calcd for $[Co(C_{16}H_{36}N_7)](O_3SCF_3)_4$: Co, 6.00; C, 24.47; H, 3.70; N, 9.99; S, 13.06. Found: Co, 5.8; C, 24.7; H, 4.1; N, 9.9; S, 13.2. pK_a (25 °C, μ = 1.0, $NaClO_4$): 3.58 ± 0.02.

Racemic $CF_3SO_3^-$ salt (0.6 g) was readily resolved on a column of SP-Sephadex C-25 resin (6 × 30 cm) with use of 0.15 M $Na_2[Sb_2((+)_{589}\text{-tart})_2]$ as the eluant. Two bands of equal size clearly separated. The eluate of the first band was sorbed on a column of Na^+-form AG 50W-X2 resin, which was washed with water (0.1 L) and 1 M HCl (0.5 L). The complex was eluted with 4 M HCl and the eluate evaporated to dryness. The chloride salt was converted to the $CF_3SO_3^-$ salt by the same method employed for the racemic complex and collected as orange crystals by dissolution in ethanol (10 mL) followed by cooling to 0 °C and gradual addition of ether (50 mL). The crystals were washed with ether and dried over P_4O_{10} at 0.1 torr. Anal. Calcd for $\Lambda(+)_{492}$-$[Co(C_{16}H_{36}N_7)](O_3SCF_3)_4\cdot C_2H_5OH$: Co, 5.73; C, 25.71; H, 4.12; N, 9.54; S, 12.48. Found: Co, 5.7; C, 25.8; H, 4.2; N, 9.1; S, 12.3. Specific rotations (0.03%, in 0.1 M HO_3SCF_3): $[\alpha]_{540}$, −593; $[\alpha]_{492}$, +2190.

The eluate of the second band was treated in the same manner, giving an almost quantitative yield of the $\Delta(-)_{492}$ enantiomer. Anal. Found: Co, 5.7; C, 26.1; H, 4.2; N, 9.3; S, 12.3. Specific rotations (0.03%, in 0.1 M HO_3SCF_3): $[\alpha]_{540}$, +596; $[\alpha]_{492}$, −2270. Visible–UV (λ_{max} (nm), ϵ_{max}, in 0.1 M HO_3SCF_3): 488, 334; 349, 269; 248, 19.6 × 10^3. CD (λ_{max} (nm), $\Delta\epsilon_{max}$, in 0.1 M HO_3SCF_3): 513, +5.31; 461, −4.57; 348, +2.80.

In a quantitative experiment, with use of the same procedure described above for the preparation of racemic $[Co(amsartacnH)]^{4+}$ but with $\Delta(-)_{490}$-$[Co(nosartacn)]_2(S_2O_6)_3\cdot 8H_2O$ as the starting material, optically pure $\Delta(-)_{492}$-$[Co(amsartacnH)]^{4+}$ was obtained. Recovery (98%) was determined by the visible and rotatory dispersion spectra of the complex obtained after evaporation of the eluate from AG 50W-X2 resin with 4 M HCl.

$\Lambda(+)_{483}$- and $\Delta(-)_{483}$-[Co(azasartacn)]$(PF_6)_3$. To a stirred suspension of Li_2CO_3 (5.0 g) and $[Co(taetacn)](ClO_4)_3$ (6.16 g) in water (30 mL) at 50–55 °C was added aqueous ammonia (6.7 M, 75 mL) and aqueous formaldehyde (10 M, 75 mL). The solutions were added separately but synchronously over 5 h with a peristaltic pump. The mixture was filtered, and the filtrate was acidified with glacial acetic acid (20 mL), diluted to 1 L with water, and sorbed on a column of H^+-form AG 50W-X2 resin (4.5 × 8.0 cm). The column was washed with H_2O (0.2 L) and 1 M HCl (0.5 L) to remove Li^+, and all complex species were removed from the column by eluting with 4 M HCl. The colored eluate was evaporated to dryness. The solid residue was dissolved in water and sorbed on a column of SP-Sephadex C-25 (6 × 20 cm). Elution with 0.13 M trisodium citrate revealed two minor pink bands followed by a major yellow band. The eluate of the yellow band was sorbed on a column of AG 50W-X2 resin, washed with 1 M HCl, and eluted with 4 M HCl as before. After concentration to 10 mL, orange crystals deposited. Crystallization was completed by addition of methanol (70 mL) followed by ether (30 mL). The product was collected and recrystallized from a mixture of 11 M HCl (6 mL) and ethanol (5 mL), yielding shiny, hygroscopic crystals, which were washed with 11 M HCl/ethanol (1/3, v/v), ethanol, and ether and dried over P_4O_{10} at 15 torr; yield 1.75 g. Anal. Calcd for $[Co(C_{17}H_{33}N_7)]Cl_3\cdot{}^1/_2H_3OCl\cdot C_2H_5OH$: Co, 10.71; C, 37.12; H, 7.42; H^+, 0.0916; N, 17.82; Cl, 22.56. Found: Co, 10.4; C, 36.4; H, 7.4; H^+, 0.0944; N, 17.7; Cl, 22.8.

