with an HP 3390A integrator. Melting points were measured with a Thomas-Hoover capillary apparatus; temperatures are uncorrected.

***N*-(3-Hydroxy-3,3-diphenylpropylidene)ethylamine** (**4a**) was prepared by the method of Wittig and Frommeld;[2b] mp 122–124 °C (lit.[2b] mp 124–125 °C).

***N*-(3-Hydroxy-1-methyl-3,3-diphenylpropylidene)cyclohexylamine** (**4d**) was prepared by a modification of the method of Wittig and Suchanek[28] using THF instead of ether as the solvent; mp 90–91 °C (lit.[28] mp 91–93 °C).

Diphenyl-*1*-^{13}*C*-methanone was prepared in 81% yield by the method of Nicodem and Marchiori[29] using 90% labeled benzoic acid (Merck) and was purified by silica gel chromatography with 1:1 hexane–methylene chloride elution.

Deprotonations of Lithium Benzhydrolate. The following procedure is representative. Into an oven-dried, 40-mL centrifuge tube which was flushed with argon and fitted with two No-Air septa was added 0.71 g (7.0 mmol) of diisopropylamine. THF (15 mL) was added and the solution was cooled to −78 °C. To the solution was added 4.50 mL of 1.56 M *n*-butyllithium in hexane. The solution was allowed to stand for 20 min at −78 °C then was warmed to 22 ± 2 °C. Benzhydrol (0.25 g, 1.4 mmol) in 1 mL of THF was added by syringe. Aliquots of the reaction mixture were removed periodically and quenched with oxygen. This was done by capping a 10-mL scintillation vial with a septum, flushing with oxygen, and then adding the aliquot and gently mixing. Saturated ammonium chloride solution (1 mL) was added after 1 min. After separation of the phases the THF layer was analyzed by GC.

Reactions of Benzophenone. The following procedure is representative. Into an oven-dried, 40-mL centrifuge tube which had been flushed with argon and fitted with two No-Air septa was added 0.68 g (6.7 mmol) of diisopropylamine. THF (15 mL) was added and the solution was cooled to −78 °C. To the solution was added 4.3 mL of 1.56 M *n*-butyllithium in hexane. The solution was allowed to stand for 20 min at −78 °C then was warmed to 22 ± 2 °C. Benzophenone (2.2 mL of a 0.95 mmol/mL solution) was added by syringe. Within 5 min a sample was removed from the reaction mixture, added to aqueous ammonium chloride solution, and analyzed by GC. Aliquots were removed periodically and analyzed by either of two methods.

(1) Analysis by oxidation: At a given reaction time an aliquot of the reaction mixture was quenched by addition to a 50% sodium hydroxide solution. A second sample was added to a vessel containing oxygen and allowed to react for 10–15 min before addition of saturated aqueous ammonium chloride. The percentage of benzhydrol and benzophenone in each sample was measured by a GC analysis. The difference in the percentage of the benzophenone detected in the two analyses represented 50% of the ketyl present after correction for autooxidation of benzhydrol. (See text for details.)

(2) Analysis by ESR: At a given time a 1-mL sample was removed and added to a 5-mm tube. The ESR spectrum of the sample was measured at 2 mW power and high modulation. The area of the curve was measured and related to those measured for a series of ketyl concentrations which had been determined by the oxidation method. All spectra were determined with constant instrument settings with the exception of the receiver gain; this effect was accounted for in the area measurements.

Rate of the Retro-Aldol Reactions. To a 10-mm NMR tube which had been flushed with argon was added 103 mg (0.33 mmol) of **4d**. After the addition of 2.5 mL of dry THF and cooling to −78 °C, 0.22 mL of 1.5 M methyllithium in ether was added. The solution was warmed to 22 ± 2 °C, and 60 mg (0.33 mmol) of the ^{13}C-labeled benzophenone was added. Spectra were obtained every 30 min, and the ratio of the carbonyl peak (δ 194.5) to the quaternary carbon (δ 79.6) was measured. A similar experiment was performed with **4a**.

Acknowledgment. We are grateful to the donors to the Petroleum Research Fund, administered by the American Chemical Society, and to the Robert A. Welch Foundation for support of this research. We thank W. G. Williams for performing preliminary studies of the reaction of benzhydrol with LDA.

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Synthesis, Chiroptical Properties, and Electron Self-Exchange Reactivity of a Rigid Pentacyclic Metal Ion Cage System with D_3 Symmetry

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Abstract: The rigid pentacyclic metal ion cages Δ-(4,9,15,20,25,30*R*)- and Λ-(4,9,15,20,25,30*S*)-[(1,12-dinitro-3,10,14,21,24,31-hexaazapentacyclo[$10.10.10.0^{4,9}.0^{15,20}.0^{25,30}$]dotriacontane)cobalt(III)](3+) ($\Delta(R,R)_3$ and $\Lambda(S,S)_3$-[Co(diNOchar)]$^{3+}$) have been synthesized by the reaction of nitromethane and formaldehyde with the corresponding [Co(chxn)$_3$]$^{3+}$ substrate (chxn = (*R,R* or *S,S*)-*trans*-1,2-cyclohexanediamine). Reduction with Zn and HCl yields the cobalt(II) complexes and also reduces the nitro substituents to amino groups. Reoxidation with H_2O_2 and O_2 then gives the $\Delta(R,R)_3$- and $\Lambda(S,S)_3$-[Co(diAMchar)]$^{3+}$ ions quantitatively. The cage complexes are configurationally and conformationally rigid and substitutionally inert in both the cobalt(II) and cobalt(III) oxidation states, and the amino derivatives are stable in aqueous solutions of strong acid or strong base at elevated temperatures (>200 °C). Reversible reduction potentials and ^{1}H NMR, ^{13}C NMR, and chiroptical spectra are reported for all of the complexes prepared. The cobalt(II,III) electron self-exchange rate constant for the $\Delta(R,R)_3$-[Co(diAMchar)]$^{2+}$, $\Lambda(S,S)_3$-[Co(diAMchar)]$^{3+}$ reaction is 1.1 M^{-1} s^{-1}, which is roughly 10^5 greater than that for [Co(en)$_3$]$^{2+/3+}$ and that inferred for the [Co(chxn)$_3$]$^{2+/2+}$ system.

We have recently developed a template approach to the encapsulation of some inert transition-metal ions, notably Co(III),[1] Pt(IV),[2] and Rh(III).[3] The procedure involves condensation of formaldehyde and either nitromethane or ammonia with the [M(en)$_3$]$^{n+}$ species at pH ~10 to yield the metal ion cage complexes (**1**, **2**).[4] The chiral cobalt center and six chiral nitrogen donors imply 16 possible diastereoisomers, only one of which is found.

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(1) (a) Creaser, I. I.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. (b) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016. (c) Geue, R. J.; Hambley, T. W.; Harrowfield, J. MacB.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.

(2) Boucher, H.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652.

(3) Bond, A. M.; Harrowfield, J. MacB.; Herlt, A. J.; Lay, P. A.; Mulac, W. A.; Sargeson, A. M.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5503.

(4) sepulchrate = sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane; sar = sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; diNOsar = 1,8-dinitrosarcophagine; diAMsarH_2 = 1,8-diaminosarcophagine; diAMsarH_2 = 1,8-diammonium sarcophagine; en = ethylenediamine.

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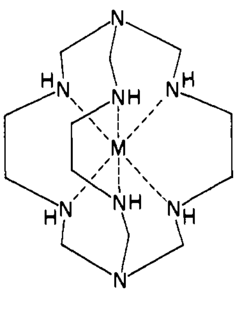
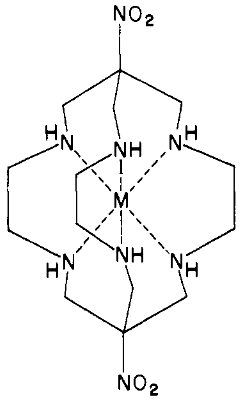


$[\mathrm{M(sepulchrate)}]^{n+}$

1

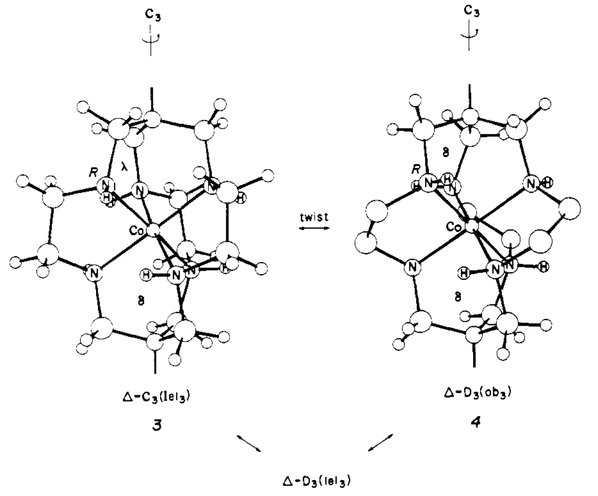


$[\mathrm{M(diNOsar)}]^{n+}$

2

The origin of this stereospecificity is clearly apparent from molecular models which show that for an octahedral chromophore, the skeletal configuration of the Δ-$[\mathrm{M(en)_3}]^{n+}$ substrate ensures a cage complex with all *R* nitrogen donors, and that of the Λ-$[\mathrm{M(en)_3}]^{n+}$ form fixes the donors in the *S* configuration.

The coordinated metal center restricts the flexibility of the cage structure except for the possibility of a complete conformational change about the C_3 molecular axis. The overall process for the Δ-[M(cage)]$^{n+}$ configuration converts all the ethylenediamine ring conformations from λ (the Δ-C_3(*lel*$_3$) form, **3**) to δ (the Δ-D_3(*ob*$_3$) form, **4**) where the "*lel*" and "*ob*" nomenclature defines the parallel (**3**) or oblique (**4**) orientation of the C–C bond of the en ligand with respect to the C_3 axis.[5] The intermediate Δ-D_3(*lel*$_3$) species is also likely to be an energetically stable conformation in many systems and has been observed in several crystal lattices.[1a,1b] Intermediate asymmetric forms may also be favored depending on the MN_6 cage cavity size and the lattice environment.