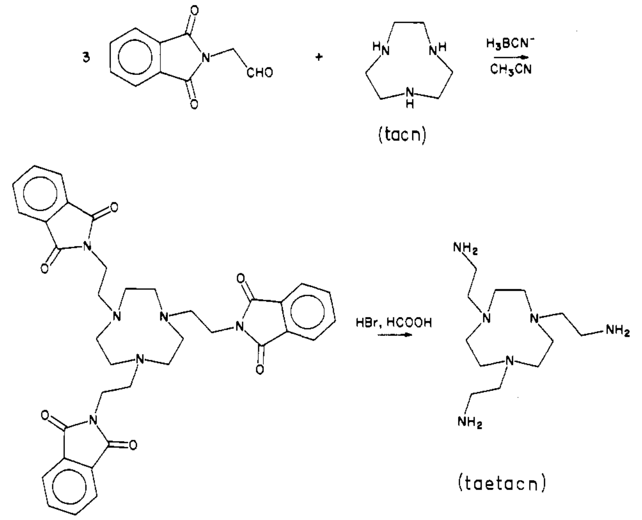
Only a partial separation was achieved in attempts to resolve $[Co(azasartacn)]^{3+}$ by ion-exchange chromatography on SP-Sephadex C-25 resin (length 75 cm) with 0.15 M $Na_2[Sb_2((+)_{589}\text{-tart})_2]$ as the eluant; the $(+)_{483}$ isomer eluted most rapidly. The chiral isomers of the complex were prepared from the corresponding isomers of $[Co(taetacn)]^{3+}$ in the following manner. Chiral $\Lambda(+)_{487}$-$[Co(taetacn)](ClO_4)_3$ (1.23 g, 2.00 mmol) was treated as described above for the preparation of racemic $[Co(azasartacn)]^{3+}$ under identical conditions, but the product was isolated as the PF_6^- salt: the yellow HCl eluate from the AG 50W-X2 resin was evaporated to dryness, the solid residue was dissolved in water (10 mL), and $NaPF_6$ (1.0 g) was added to precipitate a powdery product (0.40 g, $[M]_{483}$ +12 400). The crude product was collected and taken up in hot water (20 mL) and the solution slowly allowed to attain room temperature with the formation of crystals (0.08 g) of lower optical purity ($[M]_{483}$ = +10 200) than the mother liquor ($[M]_{483}$ = +13 300). The crystals were collected and the mother liquor concentrated to dryness, leaving a solid residue, which was redissolved in hot water (12 mL) and allowed to cool as above, yielding yellow crystals (0.08 g, $[M]_{483}$ = +12 800), which were collected. The mother liquor ($[M]_{483}$ = +13 700) was evaporated to dryness and the procedure repeated (5 mL H_2O), yielding crystals (0.08 g, $[M]_{483}$ + 13 600). The residual mother liquor ($[M]_{483}$ = +13 800) was evaporated to dryness and the solid residue recrystallized from a mixture of water (2.0 mL) and $NaPF_6$ (0.10 g), yielding large crystalline rods (20 mg). Anal. Calcd for Λ-$(+)_{483}$-$[Co(C_{15}H_{33}N_7)](PF_6)_3\cdot H_2O$: Co, 6.82; C, 20.86; H, 4.09; N, 11.36; P, 10.76. Found: Co, 6.6; C, 21.0; H, 4.9; N, 11.3; P, 10.6. Specific rotations (0.02%, in H_2O): $[\alpha]_{530}$, −413; $[\alpha]_{483}$, +1600; $[\alpha]_{360}$, +457.

The $\Delta(-)_{483}$ isomer was prepared in the same way with $\Delta(-)_{487}$-$[Co(taetacn)](ClO_4)_3$ as reagent (yield 60 mg). Anal. Found: Co, 6.3; C, 21.2; H, 5.2; N, 11.4; P, 10.8. Specific rotations (0.02%, in H_2O): $[\alpha]_{530}$, +408; $[\alpha]_{483}$, −1590; $[\alpha]_{360}$, −456. Visible–UV (λ_{max} (nm), ϵ_{max}): 482, 303; 348, 285; 243, 18.9 × 10^3. CD (λ_{max} (nm), $\Delta\epsilon_{max}$): 507, +3.40; 457, −2.43; 370, +0.65; 335, +0.78.

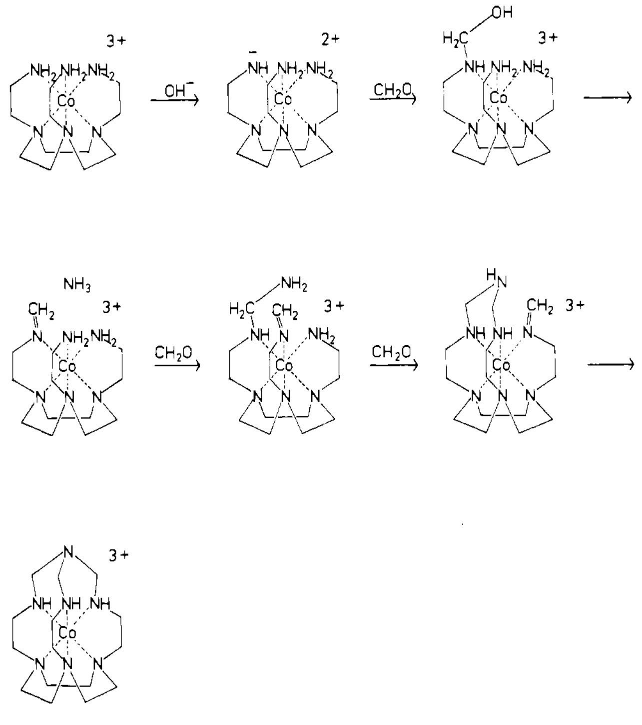
The $CF_3SO_3^-$ salts of the $[Co(taetacn)]^{3+}$, $[Co(nosartacn)]^{3+}$, and $[Co(azasartacn)]^{3+}$ ions were obtained by a common procedure from the corresponding Cl^- salts. The $[Co(taetacn)]Cl_3$ salt was obtained by evaporation to dryness of the HCl eluate. Generally, the solid complex Cl^- salts (1.5 mmol) were treated with anhydrous HO_3SCF_3 (4 mL) until all solid had dissolved and evolution of HCl had ceased. The dissolution process was accelerated by evacuating the reaction mixtures in a rotary evaporator at ~50 °C. After adequate cooling, ether (200 mL) was added with stirring to precipitate yellow flocculant products. These were collected and recrystallized from solutions of NaO_3SCF_3 (1.0 g) in water (4.0 mL) to yield, in all instances, large orange crystals, which were collected, washed with ethanol and ether, and dried over P_4O_{10} at 0.1 torr. Anal. Calcd for $[Co(taetacn)](CF_3SO_3)_3$ $(CoC_{15}H_{30}N_6S_3O_9F_9)$: Co, 7.71; C, 23.57; H, 3.95; N, 10.99; S, 12.58. Found: Co, 7.7; C, 23.7; H, 4.3; N, 10.9; S, 12.9. Calcd for $[Co(nosartacn)](CF_3SO_3)_3$ $(CoC_{19}H_{33}N_7S_3O_{11}F_9)$: Co, 6.84; C, 26.49; H, 3.86; N, 11.38; S, 11.16. Found: Co, 6.7; C, 26.6; H, 4.1; N, 11.4; S, 11.3. Calcd for $[Co(azasartacn)](CF_3SO_3)_3$ $(CoC_{18}H_{33}N_7S_3O_9F_9)$: Co, 7.21; C, 26.44; H, 4.07; N, 11.99; S, 11.77. Found: Co, 7.1; C, 26.4; H, 4.5; N, 11.9; S, 11.9.