3 **4**

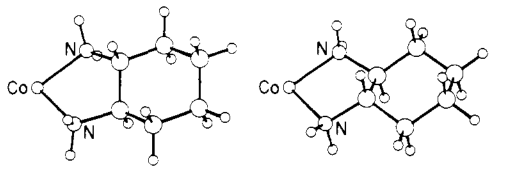
The six-membered chelate rings imposed by the caps have distorted skew boat conformations[6] in the C_3(*lel*$_3$) (**3**) and D_3(*ob*$_3$) (**4**) isomers. In the C_3(*lel*$_3$) form these rings are δ in one cap and λ in the other (δλ). A trigonal twist of the Δ-C_3(*lel*$_3$) molecule converts the five-membered chelate rings from "*lel*" (λ) to "*ob*" (δ) conformations and moves the $-CH_2-$ groups on the λ cap from one side of the Co–N–quaternary C plane to the other, so that the cap chelates have the δδ form in the Δ-D_3(*ob*$_3$) isomer. In the intermediate Δ-D_3(*lel*$_3$) species the six-membered rings are nearly eclipsed with boat conformations.

The metal ion cages derived from the $[\mathrm{Co(en)_3}]^{3+}$ substrate are substitutionally inert in both the Co(II) and Co(III) oxidation states and are readily isolated in their chiral forms. These properties have made them useful for the direct observation of Co(II,III) outer-sphere electron-transfer processes. The rates of Co(II,III) electron self-exchange reactions are simply measured by observing the change in optical rotation on mixing the chiral form of one oxidation state with the catoptric form of the other.[7]

$$\Lambda\text{-}[\mathrm{Co(cage)}]^{2+} + \Delta\text{-}[\mathrm{Co(cage)}]^{3+} \rightarrow \Lambda\text{-}[\mathrm{Co(cage)}]^{3+} + \Delta\text{-}[\mathrm{Co(cage)}]^{2+}$$

Theoretical interpretation of the Co(II,III) electron-transfer, electrochemical, and chiroptical properties has, however, been hampered in many of the cage systems by the need to consider several accessible conformations such as the symmetric D_3(*ob*$_3$), D_3(*lel*$_3$), and C_3(*lel*$_3$) forms of the $[\mathrm{Co(sep)}]^{2+/3+}$ system.[8,9] Consequently the design and synthesis of rigid-cage systems with fixed conformations and configurations is crucial for the detailed study of such phenomena. Application of the template encapsulation procedure to the rigid *lel*$_3$-$[\mathrm{Co(chxn)_3}]^{3+}$ ion would yield a high symmetry metal ion cage system which partially meets these objectives.

In the $[\mathrm{Co(chxn)_3}]^{3+}$ molecule the chelate rings are conformationally rigid since a change from λ to δ requires inversion of the chiral cyclohexane carbon atoms. This means that a *lel*$_3$ ↔ *ob*$_3$ interconversion cannot arise from a change in the chelate ring conformations but only from a change in the absolute configuration about the metal center. Such an interconversion can then only occur via Co–N bond cleavage with concomitant inversion of the secondary nitrogen configurations. This possibility would be extremely remote for the cage species.



λ-(*R*,*R*)-chxn δ-(*S*,*S*)-chxn

This paper describes the synthesis and preliminary use of the rigid cyclohexanediamine cage system for investigating a range of properties, notably electron transfer and chiroptical phenomena.

Experimental Section

All reagents used were of analytical grade. Commerical CF_3SO_3H (3M Co.) was distilled before use. $NaCF_3SO_3$ was prepared from CF_3SO_3H and NaOH. ^1H NMR spectra were recorded with a JEOL Model JNM-MH 100 Minimar spectrometer at 30 °C using sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) as the internal standard. ^{13}C NMR spectra were recorded with a JEOL JNM-FX60 Fourier transform NMR spectrometer at 25 °C relative to 1,4-dioxane as internal standard. The chemical shifts are reported in parts per million (δ) as positive downfield and negative upfield from the standard.

A Cary 118C or Hewlett-Packard 8450A UV/vis spectrophotometer was used to measure the absorption spectra. Rotary dispersion curves of the compounds were recorded with a Perkin-Elmer P22 spectropolarimeter and circular dichroism (CD) spectra were measured with a JASCO Model RD/UV instrument incorporating the SPROUL SCIENTIFIC SS20 CD modification and calibrated with d_{10}-camphorsulfonic acid: $\Delta\epsilon_{294}$ + 2.34 $M^{-1}\,cm^{-1}$ ($\Delta\epsilon_{458}$ (+1.85), $\Delta\epsilon_{424}$ (−0.127), and $\Delta\epsilon_{346}$ (+0.230) for 2-[[(+)-$\mathrm{Co(en)_3]Cl_3]NaCl{\cdot}6H_2O}$ in H_2O). All electronic spectra were of chloride salts of the compounds (~10^{-3} M) dissolved in water at 25 °C. Values of molar absorptivity (ε) and molar circular dichroism ($\Delta\epsilon = \epsilon_l - \epsilon_r$) are in units of $M^{-1}\,cm^{-1}$ and molecular rotations $[M]_\lambda$ are in units of deg $M^{-1}\,m^{-1}$.

The nitrogen gas used in oxygen-sensitive experiments was scrubbed with Cr^{2+} solutions before use. Unless otherwise stated, Bio-Rad analytical Dowex 50W-X2 (200–400 mesh, H^+ form) and SP Sephadex

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[5] IUPAC Commission on the Nomenclature of Inorganic Chemistry: *Inorg. Chem.* **1970**, *9*, 1.

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[7] Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23.

[8] Geue, R. J.; Pizer, R. D.; Sargeson, A. M., to be submitted for publication.

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C-25 (Na^+ form) ion-exchange resins were used for the cation-exchange chromatography. All evaporations were performed with Büchi rotary evaporators at ~15 torr and a bath temperature of less than 50 °C.

(+)-(*S*,*S*)- and (−)-(*R*,*R*)-*trans*-1,2-Cyclohexanediamine Dihydrochloride. {(−)chxn·H_2}{(+)-tartrate} and {(+)-chxn·H_2}{hydrogen (+)-tartrate}$_2$ salts[10] are susceptible to oxidation in the light and were therefore stored in its absence. (+)-(*S*,*S*)-chxn·2HCl and (−)-(*R*,*R*)-chxn·2HCl were obtained from the corresponding tartrates by cation-exchange chromatography on Dowex resin. The tartrate salt was dissolved in water and sorbed on the column that was washed extensively with 0.1 M HCl before elution with 1 M HCl. The eluate was evaporated to dryness and the product recrystallized by dissolution in a minimum volume of hot 6 M HCl and then dropwise addition of methanol and acetone with cooling to 0 °C. The white crystals were filtered and dried in air. Anal. Calcd for $(C_6H_{14}N_2)(HCl)_2$: C, 38.51; H, 8.62; N, 14.97; Cl, 37.89. Found: C, 38.8; H, 8.8; N, 14.8; Cl, 37.9.

Δ-[Co((−)-(*R*,*R*)-chxn)$_3$]Cl_3·4H_2O (Δ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·4H_2O). (−)-(*R*,*R*)-chxn·2HCl (85.0 g, 0.453 mol) and NaOH (30.4 g, 0.761 mol) were dissolved in methanol (1 L) at 40 °C with stirring. $CoCl_2$ (18.8 g, 0.145 mol), dissolved in methanol (600 mL), was slowly added. The orange suspension was stirred for 24 h at ~40 °C and then filtered. Air was bubbled through the solution during this period. The orange filtrate was evaporated to dryness, and the residue combined with the precipitate was dissolved in H_2O and sorbed on a CM Sephadex C-25 resin (50 × 10 cm, Na^+). After being washed with water, the column was eluted with 0.15 M Na_3PO_4 which removed a minor fast-moving brown-orange band and dispersed gray bands. The major orange band (F_1) consisting of the Δ-*lel*$_3$ complex followed. Its eluate, acidified (pH <5) and diluted (two times), was sorbed on Dowex resin, and the column was washed with water and 1 M HCl before elution with 6 M HCl. After evaporation to dryness, the complex was recrystallized by using a previously reported procedure.[11] Three batches of crystals were obtained and isolated (total yield 73.2 g, 87%). Anal. Calcd for $[Co(C_{18}H_{42}N_6)]Cl_3\cdot 4H_2O$: C, 37.28; H, 8.69; N, 14.49; Cl, 18.34; Co, 10.16. Found: C, 36.9; H, 8.6; N, 14.1; Cl, 18.4; Co, 10.1. Molecular rotations (10^{-3} M in H_2O): $[M]_{534}$ −1320, $[M]_{474}$ +9860.

A minor slow moving band (F_2) containing the Λ-*ob*$_3$ isomer separated widely from F_1 on the column. After F_1 had been eluted, F_2 was removed with 1 M NaCl, acidified (pH <5), diluted (two times), and sorbed on a Dowex column (10 × 3 cm, H^+). The column was washed with H_2O and 1 M HCl and the complex eluted with 6 M HCl. The eluate was evaporated to dryness to give the Λ-*ob*$_3$ isomer (1.5 g, 2%). Anal. Calcd for $[Co(C_{18}H_{42}N_6)]Cl_3\cdot 0.5H_2O$: C, 41.83; H, 8.39; N, 16.26; Cl, 20.58; Co, 11.40. Found: C, 41.8; H, 8.5; N, 16.3; Cl, 20.7; Co, 10.8.

Λ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·4H_2O was similarly prepared by starting with (+)-(*S*,*S*)-chxn·2HCl.

Λ-(*S*,*S*)$_3$-(1,12-Dinitro-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.0.^{4,9}0.^{15,20}0^{25,30}]dotriacontane)cobalt(III) Chloride Trihydrate (Λ-*lel*$_3$-[Co(diNOchar)]Cl_3·3H_2O). Λ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·4H_2O (5.0 g, 8.62 mmol) and HCHO (37% w/v, 134 g, 1.66 mol, 32 times excess) were dissolved in water (150 mL). The stirred solution was adjusted to pH ~11.5 with NaOH solution. The reaction mixture was left to stir for 5 min during which the deep red solution turned cloudy and darkened with an increase in temperature to ~40 °C. NO_2CH_3 (20.3 g, 0.33 mol, ~20-fold excess) was then added and the reaction mixture heated to ~55 °C. Readjustment of the solution to pH ~11.5 was carried out at 0.5-h intervals as base was consumed during the reaction. After 2, 4, and 6 h, respectively, further lots of the organic reagents were added ((HCHO, 67 g, 16 times excess) (NO_2CH_3, 10 g, ~10 times excess) each time). After 9 h of total reaction time the mixture was allowed to cool to 20 °C and quenched to pH ~4 by dropwise addition of acetic acid. Caution: *Halo acids should not be used for the quenching since carcinogenic α-halo ethers may be formed by the reaction of HX with HCHO.*

The solution was filtered to remove a small amount of brown solid, diluted with water (three times), and sorbed on Sephadex resin (65 × 10 cm) that was washed with water and eluted with 0.15 M K_2SO_4. One major pale orange band separated. Its eluate was acidified to pH <5, diluted (10 times), and resorbed on Sephadex resin (13.5 × 6 cm, H^+). After the solution was washed with water and 0.2 M HCl, it was eluted with 0.6 M HCl. The eluate was reduced to ~50 mL when it formed an orange gel. Evaporation to dryness from water gave crude product (3 g, ~50%). A sample was recrystallized by dissolution in hot water and dropwise addition of 6 M HCl. After being cooled in ice, the crystals were filtered, washed with ethanol and ether, and dried in air. Anal. Calcd for $[Co(C_{26}H_{48}N_8O_4)]Cl_3\cdot 3H_2O$: C, 41.30; H, 7.20; N, 14.82: Cl, 14.07; Co, 7.79. Found: C, 41.5; H, 6.8; N, 14.7; Cl, 14.2; Co. 7.5 (ϵ_{480} 122, ϵ_{349} 111, ϵ_{249} 20640). Molecular rotations (10^{-3} M in H_2O): $[M]_{527}$ −5600, $[M]_{455}$ +3760. ^1H NMR (acetic acid/D_2O, pD ~1.5): δ 3.58 (AB quartet, $J \approx 14$ Hz, cap-CH_2), 3.0–2.4, 1.0–1.9 (br, ring chxn protons). ^{13}C NMR (acetate salt, D_2O): δ +22.48 (quat C), −17.80 (cap-CH_2), +2.60 (chxn CH), −37.55, −42.75 (chxn CH_2).