Kinetics. Before each kinetic run all solutions of complexes were flushed for 4 h with O_2-free (aqueous Cr^{2+}) N_2 in a closed system that included a hand-operated stopped-flow mixer and its reservoirs. A spectrophotometer cell (1 cm) or a spectropolarimeter cell (5 cm), each of which had been flushed with N_2 as well, were also part of the closed system. The electron-transfer reactions were studied by following the change in optical rotation at 492 nm and 25.0 ± 0.1 °C of solutions containing Δ-$[Co(amsartacnH)]^{3+}$ and Λ-$[Co(amsartacnH)]^{4+}$ or Δ-$[Co(amsartacn)]^{2+}$ and Λ-$[Co(amsartacn)]^{3+}$. The complex $CF_3SO_3^-$ salts were used throughout. Solutions of Δ-[Co-

Scheme I



Scheme II



(amsartacnH)]$^{3+}$ in 0.20 M $NaClO_4$ or 0.20 M $LiClO_4$ were made in situ by reducing a solution of Δ-[Co(amsartacnH)]$^{4+}$ with amalgamated Zn. The Δ-[Co(amsartacnH)]$^{3+}$ solution in 0.20 M $NaClO_4$ was mixed with a solution of Λ-[Co(amsartacnH)]$^{4+}$ in 0.10 M $HClO_4$, 0.10 M $NaClO_4$, and the Δ-[Co(amsartacnH)]$^{3+}$ solution in 0.20 M $LiClO_4$ was mixed with a solution of Λ-[Co(amsartacn)]$^{3+}$ in 0.20 M Hepes buffer[8,9] at pH 7.48, μ = 0.20 M (0.10 M 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid, 0.10 M lithium 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonate, 0.10 M $LiClO_4$). Concentrations were taken as those of the starting solutions. Analogous studies have shown this technique to be satisfactory.[2] The kinetics of the oxidation of [Co(amsartacn)]$^{2+}$ and [Co(azasartacn)]$^{2+}$ with O_2 was followed spectrophotometrically at 489 nm and 25.0 ± 0.1 °C in triplicate. Solutions of [Co(amsartacnH)]$^{3+}$ in 0.20 M NaCl and [Co(azasartacn)]$^{2+}$ in 0.20 M NaCl were prepared with amalgamated Zn as above. The O_2 solutions were prepared by saturating a 2.4 mM sodium citrate–citric acid buffer[10] (pH 6.00, μ = 0.20 M (NaCl)) solution with O_2 at 25.0 ± 0.1 °C and ambient pressure of 713.4 mm. In separate experiments the concentrations of H_2O_2 formed in the oxidation reactions were determined iodometrically and the Co(III) concentrations determined spectrophotometrically after complete oxidation with excess O_2.

Results and Discussion

Synthesis. 1,4,7-Tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn) was synthesized by reductive alkylation[11] of 1,4,7-triazacyclononane (tacn) with phthalimidoacetaldehyde in the presence of $NaBH_3CN$ followed by acid hydrolysis of the recovered product to remove the protecting phthaloyl groups (Scheme I). The first reaction step was performed under anhydrous conditions in acetonitrile with molecular sieves added to scavenge the water produced in the reaction. One of the reactants, tacn·3HBr, was only sparingly soluble in the reaction medium but gradually dissolved during reaction, aided by a catalytic amount of tetramethylammonium acetate. On completion, the alkylated products were readily extracted into $CHCl_3$ and isolated as an oil.

The ^1H NMR spectrum of the oil appeared consistent with the trialkylated species 1,4,7-tris(2-phthalimidoethyl)-1,4,7-triazacyclononane, but thin-layer chromatography (neutral alumina, ethanol (1%) in dichloromethane) indicated at least two major components. Preparative-scale chromatography (Sephadex LH-20, chloroform) achieved a partial separation of the components, but this purification procedure was not pursued further since isolation and purification of the desired product was carried out readily as the Co(III) complex (if required, the free taetacn ligand can be readily obtained upon decomposition with H_2S of the purified complex). The phthaloyl protecting groups were most conveniently removed by acid hydrolysis in a HBr/acetic acid mixture. After evaporation the free amine hydrobromide was extracted into aqueous HBr and precipitated with glacial acetic acid.

Complexes. The [Co(taetacn)]$^{3+}$ complex was synthesized by aerial oxidation of Co^{2+} in the presence of activated charcoal and stoichiometric amounts of H^+ and crude taetacn in water. Ion-exchange chromatography of the mixture on AG 50W-X2 resin separated the yellow-orange fraction of [Co(taetacn)]$^{3+}$ from a red fraction, which was identified[12] as an isomeric mixture of (1,4-bis(2-aminoethyl)-1,4,7-triazacyclononane)chlorocobalt(III) complexes ([Co(baetacn)-Cl]$^{2+}$). The Co(III) complexes of the macrotricyclic cryptands 9-nitro-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane (nosartacn) and 1,4,7,9,11,14,19-heptaazatricyclo-[7.7.4.2^{4,14}]docosane (azasartacn) were synthesized on the metal by condensing [Co(taetacn)]$^{3+}$ with formaldehyde and nitromethane to give [Co(nosartacn)]$^{3+}$ or with formaldehyde and ammonia to give [Co(azasartacn)]$^{3+}$. The capping takes place through a series of intermolecular condensations and cyclizations as depicted in Scheme II. The nitro group of [Co(nosartacn)]$^{3+}$ was reduced to an amine group with Zn in HCl, yielding, upon reoxidation (with H_2O_2) of the encapsulated Co^{2+} ion, the (9-amino-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane)cobalt(III) ion, [Co(amsartacn)]$^{3+}$, which was isolated in the solid state as the protonated derivative, [Co(amsartacnH)]$^{4+}$. The pK_a of this ion (3.58 ± 0.02 at 25 °C in 1 M $NaClO_4$) is close to that determined for [Co(ammesarH)]$^{4+}$ (3.30).[13]

Resolutions. All of the hexaamine complexes obtained, except [Co(azasartacn)]$^{3+}$, were resolved into their chiral forms by ion-exchange chromatography on SP-Sephadex C-25 resin with use of chiral eluants. As a measure of the degree of separation Searle[14] has proposed R_x values (relative R_f