The insoluble mixed chloride–perchlorate salt was precipitated instantly from a dilute solution of [Co(diNOchar)]$^{3+}$ by dropwise addition of $HClO_4$ (70%). Anal. Calcd for $[Co(C_{26}H_{48}N_8O_4)]Cl_2\cdot ClO_4$: C, 40.77; H, 6.32; N, 14.63; Cl, 13.58; Co, 7.69. Found: C, 40.7; H, 6.4; N, 14.5; Cl, 13.8; Co, 7.7.

Δ-*lel*$_3$-[Co(diNOchar)]Cl_3·3H_2O was prepared by an identical route but starting with Δ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·4H_2O.

Δ-(*N*,*N*′,*N*″-[Nitromethylidynetris(methylene)]tris((*R*,*R*)-*trans*-1,2-cyclohexanediamine))cobalt(III) Chloride Pentahydrate (Δ-*lel*$_3$-[Co(NOsemichar)]Cl_3·5H_2O). Δ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·4H_2O (10 g, 0.018 mol) was dissolved in water (500 mL), and HCHO (37%, 400 g, ~4.9 mol, ~45 times excess) and CH_3NO_2 (60 g, 0.98 mol, ~27 times excess) were added to the stirred solution. The reaction mixture was adjusted to pH ~11 with NaOH solution and left stirring at 25 °C for 20 h when it was quenched to pH ~4 by dropwise addition of anhydrous acetic acid. The reaction mixture was diluted, sorbed on Sephadex resin (42 × 5 cm), washed extensively with water, and eluted with 0.1 M K_2SO_4. An orange band (F_1) was eluted first, followed by a red band and then a major yellow band (F_2) that spread out during elution. F_1 gave Δ-*lel*$_3$-[Co(diNOchar)]Cl_3·3H_2O (0.6 g). F_2 was eluted with 1 M NaCl after the other bands had been removed, diluted (~10 times), acidified to pH <5, and resorbed on Sephadex resin (55 × 10 cm). Elution with 0.25 M Na_2HPO_4 gave two major bands (F_{2a}, F_{2b}) and several minor bands. A band due to the yellow starting material (F_{2a}) eluted first, followed closely by the monocapped compound (F_{2b}). F_{2a} was resorbed on Dowex resin (16 × 5 cm), washed with water and 2 M HCl, and eluted with 6 M HCl. The eluate was evaporated to dryness to give Δ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·~4H_2O (2.1 g). *F_{2b}* was similarly isolated to give crude Δ-*lel*$_3$-[Co(NOsemichar)]Cl_3·5H_2O (3.0 g, 30% based on reacted starting material). A sample of the monocapped species was dissolved in a minimum of hot water, acidified with a few drops of HCl (11.6 M), and cooled overnight in a refrigerator. The collected crystals were washed with ether and dried in vacuo over $CaCl_2$. Anal. Calcd for $[Co(C_{22}H_{45}N_7O_2)]Cl_3\cdot 5H_2O$: C, 38.02; H, 7.97; N, 14.10; Cl, 15.30; Co, 8.48. Found: C, 37.8; H, 7.2; N, 13.8; Cl, 15.5; Co, 8.4 (ϵ_{474} 110, ϵ_{343} 116, ϵ_{230} 24 240). Molecular rotations (10^{-3} M in H_2O): $[M]_{482}$ +6600. ^1H NMR (pD 4): δ 3.58 (AB quartet, J = ~14 Hz, cap-CH_2), 1.0–2.9 (br, chxn ring protons). ^{13}C NMR (D_2O): δ +21.44 (quat C), −17.28 (cap-CH_2), +4.16, −4.16, −34.18, −37.55, −43.14 (chxn carbons).

Δ-*lel*$_3$-[Co(diNOchar)]$(ClO_4)_2$·2H_2O. Δ-*lel*$_3$-[Co(diNOchar)]Cl_3·3H_2O (0.5 g) was warmed in water (50 mL) for 0.5 h and the suspension filtered to remove the remaining solid. N_2 was bubbled through the solution for 10 min before it was vigorously shaken with Zn dust (2 g) for 60 s. The excess Zn was filtered, and a deoxygenated solution of saturated $NaClO_4$ was added dropwise until precipitation of the white solid ceased. The gray-white solid was quickly filtered, washed with deoxygenated acetone, and stored in a nitrogen atmosphere. Anal. Calcd for $[Co(C_{26}H_{48}N_8O_4)](ClO_4)_2\cdot 2H_2O$: C, 37.60; H, 6.31; N, 13.49; Cl, 8.54. Found: C, 37.3; H, 5.9; N, 13.0; Cl, 8.5.

Λ-(*S*,*S*)$_3$-(1,12-Diammonio-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.0.^{4,9}0.^{15,20}0^{25,30}]dotriacontane)cobalt(III) Pentachloride Hexahydrate (Λ-*lel*$_3$-[Co(diAMcharH$_2$)]Cl_5·6H_2O). Λ-*lel*$_3$-[Co(chxn)$_3$]Cl_3·~4H_2O (12.0 g, 21.5 mmol) was reacted with HCHO and NO_2CH_3 as described. After quenching of the reaction mixture to pH ~4, the solution was diluted and sorbed on Sephadex resin (19 × 7 cm) and the column washed with water (2 L). A large amount of brownish material eluted from the column that was then eluted slowly with 0.3 M HCl. The eluate was evaporated to dryness, the pale orange product (Λ-*lel*$_3$-[Co(diNOchar)]$^{3+}$) added to water (1250 mL), and the solution deoxygenated with N_2. Zinc powder (11 g) was added while the N_2 flow was maintained and the temperature kept at ~50 °C. HCl (11.6 M, 60 mL) was added dropwise, and after 1 h more Zn (10 g) was added. After 2 h addition of the HCl was complete and all the solid [Co(diNOchar)]Cl_3 initially present had dissolved and reacted. The reduction conditions were maintained for a further 1.5 h before H_2O_2 (30%, ~10 mL) was added. The resulting bright orange solution was aerated during heating on a steam bath for 20 min and then evaporated to dryness. The product was dissolved in water (2 L), sorbed on Sephadex resin (19 × 7 cm, H^+), and then washed with water and 0.25 M HCl that separated a pale orange front band. The major orange band was then eluted with 0.5 M HCl and evapoated to dryness. The orange solid (8.6 g, ~50%) was dissolved in hot water (60 mL, 80 °C), and HCl (11.6 M, 30 mL) was slowly added with stirring. After the solution was cooled at 3 °C for 15 h, dark orange

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crystals were collected, washed with ethanol and ether, and dried in air (7.4 g). Additional crystal were obtained by evaporating the filtrate to dryness and repeating the process (0.8 g). Anal. Calcd for $[Co(C_{26}H_{52}N_8)]Cl_3 \cdot 2HCl \cdot 6H_2O$: C, 37.94; H, 8.08; N, 13.61; Cl, 21.53; Co, 7.16. Found: C, 38.1; H, 8.2; N, 13.7; Cl, 21.7; Co, 7.0 (ϵ_{484} 144, ϵ_{350} 156, ϵ_{245} 20 360 (in 0.1 M HCl)). Molecular rotations (10^{-3} M in 0.1 M HCl): $[M]_{535}$ −4800, $[M]_{459}$ +2850. ^{1}H NMR (0.1 M DCl): δ 3.25 (AB quartet, J = 14.5 Hz, cap CH_2), 2.4–2.9, 1.0–2.0 (br complex pattern, chxn ring protons). ^{1}H NMR (D_2O/Na_2CO_3, pD 8.5): δ 2.76 (AB quartet, J = 15 Hz, cap-CH_2), 2.4–2.9, 1.0–2.0 (br, chxn ring protons). ^{13}C NMR (0.1 M DCl): δ −9.23 (quat C), −18.9 (cap-CH_2), +2.73 (chxn CH), −37.43, −42.75 (chxn CH_2). ^{13}C NMR (pD 8): δ −9.62 (quat C), −14.29 (cap-CH_2), +2.60 (chxn CH), −37.17, −42.62 (chxn CH_2). Δ-lel_3-[Co(diAMcharH$_2$)]Cl$_5 \cdot 6H_2O$ was similarly prepared by starting with Δ-lel_3-[Co(chxn)$_3$]Cl$_3 \cdot \sim 4H_2O$.

(1-Ammonio-12-nitro-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.0.^{4,9}0.^{15,20}0^{25,30}]dotriacontane)cobalt(III) Tetrachloride Hexahydrate ([Co(AMNOchar·H)]Cl$_4 \cdot 6H_2O$). Similar experiments carried out at room temperature on the same time scale gave both the [Co(diAMcharH$_2$)]$^{5+}$ ion and the partially reduced [Co(AMNOcharH)]$^{4+}$ species. The reaction mixtures were sorbed on Sephadex resin and eluted with 0.4 M HCl. The partially reduced 4+ species separated from the 5+ diammonium ion. The complex was very insoluble and was crystallized by dissolution in a minimum volume of hot water (~70 °C) and slow cooling. Anal. Calcd for $[Co(C_{26}H_{51}N_8O_2)]Cl_4 \cdot 3H_2O$: C, 40.95; H, 7.53; N, 14.70; Co, 7.73. Found: C, 41.4; H, 6.6; N, 14.4; Co, 7.0. ^{1}H NMR (D_2O): δ 3.62 (AB quartet, J = 15 Hz, H_3N^+-cap-CH_2), 3.24 (AB quartet, J = 15 Hz, O_2N-cap-CH_2), 2.4–2.9, 1.1–2.1 (br, chxn ring protons). ^{13}C NMR (0.1 M DCl): δ +22.48 (O_2N-quat C), −9.23 (H_3N^+-quat C), −17.80, −18.32 (cap-CH_2), +2.73, +2.99 (chxn CH), −37.30, −42.75 (chxn CH_2).