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Table I. ^{13}C NMR Data[a]

set no.	$[Co(taetacn)]^{3+}$ [b]	$[Co(nosartacn)]^{3+}$ [b]	$[Co(amsartacnH)]^{4+}$ [c]	$[Co(azasartacn)]^{3+}$ [b]
1, 2, 3	−2.0 −3.0 −3.9	−2.4 −2.6 −3.3	−2.4 −2.6 −3.3	-2.6_8 -2.6_3 −3.7
4	−21.3	−12.5, −13.4	−12.4, −13.6	−15.0
5				+0.4
6 (X = C)		+17.8	−13.7	

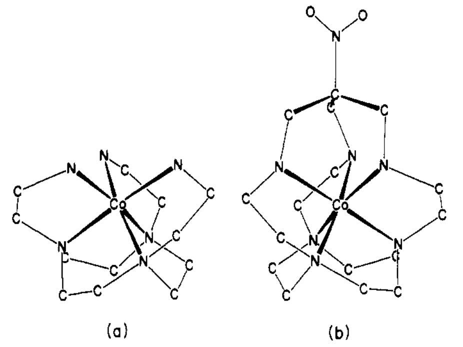
[a] Chemical shifts (ppm) are relative to 1,4-dioxane (=0 ppm). Downfield is defined as positive. [b] In D_2O. [c] In 0.01 M DO_3SCF_3, D_2O.

values) determined by measuring the distance from the top of the resin to the front of the separated bands and choosing one of the bands as a reference. The same definition of R_x has been adopted here, taking in each resolution experiment the trailing band as the reference. Admittedly, the R_x values are not reproducible quantities without detailed specification of certain variables such as flow rate, column dimensions, and eluant concentration. However, they seem useful as measures of relative elution rates for different species under the same conditions.

Sodium $(+)_{589}$-tartrate (0.2 M) was used as the eluant for $[Co(taetacn)]^{3+}$ and $Na_2[Sb_2((+)_{589}\text{-tart})_2]$ (0.15 M) for $[Co(nosartacn)]^{3+}$ and for $[Co(amsartacn)]^{3+}$. In all instances the $\Lambda(+)_{487-492}$ isomer eluted first. Alternatively, the chiral cage complexes were also synthesized from the chiral precursor $\Delta(-)_{487}$-$[Co(taetacn)](ClO_4)_3$, yielding optically pure Δ-$(-)_{490}$-$[Co(nosartacn)]^{3+}$, which in turn gave optically pure $\Delta(-)_{492}$-$[Co(amsartacnH)]^{4+}$.

In separate experiments, but under essentially identical conditions, racemic samples of the similar $[Co(amsartacn)]^{3+}$ and $[Co(nosartacn)]^{3+}$ complexes were resolved with use of 0.15 M $Na_2[Sb_2((+)_{589}\text{-tart})_2]$ as the eluant. In both instances the Δ isomers eluted first. The better separation achieved for $[Co(amsartacn)]^{3+}$ (R_x 1.6) over $[Co(nosartacn)]^{3+}$ (R_x 1.2) seems to indicate that the chiral eluant is better able to discriminate between the chiral isomers of the former complex than of the latter. Such discrimination can be ascribed to ion-pair formation,[15] and the two complexes concerned are structurally very similar except for the nature of the terminal substituent, $-NH_2$ or $-NO_2$. It seems reasonable to assume therefore that the terminal amino group of Λ-$[Co(amsartacn)]^{3+}$ is constructively engaged in the ion-pair formation of this ion with $[Sb_2((+)_{589}\text{-tart})_2]^{2-}$, most probably through hydrogen bonding. Evidence for hydrogen bonding phenomena in discrimination between such chiral forms appears in the ion-exchange and structural studies of Yoneda and co-workers[15] and of Bernal and co-workers.[16]

The resolution of $[Co(azasartacn)]^{3+}$ was also attempted with chromatography on SP-Sephadex C-25 resin, but only a partial separation within a single broad band was achieved by using a 75-cm column with 0.15 M $Na_2[Sb_2((+)_{589}\text{-tart})_2]$ as the eluant. The length of column that would have been required in order to accomplish complete separation by this method was impractical. Instead, both chiral forms of $[Co(azasartacn)]^{3+}$ were synthesized from the corresponding isomers of $[Co(taetacn)]^{3+}$, albeit in low yields. The synthesis, performed under vigorous conditions (pH 10, 50–55 °C) for a chiral Co(III) amine complex, was associated with a degree of racemization (enantiomeric excess ~80%). However, the optical purity of the product as the PF_6^- salt was improved by fractionally crystallizing the less soluble racemic component from the mixture. The chiral products thus obtained are estimated to be optically pure to within 2%.



(a) (b)

Figure 1. Drawings of the Δ-$[Co(taetacn)]^{3+}$ (a) and Λ-$[Co(nosartacn)]^{3+}$ (b) cations.

Characterization. All of the complexes gave correct elemental analyses and were further characterized by their ^{13}C NMR spectra; chemical shifts are listed in Table I. According to the spectra all four species display C_3 symmetry in solution and give rise to three closely separated peaks in the region δ −2.0 to −3.9. These are assigned to three sets of inequivalent but chemically similar carbon atoms (sets 1, 2, 3) bonded to the coordinated tertiary amine nitrogen atoms. In the spectrum of $[Co(taetacn)]^{3+}$ the remaining peak at δ −21.3 is then attributable to the set of equivalent carbon atoms (set 4) bonded to the coordinated primary amino groups. In the $[Co(azasartacn)]^{3+}$ spectrum the corresponding carbon atoms (set 4) appear as one peak at δ −15.0, but in the spectra of $[Co(nosartacn)]^{3+}$ and $[Co(amsartacnH)]^{4+}$ they appear as either of the two peaks in the region between δ −12.4 and −13.6 with the other peak in this region then due to the equivalent methylene carbon atoms (set 5) of the cap. The peak due to the single tertiary carbon atom (set 6, X = C) of the cap appears at δ +17.8 in the spectrum of $[Co(nosartacn)]^{3+}$ and, probably, as the shoulder of the signal at δ −13.7 in the spectrum of $[Co(amsartacnH)]^{4+}$. These chemical shifts correlate with those of the $[Co(dinosar)]^{3+}$ (δ +21.4)[3,17] and $[Co(diamsarH_2)]^{5+}$ (δ −10.3)[3,18] systems. The three equivalent methylene carbon atoms (set 5) of the $[Co(azasartacn)]^{3+}$ cap show up as the peak at δ +0.4, which, within experimental error, is identical with the chemical shift observed[2] for the corresponding atoms in $[Co(sep)]^{3+}$.