Δ-(R,R)$_3$-(1,12-Diamino-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.0.^{4,9}0.^{15,20}0^{25,30}]dotriacontane)cobalt(II) Tetrachlorozincate Dihydrate (Δ-lel_3-[Co(diAMchar)]ZnCl$_4 \cdot 2H_2O$). To a solution of Δ-lel_3-[Co(diAMcharH$_2$)]Cl$_5 \cdot 6H_2O$ (0.5 g) in water (50 mL) (flushed with nitrogen) was added Zn dust (0.5 g) in water (10 mL). Oxygen-free nitrogen was bubbled through the solution for 0.5 h, and then the Zn dust was filtered off under an atmosphere of nitrogen. The near colorless solution was treated with an oxygen-free solution of Li_2ZnCl_4 (5 mL of 2 M in 0.1 M HCl). After 5 min, the shiny gray plates that formed were filtered under nitrogen, washed with oxygen-free acetone, and dried in vacuo (0.35 g, 74%). Anal. Calcd for $[Co(C_{26}H_{52}N_8)]ZnCl_4 \cdot 2H_2O$: C, 40.00; H, 7.48; N, 14.35; Cl, 18.16. Found: 40.3; H, 7.4; N, 13.9; Cl, 17.8 (ϵ_{576} 14, ϵ_{464} 26, ϵ_{348} ~15 (sh)).

Trifluoromethanesulfonate (Triflate) Salts. The triflate salts were prepared by dissolution of the compound (1 g) in water (20 mL) and addition of trifluoromethanesulfonic acid (triflic acid) (~1.5 times excess). The solution was concentrated to crystallization by evaporation (~40 °C), filtered, and dried in the air. The product was dissolved in a minimum volume of hot (60–70 °C) $NaCF_3SO_3$ solution (1 g in 5 mL H_2O), and a few drops of triflic acid were added. The crystals that formed on cooling were filtered, washed with a small amount of ice cold water and then ether, and dried for at least 10 h in vacuo over P_2O_5 (0.1 torr). Δ-lel_3-[Co(chxn)$_3$]$^{3+}$: Anal. Calcd for $[Co(C_{18}H_{42}N_6)](CF_3SO_3)_3 \cdot 2H_2O$: C, 28.51; H, 5.24; N, 9.50; S, 10.87. Found: C, 28.6; H, 5.0; N, 9.7; S, 10.6. Λ-ob_3-[Co(chxn)$_3$]$^{3+}$: Anal. Calcd for $[Co(C_{18}H_{42}N_6)](CF_3SO_3)_3 \cdot H_2O$: C, 29.10; H, 5.12; N, 9.70; S, 11.10. Found: C, 29.2; H, 5.3; N, 9.8; S, 10.7. Δ-lel_3-[Co(NOsemichar)]$^{3+}$: Anal. Calcd for $[Co(C_{22}H_{45}N_7O_2)](CF_3SO_3)_3 \cdot 2H_2O$: C, 30.58; H, 5.03; N, 9.99. Found: C, 30.7; H, 5.1; N. 9.6. Δ-lel_3-[Co(diNOchar)]$^{3+}$: Anal. Calcd for $[Co(C_{26}H_{48}N_8O_4)](CF_3SO_3)_3$: C, 33.40; H, 4.64; N, 10.75; S, 9.22; Co, 5.65. Found: C, 33.2; H, 4.8; N, 10.5; S, 9.2; Co, 5.4. Λ-lel_3-[Co(diAMcharH$_2$)]$^{5+}$: Anal. Calcd for $[Co(C_{26}H_{54}N_8)](CF_3SO_3)_5 \cdot 4H_2O$: C, 27.47; H, 4.61; N, 8.27; S, 11.83: F, 21.03: Co, 4.35. Found: C, 27.6; H, 4.5; N, 8.2; S, 11.8; F, 20.9; Co, 4.2.

Reactivity. Δ-lel_3-[Co(diAMchar)]$^{3+}$ was heated at 200 °C in 5 M NaOH in an autoclave for 3 days. The reaction mixture was then cooled and neutralized, and the products were isolated by ion-exchange chromatography. Several minor products appear to be cage-opened species, but the major product was the starting material (50–60%). Δ-lel_3-[Co(diAMchar)]$^{3+}$ was reduced to the Co(II) form with Zn powder in 5 M NaOH and refluxed for 5 h. No loss of starting material was observed. The Δ-lel_3-[Co(diAMcharH$_2$)]$^{4+}$ species was heated for 24 h at ~270 °C in a sealed ampule with HCl (11.6 M). Negligible decomposition occurred, but the Co(II) salt was slowly oxidized to the Co(III) species during heating.

The system containing the solutions of the two oxidation states and the stopped-flow reactor in which they were mixed was flushed with nitrogen for at least 4 h before each kinetic run. The electron-transfer reactions were followed by the change in optical rotation after solutions of Λ-lel_3-[Co(diAMcharH$_2$)]$^{5+}$ or Λ-lel_3-[Co(diAMchar)]$^{3+}$ were mixed with Δ-lel_3-[Co(diAMchar)]$^{2+}$. Δ-lel_3-[Co(diAMchar)]$^{2+}$ solutions were prepared in situ by reducing the Co(III) ion with Zn amalgam under a nitrogen flow. Λ-lel_3-[Co(diAMcharH$_2$)]$^{5+}$ solutions in 0.1 M $NaClO_4$ and 0.1 M $HClO_4$ were mixed with Δ-lel_3-[Co(diAMchar)]$^{2+}$ solutions in 0.2 M $NaClO_4$ in a stopped-flow apparatus coupled to a 5-cm polarimeter cell. Also, solutions of Λ-lel_3-[Co(diAMchar)]$^{3+}$ in 0.2 M N-(2-hydroxyethyl)piperazine-N-2-ethanesulfonic acid (HEPES) and Δ-lel_3-[Co(diAMchar)]$^{2+}$ in 0.2 M $NaCF_3SO_3$ were mixed to follow the rate of electron transfer for the 3+/2+ couple. The reactions were studied at 520 nm and 25.0 ± 0.1 °C. For experiments conducted with chloride salts, the values of $[Co]_{total}$ and $[Co(III)]t_o/[Co(II)]t_o$ were determined from the concentrations of starting complex by assuming complete reduction of the Δ-lel_3-[Co(diAMchar)]$^{3+}$ solutions. For the reactions using the triflate salts, $[Co]_{total}$ was determined by atomic absorption spectroscopy.

Electrochemical measurements were made by using a three-electrode, iR-compensated system with a platinum auxiliary electrode and a PAR Model 170 electrochemical system. The reference electrodes were the saturated calomel electrode (SCE) (aqueous) or Ag/AgCl/saturated LiCl (acetone) electrode (nonaqueous). The salt bridge was filled with the solvent and electrolyte used in the working compartment. The working electrodes were a dropping mercury electrode (DME) PAR Model 172A, hanging mercury drop electrode (HMDE), or a PAR Model 303 static mercury drop electrode (SMDE). A Ag/AgCl/saturated KCl·AgCl reference electrode was used with the PAR 303 SMDE system. The coulometric measurement was performed by using an Amel Model 731 digital integrator in conjunction with an Amel Model 551 potentiostat. A PAR Model 377A coulometry cell system using a Pt basket working electrode was also employed. The measurements were made at 20 °C after the solutions had been degassed with argon. Distilled water and dry dimethyl sulfoxide (Me_2SO) were the solvents used. The supporting electrolytes employed were $NaCF_3SO_3$ (recrystallized), $NaClO_4 \cdot H_2O$ (AR), $Me_4NCF_3SO_3$, and distilled CF_3SO_3H. The triflate salts of the complexes were used, except in one instance, in millimolar concentrations.

Results

Syntheses. The [Co(chxn)$_3$]$^{3+}$ ion used in the synthesis was prepared by using the optically pure ligand hydrochlorides and separating the ob_3 and lel_3 complex species.[11] The synthesis may also be carried out in methanol by using the tartrate salts of the ligand ({(+)-chxnH$_2$}{H(+)-tart}$_2 \cdot H_2O$ or {(−)-chxnH$_2$}{(+)-tart}), but this gives lower yields than the method described here. The presence of tartrate did not significantly alter the distribution of ob_3 and lel_3 conformers.

The [(1,12-dinitro-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.0^{4,9}0.^{15,20}0^{25,30}]dotriacontane)cobalt(III)](3+) ion ([Co(diNOchar)]$^{3+}$) has been synthesized in both the Δ-(R,R)$_3$ and Λ-(S,S)$_3$ forms (Scheme I). The reaction of optically pure (−)-(R,R)-chxn with $CoCl_2$ in methanol lead to the isolation of Δ-[Co((R,R)-chxn)$_3$]$^{3+}$ (Δ-lel_3 isomer) and Λ-[Co((R,R)-chxn)$_3$]$^{3+}$ (Λ-ob_3 isomer) ions by cation-exchange chromatography. Δ-lel_3[Co((R,R)-chxn)$_3$]Cl$_3 \cdot 4H_2O$ was then capped with CH_2O and NO_2CH_3 at pH ~11.5 and ~55 °C by addition of the organic reagents in several portions over a 9-h period to yield Δ-lel_3-[Co(diNOchar)]Cl$_3 \cdot 3H_2O$ (~50%). NaOH was used as the base in preference to Na_2CO_3 that precipitated the starting complex as a carbonate salt.

The (N,N',N''-[nitromethylidynetris(methylene)]tris(*trans*-1,2-cyclohexanediamine))cobalt(III)](3+) ion ([Co(NOsemichar)]$^{3+}$) was also synthesized in reasonable yield under less forcing conditions.

The chloride salt of [Co(diNOchar)]$^{3+}$ was difficult to crystallize as it formed a gelatinous precipitate, and the mixed chloride-perchlorate salt was readily isolated but very insoluble. The triflate salts of the compounds containing nitro substituents were sparingly soluble in water although the diamine complexes were quite soluble. The triflate salts of all compounds were soluble in ethanol, Me_2SO, dimethyl formamide (DMF), acetone, and sulfolane.