An X-ray crystallographic analysis by Snow and Taylor[19] has confirmed the identity of the $\Delta(-)_{487}$-$[Co(taetacn)]^{3+}$ ion and has also established the absolute configuration of this ion to be that illustrated in Figure 1. The existing IUPAC nomenclature[20] for the absolute configuration of tris- and bis-bidentate complexes based on the octahedron is inapplicable for the $(-)_{487}$-$[Co(taetacn)]^{3+}$ ion. The complex gives rise to an equal number of Δ and Λ pairs of skew lines, as defined

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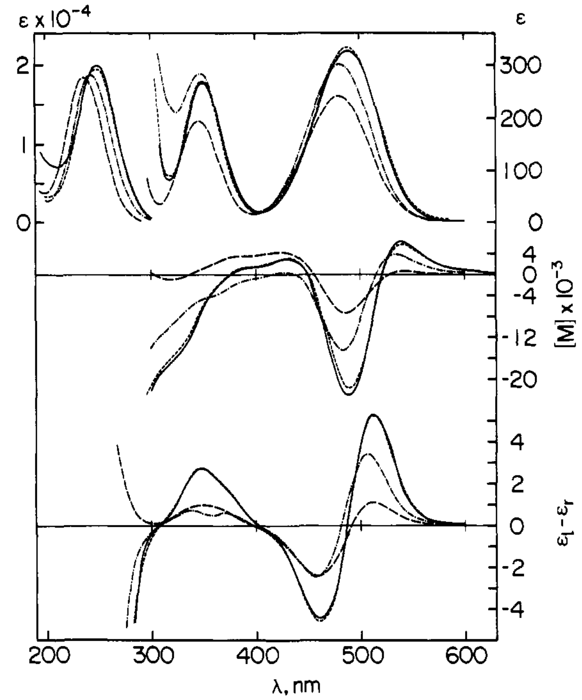

Figure 2. Absorption, rotatory dispersion, and circular dichroism spectra of $\Delta(-)_{487}$-[Co(taetacn)]$(ClO_4)_3$ (– – –), $\Delta(-)_{490}$-[Co(nosartacn)]$(S_2O_6)_{1.5}$ (—), and $\Delta(-)_{483}$-[Co(azasartacn)]$(PF_6)_3$ (–·–), all in water, and $(-)_{492}$-[Co(amsartacnH)]$(O_3SCF_3)_4$ in 0.1 M HO_3SCF_3 (- - -).

by the octahedral edges spanned by a chelate ring. However, a truncated convention has been adopted. The $(-)_{487}$-[Co(taetacn)]$^{3+}$ ion can be regarded as being derived from Δ-[Co(en)$_3$]$^{3+}$ and thus assigned the absolute configuration Δ on the basis of the chirality defined by the "Co(en)$_3$" element of the molecule. This convention is also applied to the chiral derivatives of [Co(taetacn)]$^{3+}$ reported in this paper.

An X-ray crystallographic analysis[19] has also confirmed the structural features and absolute configuration of the Λ-$(+)_{490}$-[Co(nosartacn)]$^{3+}$ ion, illustrated in Figure 1. On the basis of these results and the results from the chiral derivative syntheses, the chiralities of all four complex species of this study can be correlated. The crystal structure determinations establish the absolute configurations of $\Delta(-)_{487}$-[Co(taetacn)]$(ClO_4)_3$ and $\Lambda(+)_{490}$-[Co(nosartacn)]$(S_2O_6)_{1.5}\cdot 4H_2O$ in agreement with the correlation derived from the synthesis of $\Lambda(+)_{490}$-[Co(nosartacn)]$^{3+}$ from $\Lambda(+)_{487}$-[Co(taetacn)]$(ClO_4)_3$. The synthesis occurs with retention of chirality and absolute configuration, in a manner analogous to the synthesis of [Co(sep)]$^{3+}$ from [Co(en)$_3$]$^{3+}$ (Scheme II). Similarly, reduction of the nitro group in $\Delta(-)_{490}$-[Co(nosartacn)]$^{3+}$ afforded optically pure $\Delta(-)_{492}$-[Co(amsartacnH)]$^{4+}$.

By contrast, some racemization took place in the synthesis of the $(+)_{483}$-[Co(azasartacn)]$^{3+}$ ion (~80% enantiomeric excess) from the $\Lambda(+)_{487}$-[Co(taetacn)]$^{3+}$ complex. The high enantiomeric yield, however, leaves no doubt that the product $(+)_{483}$ isomer also has the absolute configuration Λ.

Spectra. Figure 2 shows the visible and near-UV absorption, the rotatory dispersion, and the CD spectra of all four molecules in the Co(III) oxidation state. Numerical data are given in the Experimental Section. The spectra are characteristic of chiral Co(III) hexaamine complexes.

As might be expected from their close structural similarity, the ions Δ-[Co(nosartacn)]$^{3+}$ and Δ-[Co(amsartacnH)]$^{4+}$ have almost identical absorption, rotatory dispersion, and CD spectra.

The CD sign variation in the region of the first and second ligand field bands qualitatively remains the same for the parent Δ-[Co(taetacn)]$^{3+}$ ion and its capped derivatives of the same chirality. In other words, the addition of the cap does not alter the sign variation in the CD spectra.