Exhaustive reduction with Zn in HCl and then reoxidation with H_2O_2 converted chiral [Co(diNOchar)]$^{3+}$ into [Co(diAMcharH$_2$)]$^{5+}$ with complete retention of chirality. The [Co(diNOchar)]$^{2+}$ species was isolated by controlled reduction of [Co(diNOchar)]$^{3+}$ in water. The reduction of the chiral

Table I. Electrochemical Data vs. SHE

			DC		AC[b]	cyclic DC[c]			
compd	solv[a]	process	$E_{1/2}$, V	$F_{1/4} - E_{3/4}$, V	E_p, V	E_R, V	E_O, V	ΔE, mV	i_O/i_R
$[Co(NOsemichar)]^{3+}$	pH 5	Co(III) → Co(II)	−0.13	84	−0.20				
		NO_2 → NHOH	−0.53		−0.56				
$[Co(diNOchar)]^{3+}$	pH 1.5	Co(III) → Co(II)	0.00	58	0.00				
		$NO_2 \rightarrow NH_2OH$	−0.27		−0.27				
$[Co(diNOchar)]^{3+}$	pH 5	Co(III) → Co(II)	+0.02	58	+0.01				
		NO_2 → NHOH	−0.54		−0.55				
$[Co(diNOchar)]^{3+}$	pH 9	Co(III) → Co(II)	−0.14	63	−0.14				
		NO_2 → NHOH	−0.52		−0.54				
$[Co(diAMcharH_2)]^{5+}$	pH 1	Co(III) → Co(II)	0.00	71	−0.01	+0.02	−0.05	70	~1
$[Co(diAMchar)]^{3+}$	pH 10 (pH 7.5)	Co(III) → Co(II)	−0.35	62	−0.36	−0.40	−0.33	70	~1
$[Co(diAMchar)]^{3+}$	Me_2SO $(Me_4NCF_3SO_3)$	Co(III) → Co(II)			−0.46				

[a] Triflato salts used with aqueous $NaCF_3SO_3/CF_3SO_3H$ ($\mu = 0.1$) as supporting electrolytes except where indicated. [b] Peak voltages measured at 20 or 40 Hz in phase; ΔE = 10 mV. [c] 20 mV/s.

$[Co(diAMchar)]^{3+}$ ion in H_2O under a N_2 atmosphere yielded shiny gray plates of the chiral cobalt(II) salt $[Co(diAMchar)]ZnCl_4 \cdot 2H_2O$ that was stable for several days in oxygen-free conditions. An average value for the pK_a of the amino groups in $[Co(diAMcharH_2)]^{5+}$ was determined by pH titration as 3.1 (25 °C, 0.2 M $NaCF_3SO_3$). This value is close to the value of ~3 measured for $[Co(diAMsarH_2)]^{5+}$.[4,12]

^1H NMR and ^{13}C NMR Spectra. The ^1H NMR spectrum of $[Co(diNOchar)]^{3+}$ in D_2O showed an AB doublet pair centered at δ 3.58 ($J \approx 14$ Hz) corresponding to the protons of the methylene groups on the caps. The unresolved resonances at δ 1–3 are attributed to the complex set of signals expected for the cyclohexane ring protons. The ^{13}C NMR spectrum in D_2O was readily interpreted and gave three signals associated with the cyclohexane ring carbons at δ 3.12, −37.10, and −42.73. The methylene cap carbons appeared at δ −17.80, and the quaternary cap carbons gave a low-field resonance at δ +22.18. The simplicity of the spectra is consistent with an effective D_3 symmetry for the ion over both ^1H and ^{13}C NMR time scales[13] in solution.

$[Co(NOsemichar)]^{3+}$ gave a ^1H NMR spectrum (D_2O) with similar shifts to that of the cage complex but with half the intensity for the AB pattern of the cap protons. The ^{13}C NMR spectrum (D_2O) showed six distinct resonances, at δ +4.16 and −4.16 for the cyclohexane methine carbon atoms and at δ −34.18, −37.55, and −43.15 for the cyclohexane methylene carbon atoms. The quaternary carbon resonance was at δ +21.44.

Figure 1 shows the ^1H and ^{13}C NMR spectra of *lel*$_3$-$[Co(diAMcharH_2]^{5+}$ in 0.1 M DCl. The ^1H NMR signals of the cap protons in the $[Co(diAMchar)]^{3+}$ ion showed a significant variation in chemical shift with pH. In 0.1 M DCl the AB doublet pair centered at δ 3.25 (J = 14.5 Hz) almost completely separated from the cyclohexane proton resonances. At pD 8.5 (D_2O/Na_2CO_3) the AB doublet pair centered at δ 2.76 ($J \approx 15$ Hz) partially overlapping the high-field resonances.

As for $[Co(diNOchar)]^{3+}$, the effective D_3 symmetry of the $[Co(diAMcharH_2)]^{5+}$ and $[Co(diAMchar)]^{3+}$ ions leads to a simple ^{13}C NMR spectrum with five peaks. The quaternary carbon resonances were observed at δ −9.23 and −9.62 for the diprotonated and free diamine complexes, respectively.

Electrochemistry. The electrochemical data (Table I) shows that the Co(III)/Co(II) reduction process was essentially reversible for all the complexes except the partially encapsulated sexidentate species $[Co(NOsemichar)]^{3+}$. The one-electron reduction was confirmed by a coulometry experiment using $[Co(diAMchar)]^{3+}$ in acetonitrile with $Me_4NCF_3SO_3$ as the supporting electrolyte. For DC polarography, the Heyrovsky–Ilkovic equation was used to indicate the degree of electrochemical reversibility of the processes ($E_{1/4} - E_{3/4} \approx 56/n$ mV for reversibility) and also to obtain $E_{1/2}$ values. AC polarography and DC cyclic voltammetry showed quasi-reversible behavior for the metal centered reductions.

The electrochemical measurements were partially obscured in aqueous solution by the presence of adsorption processes. Preadsorption waves were observed with all complexes, were pH dependent, and were most dominant for the compounds containing nitro substituents. Interfering adsorptions at pH 1 were less significant than at pH 10 for the Co(III)/Co(II) reduction of $[Co(diAMcharH_2)]^{53}$. Phase-sensitive AC polarography was used to distinguish between the adsorptions and genuine metal ion reduction. Hence, the best method for determining $E_{1/2}$ potentials for these complexes was AC polarography where E_p was $\sim E_{1/2}$ at low frequencies. The $[Co(diAMchar)]^{2+}$ ion showed no indication of reduction even down to −2.6 V vs. Ag/AgCl in Me_2MSO. There was also no sign of oxidation of [Co(diAMc-

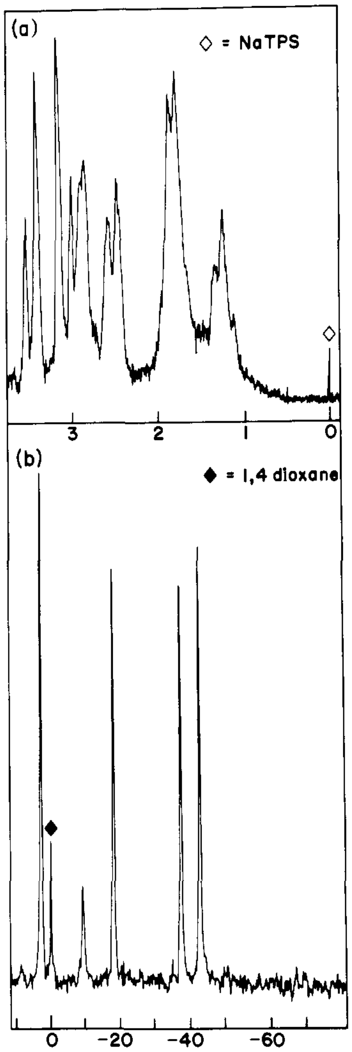

Figure 1. ^1H NMR (a) and ^{13}C NMR (b) of *lel*$_3$-$[Co(diAMcharH_2)]^{5+}$ in 0.1 M DCl.

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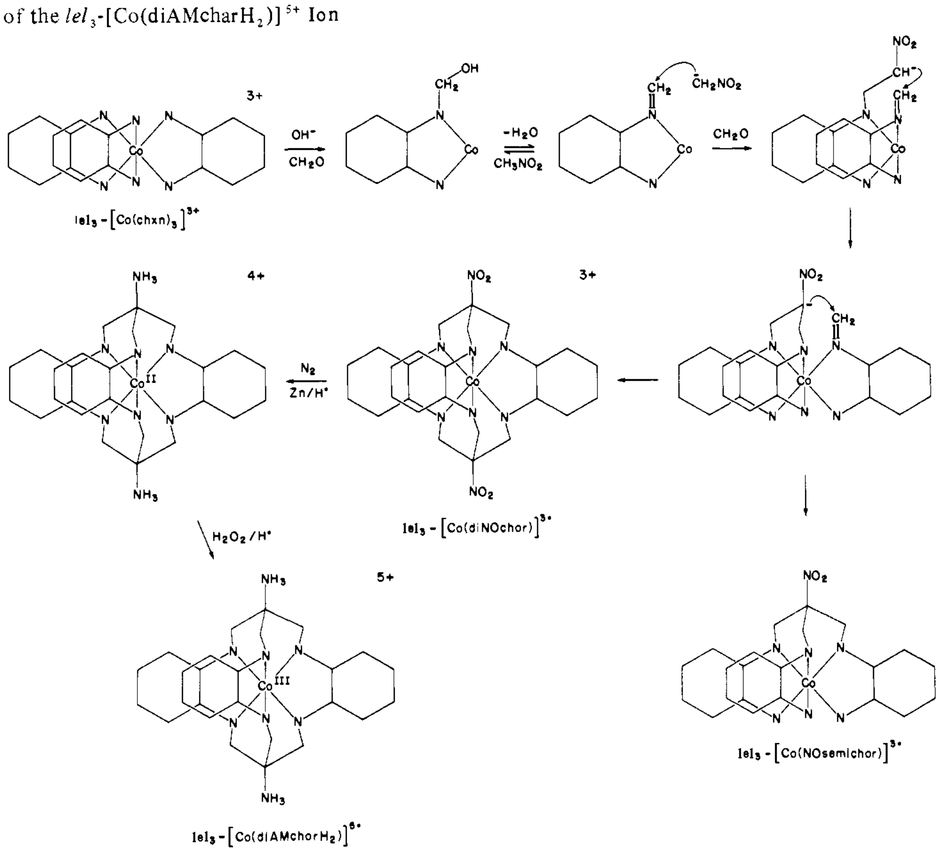
(12) Lawson, P. J. pH titration, unpublished work.
(13) Bryant, R. G. *J. Chem. Educ.* **1983**, *60*, 933.

Scheme I. Synthesis of the *lel*$_3$-[Co(diAMcharH$_2$)]$^{5+}$ Ion



har)]$^{3+}$ to a Co(IV) species up to +1.4 V vs. SCE (Me$_2$SO).

Electron-Transfer Kinetics. The racemization of solutions containing Λ-*lel*$_3$-[Co(diAMcharH$_2$)]$^{5+}$ or Δ-*lel*$_3$-[Co(diAMchar)]$^{3+}$ and Λ-*lel*$_3$-[Co(diAMcharH$_2$)]$^{4+}$ or Δ-*lel*$_3$-[Co(diAMchar)]$^{2+}$ was used to follow the kinetics of the Co(III)/Co(II) electron-transfer process. For a second-order electron transfer between Λ-Co(III) and Δ-Co(II) species the optical rotation (α) varies according to the relationship

$$-\mathrm{d}\ln(\alpha_t-\alpha_\infty)/\mathrm{d}t = k_{\mathrm{et}}[\mathrm{Co}]_{\mathrm{total}} \tag{1}$$

The rate constants for electron transfer (k_{et}) were determined from plots of ln ($\alpha_t - \alpha_\infty$) vs. time (t), which were linear for at least 3 half-lives (Table II). The *lel*$_3$-[Co(diAMcharH$_2$)]$^{5+}$ racemate was recovered intact after the reaction, and ^{1}H NMR spectra and ion-exchange chromatography on the racemate showed no sign of isomerization or degradation during the process.

Table II. Rate Constants for Electron-Transfer Reactions

Λ-*lel*$_3$-[Co(diAMchar)]$^{3+}$ + Δ-*lel*$_3$-[Co(diAMchar)]$^{2+}$

$10^3[\mathrm{Co}]_{\mathrm{total}}$[a]	10^3k_{obsd}, s^{-1}	k_{et}, M^{-1} s^{-1}
2.28	3.28	1.44
2.34	2.62	1.12
2.69	2.80	1.04
3.36	3.24	0.96

Λ-*lel*$_3$-[Co(diAMcharH$_2$)]$^{5+}$ + Δ-*lel*$_3$-[Co(diAMcharH$_2$)]$^{4+}$

$10^3[\mathrm{Co}]_{\mathrm{total}}$[b]	10^4k_{obsd}, s^{-1}	10^2k_{et}, M^{-1} s^{-1}
2.89	1.13	3.89
3.30	1.36	4.13
3.96	1.34	3.39

$10^3[\mathrm{Co}]_{\mathrm{total}}$[c]	$[\mathrm{Co(III)}]t_0/[\mathrm{Co(II)}]t_0$	10^4k_{obsd}, s^{-1}	10^2k_{et}, M^{-1} s^{-1}
2.00	1.00	0.72	3.60
2.13	1.13	0.85	3.99
2.25	1.25	0.84	3.74

[a] μ = 0.2 (0.1 M HEPES (pH 7.45), 0.1 M NaCF$_3$SO$_3$); [Co]$_{\mathrm{total}}$ determined by AA spectroscopy; k_{obsd} values are the average of at least three equivalent measurements. [b] μ = 0.2 (0.15 M NaCF$_3$SO$_3$, 0.05 M CF$_3$SO$_3$H); [Co]$_{\mathrm{total}}$ determined by AA spectroscopy. [c] μ = 0.2 (0.15 M NaClO$_4$, 0.05 M HClO$_4$).

Discussion

Syntheses. The synthetic methodology developed for the preparation of cobalt cage compounds has been used to give the first conformationally rigid-cage complexes with high symmetry. The most probable reaction path for the formation of the [Co(diNOchar)]$^{3+}$ molecule is shown in Scheme I, and the mechanism is similar to that proposed for the synthesis of [Co(sep)]$^{3+}$ [1b] except that NH$_3$ is replaced here by the nitromethane carbanion (−)-CH$_2$NO$_2$. The evidence for such a mechanism comes from the results of the reactivity of coordinated imines[1,14-16] and the isolation of reaction intermediates.[1c]

In this system ^{1}H NMR spectra were used to identify several intermediates. Monoimine species with characteristic resonances at δ 8–9 ppm were found in reactions that had not been taken to completion. In addition, N-methylated species that were probably formed via crossed Canizzarro reactions were observed.[1b] The ^{1}H NMR of such species give doublets at δ ~2.4 ppm in DCl/D$_2$O due to coupling with the N–H protons, and the resonance collapses to a singlet when the N–H protons are exchanged in D$_2$O.

The synthesis of the [Co(diNOchar)]$^{3+}$ cage is more difficult than that for the more flexible [Co(diNOsar)]$^{3+}$ analogue. Under temperature conditions similar to those used to prepare the latter,[1c] the monocapped [Co(NOsemichar)]$^{3+}$ species is the only significant condensation product, and elevated temperatures and controlled addition of organic reagents were required to produce reasonable yields of the desired cage. Reactions at elevated temperatures also caused some decomposition and an increase in

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the quantity of N-methylated species. Both these processes compete with the capping reaction.

The exchange rate of the coordinated N–H protons appears to be important in determining the reactivity of the complex ions with the HCHO electrophile in these reactions. At a given pH the exchange rates for the N–H protons of the *lel*$_3$-[Co(chxn)$_3$]$^{3+}$ ion are slower than for the [Co(en)$_3$]$^{3+}$ ion by ^{1}H NMR spectroscopy, and this is one reason for the quite different reactivity of the two complex ions.

Differences in the conformational flexibility of these species may also contribute to the reactivity differences. The rigid nature of the chelate rings in *lel*$_3$-[Co(chxn)$_3$]$^{3+}$ means that the intermediates involved in the capping process have less flexibility than the analogous [Co(en)$_3$]$^{3+}$ based intermediates. Hence the ideal stereochemistry required for the intramolecular condensations in the capping process is expected to be more difficult to achieve for the *lel*$_3$-[Co(chxn)$_3$]$^{3+}$ species.

The [Co(diNOchar)]$^{3+}$ ion is formed with complete retention of the configuration and conformations imposed by the starting complex. The reduction of the nitro cap substituents is accompanied by reduction of the Co(III) center to Co(II). Upon reoxidation of the metal center, no changes in the configuration of the cage or the five-membered ring conformations occur. The nitro groups are more difficult to reduce in this system than those of the [Co(diNOsar)]$^{3+}$ analogue with the Zn/HCl reagent, and it is possible to isolate the complex [Co(AMNOcharH)]$^{4+}$ where only one of the nitro groups has been reduced. The electrochemical reduction $-NO_2 \rightarrow NHOH$ in analogous complexes support this observation. For this reduction, a $E_{1/2}$ for [Co(diNOchar)]$^{3+}$ (pH 5) of −0.54 V vs. SHE. (Table I) may be compared with $E_{1/2}$ for [Co(diNOsar)]$^{3+}$ (pH 5–6), −0.45 vs. SHE.[17]

The electronic spectra of these complexes are similar to those for the analogous cage species derived from [Co(en)$_3$]$^{3+}$,[1c] except that the first ligand field band of O_h parentage ($^1A_{1g} \rightarrow {}^1T_{1g}$) and the charge-transfer band are shifted to slightly longer wavelengths[1] (Figure 2).

The isolation of the *ob*$_3$ cage complex is of some importance in effecting the maximum utility of this system as a probe for understanding the outer-sphere electron-transfer properties of metal complexes. In the [Co(chxn)$_3$]$^{3+}$ synthesis used here, only a 2% yield of the *ob*$_3$-[Co(chxn)$_3$]$^{3+}$ was obtained. However, an equilibrium amount of 7% of the *ob*$_3$-[Co(chxn)$_3$]$^{3+}$ may be obtained when a solution of the *lel*$_3$-[Co(chxn)$_3$]$^{3+}$ ion is refluxed with activated charcoal (pH 7).[11] Several reactions of this species with HCHO and CH_3NO_2 were conducted but the *ob*$_3$-[Co(diNOchar)]$^{3+}$ complex has not yet been isolated. Analysis of the reaction products by ^{1}H NMR indicate significant condensation has occurred although species involving dissociation of a diamine are major reaction components. Dreiding models indicate that the stereochemistry for the capping process, via the proposed mechanism of imine formation and subsequent reaction with (−)-CH_2NO_2 would be more difficult in this case, especially for the final ring closures to give the caps.

Attempts to convert the *lel*$_3$-[Co(cage)]$^{3+}$ to the corresponding *ob*$_3$ form via the vigorous methods described in the reactivity section were not successful, but they have demonstrated a remarkable stability for these compounds. Several other synthetic approaches to the *ob*$_3$ system are currently being investigated.

^{1}H NMR and ^{13}C NMR Spectra. The ^{1}H NMR and ^{13}C NMR spectra, exemplified in Figure 1, are useful for characterization of the cage compounds. All complexes have the *lel*$_3$ conformation for the five-membered chelate rings, and the molecules may be in the D_3 or C_3 forms depending on the cap conformations. In the C_3 form the caps have distorted skew-boat conformations in which the methylene protons are staggered with respect to the proton on the secondary nitrogen. In the D_3 form these protons are nearly eclipsed. Although both the ^{1}H NMR and ^{13}C NMR spectra indicate an effective D_3 molecular symmetry, these techniques give only an average value for the cap resonances, as the $D_3(lel_3) \leftrightarrow C_3(lel_3)$ interconversion is likely to be facile on the NMR time scales (^{1}H NMR (60 mHz) $>10^2$ s^{-1}; ^{13}C NMR (60 mHz) $> 10^3$ s^{-1}).[13] Previous work has shown that in [Co(sep)]$^{3+}$ the individual D_3 and C_3 forms are not observed on a ^{13}C NMR time scale even at low temperatures[18] (−95 °C).