However, the CD sign variation observed for the Δ-[Co(en)$_3$]$^{3+}$ ion in the first ligand field band region is qualitatively opposite to that seen for the Δ-[Co(taetacn)]$^{3+}$ ion (and capped derivatives),[21] even though both ions have the same chirality as defined by the "Co(en)$_3$" element. The solution CD spectra of Co(III) hexaamines with D_3 symmetry such as [Co(en)$_3$]$^{3+}$ are generally considered as an averaged superposition (due to the random orientation of the molecules) of two almost equal and symmetrical CD components with opposite signs.[22] These components are associated with the electronic transitions to the $A_2(D_3)$ (polarized along the C_3 axis) and the $E(D_3)$ (polarized perpendicular to the C_3 axis) excited levels. Axial CD measurements on single uniaxial crystals of Λ-[Co(en)$_3$]$^{3+}$ and Λ-[Co(sep)]$^{3+}$ have shown the E component to be of positive sign in both compounds and consequently of negative sign for the Δ absolute configuration.[23] This situation is assumed to remain unchanged in solution. On that basis the negative band (at lower energy) in the CD spectrum of Δ-[Co(en)$_3$]$^{3+}$ is regarded as a wing of the negative E component and the much smaller but positive band in the spectrum is regarded as a wing of the A_2 component, which thus must be less intense than the E component. The two components are centered at slightly different energies due to the trigonal splitting, with the E component at lowest energy. If the effective symmetry governing the CD in Δ-[Co(taetacn)]$^{3+}$ is D_3 and if the skew configuration of the chelate rings in the "Co(en)$_3$" element is dominating the CD, then, by analogy to Δ-[Co(en)$_3$]$^{3+}$ and Δ-[Co(sep)]$^{3+}$, the negative band in the CD spectrum of Δ-[Co(taetacn)]$^{3+}$ is likely to be a wing of the E component. The implication in this analysis is that the relative positions of the E and A_2 components are inverted in Δ-[Co(taetacn)]$^{3+}$ compared to the situation in Δ-[Co(en)$_3$]$^{3+}$. In the solution CD spectrum of Δ-[Co(sep)]$^{3+}$, only a positive band is observed and this has been ascribed to the A_2 component dominating entirely the E component.

If these arguments are correct, then the variation in CD arises from quite subtle changes in the structures of the different ions. Clearly the "Co(en)$_3$" structural unit does not dominate the issue and small variations in atomic positions may be crucial to the ordering of the A_2 and E energy levels and their rotatory strengths.

Redox Properties. Results from the electrochemical studies of the Co(III)/Co(II) reduction process for the [Co(taetacn)]$^{3+}$ ion and its ligand-cage derivatives in water (0.1 M $NaClO_4$), acetone (0.1 M TMAT), and acetonitrile (0.1 M TMAT) are listed in Table II. In all three solvent systems the polarograms of all complex species investigated showed essentially reversible one-electron reduction waves ascribable to Co(III) → Co(II) reduction. In the aqueous system this electrochemical reversibility was confirmed by cyclic voltammetry at Hg. With similar diffusion coefficients for the electroactive species, the experimental $E_{1/2}$ values would closely approximate the thermodynamic reduction potentials in the relevant media.

The reduction potentials of the [Co(amsartacn)]$^{2+/3+}$ and the [Co(amsartacnH)]$^{3+/4+}$ redox couples differ by 0.15 V. Protonation renders the system less reducing. It is evident that the substituents on the caps are able to modulate the redox properties of the cobalt cages quite markedly. The point is clearly illustrated by the series of [Co(sarcophagine)]$^{2+/3+}$ derivatives. Here the complexes all have the same basic

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Table II. Electrochemical Data at 22 °C

	Co(III)/Co(II) reduction potentials						
	water[a]					acetone[b] polarography, $E_{1/2}$, V[f]	acetonitrile[b] polarography, $E_{1/2}$, V[f]
	polarography		cyclic voltammetry at Hg[c]				
compd[d]	$E_{1/2}$, V[e]	$E_{1/2}$, V	$E_{1/2}$, V[e]	ΔE_p, V	i_{pf}/i_{pb}		
$[Co(taetacn)]^{3+}$	−0.36	−0.12	−0.36	0.07	0.7	−0.05	+0.04
$[Co(nosartacn)]^{3+}$	−0.18	0.06	−0.18	0.06	0.9	+0.12	+0.22
$[Co(amsartacnH)]^{4+}$, pH 2[g]	−0.17	0.07	−0.17	0.08	1.0	+0.17	+0.24
$[Co(amsartacn)]^{3+}$, pH 9[h]	−0.30	−0.08	−0.32	0.07	0.8		
$[Co(azasartacn)]^{3+}$	−0.30	−0.06	−0.31	0.07	1.0	+0.02	+0.07

[a] With 0.1 M $NaClO_4$. [b] With 0.1 M TMAT. [c] Scan rate 50 mV/s. [d] Anhydrous $CF_3SO_3^-$ salts were used throughout; concentration of complex 10^{-3} M. [e] Vs. SCE. [f] Vs. Ag/AgCl, 0.1 M LiCl in acetone. [g] $HClO_4$, added in aqueous system only. [h] NaOH.

structure and differ from each other only by the nature of the substituents on the caps. Nevertheless, their reduction potentials span a range of ~0.5 V with the potentials decreasing in the order diamsarH_2 (+0.06 V) > dinosar (+0.04 V) >> ammesarH (−0.19 V) = nomesar (−0.19 V) >> diamsar (−0.30 V) > ammesar (−0.35 V) > sar (−0.40 V).[3,13]

In all instances the reduction potential of a $-NO_2$ substituted redox couple is very close to the reduction potential of the $-NH_3^+$ substituted equivalent. This apparent similarity in the effect of the $-NO_2$ and the $-NH_3^+$ substituent could be attributed to the similar electron-withdrawing effects generally observed in organic chemistry.[24]

Reduction of O_2. Quantitatively, $\Delta(-)_{490}$-$[Co(nosartacn)]^{3+}$ was reduced with Zn in HCl. On reoxidation (with H_2O_2) optically pure $\Delta(-)_{492}$-$[Co(amsartacnH)]^{4+}$ was recovered in a yield better than 98%.

Both $[Co(amsartacn)]^{2+}$ and $[Co(azasartacn)]^{2+}$ reduce O_2 in aqueous solution to give H_2O_2 and $[Co(amsartacn)]^{3+}$ and $[Co(azasartacn)]^{3+}$, respectively. In each instance iodometric titrations detected >78% of the theoretical amount of generated H_2O_2 according to the stoichiometry $2Co(II) + O_2 + 2H^+ \rightarrow 2Co(III) + H_2O_2$. For both Co(II) complexes (0.1 mM) the kinetics of the oxidation reaction was followed spectrophotometrically (489 nm) at one O_2 concentration under pseudo-first-order conditions with O_2 in 2.4 mM citrate buffer (pH 6.0, μ = 0.2 M) at 25.0 ± 0.1 °C. The O_2 concentration (1.14 mM) of the saturated reactant solution was calculated on the basis of the ambient pressure (713.35 mmHg) and published values[25] for the solubility of O_2 in 0.2 M NaCl. For both reactions, plots of log $(A_\infty - A)$ against time were linear for at least 3 half-lives, leading to observed first-order rate constants $k_{obsd} = (1.6 \pm 0.1) \times 10^{-4}$ s^{-1} for the oxidation of $[Co(amsartacn)]^{2+}$ and $k_{obsd} = (0.9 \pm 0.1) \times 10^{-4}$ s^{-1} for $[Co(azasartacn)]^{2+}$.