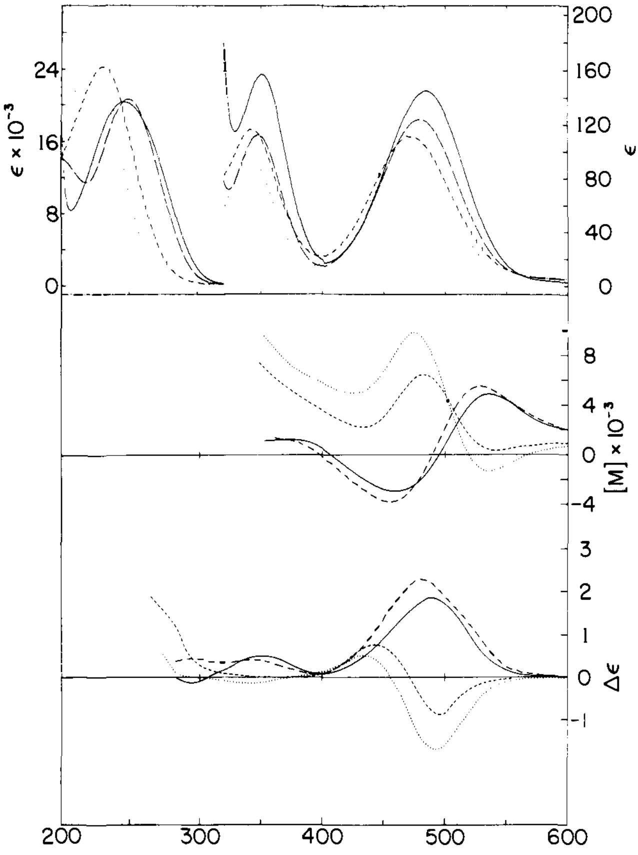

Figure 2. Absorption, rotary dispersion, and circular dichroism spectra of Δ-*lel*$_3$-[Co(chxn)$_3$]$^{3+}$ (···), Δ-*lel*$_3$-[Co(NOsemichar)]$^{3+}$ (- - -), Δ-*lel*$_3$-[Co(diNOchar)]$^{3+}$ (-·-·) (in H_2O), and Δ-*lel*$_3$-[Co(diAMcharH$_2$)]$^{5+}$ (in 0.1 M HCl) (—).

The AB doublet pair in the ^{1}H NMR of the Δ-*lel*$_3$-[Co(diAMcharH$_2$)]$^{5+}$ ion (Figure 1a) is diagnostic of the capped species since it is separated from the cyclohexane ring proton resonances.

The ^{13}C{^{1}H} NMR spectra of both [Co(diNOchar)]$^{3+}$ and [Co(diAMcharH$_2$)]$^{5+}$ species (Figure 1b) show a simple pattern containing five peaks and are consistent with an effective D_3 symmetry for the molecule. The resonances of the methylene carbon atoms on the cyclohexane rings are virtually identical for the cage molecules and the parent *lel*$_3$-[Co(chxn)$_3$]$^{3+}$ ion (carbons γ to N donor, δ −42.75, β carbons, δ ∼−37.4 relative to 1,4-dioxane). Resonances for the cage complexes were assigned from a consideration of the ^{1}H-coupled ^{13}C NMR spectra to determine ^{13}C NMR resonances of the cyclohexane ring carbon atoms and from general comparisons with the spectra of other cage systems derived from the [Co(en)$_3$]$^{3+}$ ions.[1,17]

The chemical shifts of quaternary carbon atoms are very sensitive to the apical substituent. In the ^{13}C NMR spectra there is an upfield shift of ∼32 ppm when the nitro group is changed to the protonated amino group and a further shift of 0.4 ppm for the free amino substituent. The intermediate complex [Co(AMNOcharH)]$^{4+}$ containing both a nitro and a protonated amino substituent shows both resonances for the quaternary carbon atoms.

The structure and absolute configuration of the cages have been confirmed by a single-crystal X-ray analysis of Δ-(*R*,*R*)$_3$-[Co(diAMchar)](NO$_3$)$_3$·H$_2$O.[19]

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Circular Dichroism. The changes in structural and electronic environment of the CoN_6 chromophore on going from the $[Co(chxn)_3]^{3+}$ parent ion to the caged species are associated with some extraordinary changes in the visible circular dichroism (CD) and rotatory dispersion (RD) spectra (Figure 2). The trends observed here may be compared with the changes in the CDs of the ligand field bands for the $[Co(en)_3]^{3+} \rightarrow [Co(sen)]^{3+}$ system[20] and the $[Co(en)_3]^{3+} \rightarrow [Co(sep)]^{3+}$ system.[1b]

The solution CD of Δ-$[Co(en)_3]^{3+}$ in the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ spectral region shows a negative band at low energy and a higher energy positive band of lower intensity. These bands are considered to derive from the net sum of two much larger transitions that have nearly equal magnitudes and opposing signs and are closely similar in energy.[21,22]

Single-crystal axial CDs of Λ-$[Co(en)_3]^{3+}$ and Λ-$[Co(sep)]^{3+}$ at 298 K both give a positive sign for the ${}^1A_1 \rightarrow {}^1E$ transition.[23] Consequently, the E component of the CD for the first ligand field band is most probably negative for the Δ absolute configuration of the caged species in solution. On the basis of this result, the observation that the Δ-*lel*$_3$-$[Co(chxn)_3]^{3+}$ ion exhibits a CD of the same form as the Δ-$[Co(en)_3]^{3+}$ complex means the low-energy negative wing in the CD of Δ-*lel*$_3$-$[Co(chxn)_3]^{3+}$ is due to the ${}^1A_1 \rightarrow {}^1E$ component and the high-energy positive wing of lower intensity to the ${}^1A_1 \rightarrow {}^1A_2$ component.

The effect of one cap on the complex (Δ-$[Co(NOsemichar)]^{3+}$) is to increase the overlapping of the component transitions and to decrease the intensity of the E wing while that of the A_2 wing is increased (Figure 2). Further changes in the CD occur for the fully formed cage species where the net intensity of the two components is enhanced and of opposite sign compared with that of the parent Δ-$[Co(chxn)_3]^{3+}$ ion. Only a positive band of ${}^1A_{1g} \rightarrow {}^1T_{1g}$ origin is present in the CD spectrum of Δ-$[Co(sep)]^{3+}$ in solution.[1a,b] With use of the result of the room temperature single-crystal study, we may argue that the A_2 component dominates the E component in the Δ-$[Co(sep)]^{3+}$ cage species. If the same result holds for $[Co(diAMchar)]^{3+}$, then the capping process results in an inversion of the relative intensities of the A_2 and E components as compared with the Δ-$[Co(chxn)_3]^{3+}$ ion and again the A_2 component is dominant.

The effect of protonation of the cap amino groups on the CD of the Δ-*lel*$_3$-$[Co(diAMchar)]^{3+}$ ion is to decrease the energy and intensity of the first ligand field band by ~30% (Δ-*lel*$_3$-$[Co(diAMchar)]^{3+}$ $\Delta\epsilon_{474} = +2.66\ M^{-1}\ cm^{-1}$ (H_2O, pH 7); Δ-*lel*$_3$-$[Co(diAMcharH_2)]^{5+}$ $\Delta\epsilon_{489} = +1.86\ M^{-1}\ cm^{-1}$ (0.1 M HCl)). This change in the CD may be interpreted as being entirely due to the protonation and the consequent increase in concentration of contact ion pairs, since the compounds are conformationally locked and hence changes in the CD due to conformational variations can be neglected. The rigidity of this system makes it very useful for studying changes in dichroism due to both different ionic environments and to different charge distributions within the complex ions. The latter are induced by different cap substituents, and such changes are expected to lead to considerable variations in the visible CD intensities.[24] This is exemplified by the CD differences for the Δ-*lel*$_3$-$[Co(diAMchar)]^{3+}$ and Δ-*lel*$_3$-$[Co(diAMcharH_2)]^{5+}$ ions discussed above, and further work is in progress in this area.

Table III. Rate Constants for Self-Exchange Reactions and Redox Potentials

reaction	k_{et}, $M^{-1}\ s^{-1}$	condtns (μ)[a]	E, V (vs. SHE)
$[Co(NH_3)]_6^{2+/3+}$	$\sim 10^{-7}$[b]		-0.02[c]
$[Co(en)_3]^{2+/3+}$	3.4×10^{-5}[d]	0.2	-0.18[c]
$[Co(chxn)_3]^{2+/3+}$	$\sim 10^{-5}$[e]		-0.19[f]
$[Co(diAMsar)]^{2+/3+}$	0.5[g]	0.2 ($LiClO_4$, pH 7.5)	-0.31[c]
lel$_3$-$[Co(diAMchar)]^{2+/3+}$	1.1 (0.2)	0.2 ($NaCF_3SO_3$, pH 7.5)	-0.36[h]
$[Co(diAMsarH_2)]^{4+/5+}$	0.024[g]	0.2 ($LiClO_4$, $HClO_4$, pH 1)	-0.04[c]
lel$_3$-$[Co(diAMcharH_2)]^{4+/5+}$	0.038 (0.002)	0.2 ($NaClO_4$, $HClO_4$)	
	0.038 (0.004)	0.2 ($NaCF_3SO_3$, CF_3SO_3H)	-0.01[h]

[a] Measured at 25.0 ± 0.1 °C. [b] Geselowitz, G.; Taube, H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*. Hammershøi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979. [c] Table I, ref 29. [d] Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892. [e] Reference 27. [f] Reference 15. [g] Reference 29. [h] Measured under conditions identical with those for electron-transfer experiments.

Electrochemistry. The reduction potentials for the cyclohexane systems are similar to those for the corresponding $[Co(diNOsar)]^{3+}$ cage species under similar conditions.[17] Energy minimization calculations have shown that the relative cavity sizes of the cobalt cage complexes are partly reflected by their respective redox potentials, although ligand rigidity effects are also important.[25] Because of their similar Co(III)/Co(II) redox potentials ($E_{1/2}[Co(diAMsarH_2)]^{5+} = -0.18$ V vs. SCE[17]), we infer that the $[Co(diAMcharH_2)]^{5+}$ and $[Co(diAMsarH_2)]^{5+}$ ions probably have similar cavity sizes and hence Co–N bond distances in solution. However, $[Co(diAMsarH_2)]^{4+}$ shows a two-electron reduction at $E_{1/2} = -1.9$ V in acetonitrile vs. Ag/AgCl accompanied by decomposition of the complex.[17] $[Co(diAMcharH_2)]^{5+}$ is not reduced even down to −2.6 V vs. Ag/AgCl in Me_2SO. Although both cage complexes have ideal similar cavity sizes under unstrained conditions, the $[Co(diAMcharH_2)]^{5+}$ species is rigid in conformation and may not readily accommodate additional ligand strain. It is then apparent that the reduction of the Co(II) center to the larger Co(I) or Co(0) state is not accessible in the cyclohexanediamine cage system. This may arise as a result of the rigid diamchar cage that would resist the deformations required to accept more electrons.