The reduction of O_2 to H_2O_2 is an interesting property of the Co(II)–cage complexes and is in keeping with the observations[2] for $[Co(sep)]^{2+}$. Usually Co(II)–amine complexes react with O_2 to give Co(III)–peroxy dimers[26] such as $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+}$, but the tightness and steric bulk of the cage ligand structures prevent access of O_2 to the encapsulated Co(II) center. This would then imply an outer-sphere redox process. The first and rate-determining step in the oxidation of $[Co(sep)]^{2+}$ has been established as

$$[Co(sep)]^{2+} + O_2 \rightarrow [Co(sep)]^{3+} + O_2^-$$

The superoxide ion and another $[Co(sep)]^{2+}$ ion then react rapidly to give peroxide.[2] The derived rate law for this mechanism has the form $-d[O_2]/dt = -{}^1/_2 d[Co(II)]/dt = k_{ox}[Co(II)][O_2]$. For the $[Co(sep)]^{2+} + O_2$ reaction k_{ox} = 43 ± 5 M^{-1}·s^{-1} was obtained at 25 °C, μ = 0.2 M.[2]

Although it is not substantiated, the same rate law is assumed to hold here for the reaction of O_2 with $[Co(amsartacn)]^{2+}$ or $[Co(azasartacn)]^{2+}$, and the second-order rate constants are calculated from the observed first-order rate constants on that basis to give k = 0.14 M^{-1}·s^{-1} for $[Co(amsartacn)]^{2+} + O_2$ and k = 0.08 M^{-1}·s^{-1} for $[Co(azasartacn)]^{2+} + O_2$ at 25 °C. If this is correct, these ions are reacting ~300-fold slower with O_2 than does $[Co(sep)]^{2+}$. This is consistent with the fact that $[Co(sep)]^{2+}$ ($E°$ = −0.26 V vs. NHE) is a better reducing agent than $[Co(amsartacn)]^{2+}$ ($E°$ = −0.08 V vs. NHE), which, in turn, is a slightly better reducing agent than $[Co(azasartacn)]^{2+}$ ($E°$ = −0.06 V vs. NHE).

The demonstrated kinetic inertness and optical stability of the $[Co(amsartacn)]^{2+}$ ion is analogous to the behavior of $[Co(sep)]^{2+}$ and $[Co(ammesar)]^{2+}$. Although Co(II) complexes usually exchange their ligands on the microsecond time scale,[27] the observed inertness in this instance is most probably due to the connectivity and the tight packing of the strands of the stable sexidentate cage ligands, which limit substitution reactions at the metal ion. This aspect is revealed by space-filled Leybold models. The rigidity of the cage structures is also manifested in the optical stability of the Co(II) cages. Synchronous rupture of all three Co(II)–N(*sec*-amine) bonds and a trigonal twist of the cage would lead to inversion of configuration provided the three nitrogen configurations also inverted. Also, synchronous deprotonation of all three *sec*-amine nitrogen centers coupled with a twist of the complex ion about the C_3 axis and inversion at the deprotonated nitrogen centers would lead to racemization. The improbability of both processes indicates why the Co(II) complex is unusually optically stable. The cage structure makes it difficult for the Co(II)–N bonds to be broken, and the close packing of the ligand strands makes the synchronous triple deprotonation followed by triple inversion and trigonal twist a necessity. The overall inversion process could not be accomplished by successive deprotonations and inversions at individual nitrogen centers coupled with a trigonal twist because of the steric strain introduced by each separate inversion.

Electron Self-Exchange Process. The kinetic inertness and optical stability of the $[Co(amsartacn)]^{2+/3+}$ and the $[Co(amsartacnH)]^{3+/4+}$ couples in both of their oxidation states enabled the electron exchange-rate measurements to be performed quite simply with use of the method described by Dwyer and Gyarfas.[28] For each couple a chiral form of one oxidation state was mixed with the catoptric form of the other oxidation state:

$$\Lambda\text{-}Co^{III}L + \Delta\text{-}Co^{II}L \rightleftarrows \Lambda\text{-}Co^{II}L + \Delta\text{-}Co^{III}L$$

For equal concentrations of the two oxidation states a net

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Table III. Rate Constants for the Electron Transfer at 25.0 ± 0.1 °C[a]

$10^3 \times [\mathrm{Co}]_{\mathrm{total}}$, M	$[\mathrm{Co(III)}]_{t_0}/[\mathrm{Co(II)}]_{t_0}$	$10^4 k_{\mathrm{obsd}}$, s^{-1}	$10^2 k$, $\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$
Δ-[Co(amsartacnH)]$^{3+}$/Λ-[Co(amsartacnH)]$^{4+}$ [b]			
3.06	0.26	1.09	3.56
2.22	0.40	0.997	4.49
3.17	1.00	1.24	3.91
2.22	2.50	0.834	3.76
2.95	3.66	1.31	4.44
			k_{av} 0.040 ± 0.004
Δ-[Co(amsartacn)]$^{2+}$/Λ-[Co(amsartacn)]$^{3+}$ [c]			
2.95	0.27	2.48	8.41
2.92	0.52	2.49	8.53
3.17	1.00	3.06	9.65
2.66	1.11	2.29	8.60
2.91	3.59	2.29	7.87
			k_{av} 0.086 ± 0.006

[a] Rates measured spectrophotometrically at 492 nm. [b] In 0.005 M $HClO_4$, 0.15 M $NaClO_4$. [c] In 0.2 M Hepes buffer, pH 7.5, μ = 0.20 M ($LiClO_4$).

rotation is observed, which decays through electron transfer to give (finally) an equilibrium mixture with zero optical rotation. Since electron exchange between species of the same chirality leads to no change in the optical rotation, the electron-transfer rate is only measured through electron exchange between species of opposite chirality. The kinetics of the electron-transfer reactions were studied by measuring the rate of change in optical rotation, α, at 492 nm of solutions that initially contained the ions Δ-[Co(amsartacnH)]$^{3+}$ and Λ-[Co(amsartacnH)]$^{4+}$ or Δ-[Co(amsartacn)]$^{2+}$ and Λ-[Co(amsartacn)]$^{3+}$. Plots of ln ($\alpha - \alpha_\infty$) vs. time were linear for at least 4 half-lives to yield a rate law of the form

$$\frac{\mathrm{d}\ln(\alpha - \alpha_\infty)}{\mathrm{d}t} = -kC_{\mathrm{Co}} = -k_{\mathrm{obsd}}$$

where C_{Co} is the total cobalt concentration and k the second-order rate constant for electron transfer. Values of k_{obsd} and k for the [Co(amsartacnH)]$^{3+}$/[Co(amsartacnH)]$^{4+}$ and [Co(amsartacn)]$^{2+}$/[Co(amsartacn)]$^{3+}$ couples are given in Table III. The rate law is independent of the Co(II)/Co(III) ratio, consistent with a second-order exchange process, the derived rate law of which is deposited in the supplementary material. The rate constants obtained for the two systems fall within the range covered by other Co(II)/Co(III)–hexaamine cage systems ([Co(sep)]$^{2+/3+}$, k = 5.1 $\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$; [Co(diamsarH)]$^{4+/5+}$, k = 0.024 $\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$)[2,13] and should be compared with the rate constants for the [Co(diamsar)]$^{2+/3+}$ (k = 0.50 $\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$)[13] and [Co(diamsar$H_2$)]$^{4+/5+}$ systems; no gross differences are seen.

A 2-fold decrease in rate was observed on protonating the primary amine group of the [Co(amsartacn)]$^{2+/3+}$ couple. A similar effect was seen for the [Co(diamsar)]$^{2+/3+}$ and [Co(diamsarH_2)]$^{4+/5+}$ couples, where a 20-fold decrease in the rate was observed after double protonation. It would be unsafe to interpret this effect solely in terms of the stronger repulsive interaction between the exchanging ions due to the increased positive charge, because the protonation also affects the redox properties of the redox couples, as pointed out earlier.

The spectroscopic properties of the Co(III)–hexaamine cage complexes are not significantly different from those of the [Co(en)$_3$]$^{3+}$ ion. Therefore, it is striking that the Co(II)/Co(III)$^{2+/3+}$ hexaamine cages exchange their electrons between 10^3- and 10^5-fold faster than does the [Co(en)$_3$]$^{2+/3+}$ couple ($k = 3.4 \times 10^{-5}$ $\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$, extrapolated to 25 °C, μ = 0.2 M).[29]

The arguments that have been advanced earlier to explain the observed slow electron-transfer rates in Co(II)/Co(III)–amine systems have centered on the restrictions arising from forbidden spin-state changes.[30] These explanations do not seem to hold for the cobalt(III) cage systems in general as discussed elsewhere.[2] The aza capped cage ions might have been considered to communicate more readily through the lone pair of electrons, but experiments with C–H substituting for the tertiary N center barely alter the electron-exchange rates. One of the reasons for making the current complexes was that the tacn ring might allow more ready access to the metal ion d orbitals along the C_3 axis and thereby a more facile electron transfer. Clearly, this prospect was not realized and the tacn cage complexes are not substantially different from the other cage complexes in this respect.

To date the bond length differences for Co(II) and Co(III) have been essentially constant for the saturated hexaamine complexes and so have the ligand field spectroscopic properties. Neither of these factors therefore can accommodate the rate differences. The sizes of the hexaamine ions [Co(NH$_3$)$_6$]$^{2+/3+}$, [Co(en)$_3$]$^{2+/3+}$, [Co(chxn)$_3$]$^{2+/3+}$,[31] and [Co(cage)]$^{2+/3+}$ do vary considerably and thence the hydration energies, but there is still no correlation with rates and the size of the ion. By implication this indicates that the hydration energies are not significant in accounting for the rate differences. The change in charge does affect the rate within the cage systems in a relatively minor way, and that could be ascribed to work terms or the effect of the $-NH_2$ and $-NH_3^+$ substituents on the redox potential for the couples or both. It seems likely that the internal reorganizational energies are a critical factor in explaining the differences observed although they are not reflected in the Co–N bond lengths. To assess this factor, the strain energies of the Co(II)/Co(III)–amine complexes are at present being explored with use of molecular mechanics calculations.[32]

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Registry No. **1**, 87262-58-6; **1**(CF_3SO_3)$_3$, 87262-66-6; **1**(ClO_4)$_3$, 87262-59-7; $\Lambda(+)_{487}$-**1**(ClO_4)$_3$, 87332-45-4; $\Delta(-)_{487}$-**1**(ClO_4)$_3$, 87332-47-6; **2**, 87262-67-7; **2**(CF_3SO_3)$_3$, 87262-68-8; **2**Cl_3, 87262-60-0; $\Lambda(+)_{490}$-**2**(S_2O_6)$_{3/2}$, 87333-68-4; $\Delta(+)_{490}$-**2**(S_2O_6)$_{3/2}$, 87333-70-8; **3**, 87332-53-4; Λ-**3**, 87391-71-7; **3**(O_3SCF_3)$_4$, 87332-50-1; $\Lambda(+)_{492}$-**3**-(O_3SCF_3)$_4$, 87333-72-0; $\Delta(+)_{492}$-**3**(O_3SCF_3)$_4$, 87262-63-3; **4**, 87332-54-5; **4**(CF_3SO_3)$_3$, 87391-70-6; **4**Cl_3, 87333-73-1; $\Lambda(+)_{483}$-**4**-(PF_6)$_3$, 87262-65-5; $\Delta(-)_{483}$-**4**(PF_6)$_3$, 87332-52-3; Δ-[Co(amsartacnH)]$^{3+}$, 87262-69-9; Δ-[Co(amsartacn)]$^{2+}$, 87262-70-2; Λ-[Co(amsartacn)]$^{3+}$, 87332-55-6; taetacn·6HBr, 87262-57-5; 1,4,7-triazacyclononane trihydrobromide, 35980-59-7; phthalimidoacetaldehyde, 2913-97-5.

Supplementary Material Available: The derivation of the rate law for electron exchange between the metal complexes (2 pages). Ordering information is given on any current masthead page.

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