The $-NO_2 \rightarrow NHOH$ reductions were pH dependent, shifting to more negative potentials with increasing pH. AC polarography and cyclic DC voltammetry both indicated that the nitro reductions were irreversible. The electrochemistry of $[Co(diNOchar)]^{3+}$ showed a difference in reduction potential between the Co(III)/Co(II) couple and the nitro reduction of up to ~0.55 V (Table I). The possibility of obtaining the Co(II) species without reduction of the nitro groups is then feasible electrochemically, and the Co(II) nitro compound has been prepared chemically by using the mild reducing conditions of Zn dust in water.

Considerable adsorption on the surface of the mercury electrode occurred with these compounds. In both AC and DC polarography the adsorption always appeared at more positive potentials than the Co(III)/Co(II) reduction. Where adsorption gives a prewave, it is due to the fact that a reversible reduction is more facile if the reduced species is bound to the electrode.[26] The likely process here is therefore reduction of the Co(III) ion to the Co(II) that is adsorbed on the mercury electrode before reoxidation. Adsorption of the Co(III) species would result in an adsorption wave more negative in potential than that for the reduction of the free Co(III) ion.[26] This is consistent with the observation that few examples of adsorption of the oxidized form (Co(III) here) have been seen in polarography studies on such metal complexes.[26]

We note that the cage complexes described here qualitatively seem to exhibit stronger adsorption waves than for the other cage ions studied with similar core structures. The difference could be attributed to their greater hydrophobic character arising from the aliphatic cyclohexane rings.

Electron Transfer. The Co(III)/Co(II) electron self-exchange rates have been measured for this system and are presented in

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[26] Crow, D. R. "Polarography of Metal Complexes"; Academic Press: New York, 1969; Chapter 9.

Table III where the observed rate constants are compared with those for related systems. The most striking result is the factor of $\sim 10^5$ between the $[Co(en)_3]^{3+/2+}$ and $[Co(chxn)_3]^{3+/2+}$ self-exchange rates and that of *lel*$_3$-$[Co(diAMchar)]^{3+/2+}$. Increasing the bulkiness of the basic $[Co(en)_3]^{3+}$ structure both in the axial direction by the capping procedure and in the equatorial plane by addition of the cyclohexane rings has not diminished the rate of electron transfer as might be expected from a naive view but has actually increased it by a factor of about 10^5.

Dreiding models of the Λ,Λ reactant pairs give some useful qualitative information about the nature of the possible close contact distances and orientations in the bimolecular transition states for these electron self-exchange reactions. The models show that the distance of closest approach for the metal centers of the two reactants occurs when their C_3 axes are approximately at right angles in the cage systems or when they are aligned axially for the uncaged $[Co(en)_3]^{3+/2+}$ and $[Co(chxn)_3]^{3+/2+}$ pairs. The closest approach configuration was chosen as the bimolecular configuration with the shortest apparent distance that can be achieved between cobalt centers while intermolecular contacts at distances greater than the sums of van der Waals radii of contacting atoms were maintained. For both the Λ,Δ reactant pairs of the *lel*$_3$-$[Co(en)_3]^{3+/2+}$ and *lel*$_3$-$[Co(chxn)_3]^{3+/2+}$ systems the distance of closest equatorial approach appears to be similar at about 7.5 Å when the C_3 axes are approximately at right angles. Both systems of course have similar closest axial approach distances (~6 Å).

An expected effect of adding the cap moieties to the $[Co(en)_3]^{3+}$ and $[Co(chxn)_3]^{3+}$ ions would be to increase the close contact distance for the reactant molecules along the C_3 axis and so inhibit electron transfer in that direction. However, both $[Co(diAMsar)]^{3+/2+}$ and *lel*$_3$-$[Co(diAMchar)]^{3+/2+}$ pairs have self-exchange rates of $\sim 10^5$ greater than that measured for $[Co(en)_3]^{3+/2+}$ and deduced[26] for $[Co(chxn)]^{3+/2+}$. This means that the limiting axial approach model suggested by Beattie and co-workers[27] is unlikely to be an important contributor to the mechanism for electron transfer in these systems. Dreiding models also indicate that the distance of closest approach for catoptric $[Co(diAMsar)]^{3+/2+}$ pairs and $[Co(diAMchar)]^{3+/2+}$ pairs are similar but are dependent on the five- and six-membered chelate ring conformations. In the $[Co(diAMchar)]^{3+}$ molecule the cyclohexane rings are quite flexible between chair, skew, and boat forms and would move to minimize repulsions between rings in the reactant pairs.

The range of values for the rate constants of the species in Table III is not explained by the variations in bond length changes between the Co(II) and Co(III) reactant pairs.[1b,7,8] Alternatively, spin-state changes do not provide an explanation since the spectroscopic properties of all the cages and the parent $[Co(en)_3]^{3+}$ ion are very similar.[1,7]

A theoretical treatment of outer-sphere electron-transfer rates has recently been applied to several cobalt–amine systems.[8,9,25] The inner-sphere reorganization energies were determined from a molecular mechanics treatment of the bimolecular transition states, which were bounded by the Frank–Condon restrictions on electron transfer. The calculated reorganization energies largely account for the variation in rate constant over a range of 7 orders of magnitude in the electron self-exchange and cross-reaction rates of cobalt–amine systems, including several flexible metal ion cage systems. The results however are somewhat ambiguous for some of the flexible cage species. This is particularly apparent in the $[Co(sep)]^{3+/2+}$ self-exchange system and its cross-reaction rates, where the calculated reorganization terms are quite different for *lel*$_3$ and *ob*$_3$ conformational types. Since the equilibrium thermodynamic parameters are not yet known for the interconversion of these species and cannot be estimated with any confidence in aqueous solution at present, the inner-sphere contributions to the reorganization energy in this system cannot be determined uniquely, although upper and lower bounds can be established. In the cyclohexanediamine cage systems, however, only the *lel*$_3$ conformations need to be considered and so the theoretical treatment is less ambiguous than that for the flexible cage molecules. These calculations are in progress and will provide a more rigorous test for this treatment of the relative electron-transfer rates of the various cobalt–amine systems.

A study of the electron-transfer cross reactions between the rigid *ob*$_3$ and *lel*$_3$ forms of the $[Co(diAMchar)]^{3+/2+}$ system, as well as the self-exchange rates of the *ob*$_3$ species, would lead to further direct information on the intramolecular reorganization energies involved for different conformers and work is continuing on this aspect.

As expected, the rate of electron self-exchange for the protonated *lel*$_3$-$[Co(diAMcharH_2)]^{5+/4+}$ system is a factor of about 10^2 slower than that for the *lel*$_3$-$[Co(diAMchar)]^{3+/2+}$ reaction. This is probably mainly due to differences in the work required to bring the 5+/4+ and 3+/2+ ions together in the encounter complex prior to electron transfer.

Owing to the rigidity and hydrophobic characteristics of the $[Co(diAMchar)]^{3+}$ and $[Co(diAMchar)]^{2+}$ molecules, this system may also be amenable to an investigation of the total outer-sphere contribution to the electron-transfer rates. Furthermore, the study of asphericity effects on the dielectric continuum contributions to the outer-sphere reorganization may be important in this context. *Variations* in rate due to different solvent and ionic environments could be uniquely interpreted in terms of inner- and outer-sphere contributions, since the crucial conformations are fixed and inner-sphere reorganization energies and experimental rate constants are independently accessible. A recent study[28] has indicated that solvent *variations* have only a minor effect on the cross-reaction rate of the conformationally rigid $[Co(terpy)_2]^{2+}$ and $[Co(bpy)_3]^{3+}$ ions. Ion pairing effects may also be of importance in some solvents for the cage systems,[29] but we observe no difference in the *lel*$_3$-$[Co(diAMcharH_2)]^{5+/4+}$ self-exchange rate between aqueous triflate and aqueous perchlorate media at $\mu = 0.2$.

The study and interpretation of stereoselectivity effects in outer-sphere electron-transfer processes has not yet proved a particularly fruitful area of research.[30] In cases where stereoselectivity has been observed,[31] the effect has not been great. The reactions of individual enantiomers of $[Co(sep)]^{2+}$ with (−)-Λ-$[Co(diAMsarH_2)]^{5+}$ showed only a small selectivity.[29] However, this system is again complicated by the contributions of both *ob*$_3$ and *lel*$_3$ conformers of (−)-$[Co(diAMsarH_2)]^{5+}$ and $[Co(sep)]^{2+}$ to the electron-transfer rates. The intramolecular reorganization energy calculations previously discussed show that different combinations of D_3(*ob*$_3$), C_3(*lel*$_3$), and D_3(*lel*$_3$) reactant pairs may have quite different reorganization energies and contribute significantly to the rate whether or not they are observable in solution. Once again the $[Co(diAMchar)]^{3+}$ system is a more tractable one for probing the importance of such stereoselectivity. The molecules are constrained to be in the *lel*$_3$ conformation in both the Co(II) and Co(III) forms, and the large cyclohexane blades would be expected to enhance the chiral recognition properties of the reacting species. Experiments to clarify these aspects are currently under investigation.

The aza-capped analogue of the *lel*$_3$-$[Co(diAMchar)]^{3+}$ ion has recently been prepared[32] and may also prove to be an important

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molecule for probing the reorganization and stereoselective contributions to the electron-transfer process. The results of synthetic and electron-transfer experiments involving this ion will be presented in a subsequent publication.

Acknowledgment. We are thankful to J. Springborg and B. Søndergaard for providing some of the resolved cyclohexanediamine ligand and to the ANU Microanalytical Service. M.G.M. is grateful to the Australian National University for a Postgraduate Research Award.

Registry No. (*R*,*R*)-chxn, 20439-47-8; (*S*,*S*)-chxn, 21436-03-3; (–)-(*R*,*R*)-chxn·2HCl, 35018-63-4; (+)-(*S*,*S*)-chxn·2HCl, 35018-62-3; {(–)-chxn·H$_2$}{(+)-tartrate}, 39961-95-0; {(+)chxn·H$_2$}{hydrogen (+)-tartrate}$_2$, 39961-96-1; Δ-*lel*$_3$-[Co(chxn)$_3$]Cl$_3$, 37381-44-5; Δ-*lel*$_3$-[Co(chxn)$_3$](CF$_3$SO$_3$)$_3$, 92097-48-8; Λ-*ob*$_3$-[Co(chxn)$_3$]Cl$_3$, 31537-08-3; Λ-*ob*$_3$-[Co(chxn)$_3$](CF$_3$SO$_3$)$_3$, 92216-20-1; Λ-*lel*$_3$-[Co(chxn)$_3$]Cl$_3$, 59617-81-7; Λ-*lel*$_3$-[Co(diNOchar)]Cl$_3$, 92097-45-5; Λ-*lel*$_3$-[Co(diNOchar)]Cl$_2$·ClO$_4$, 92216-17-6; Δ-*lel*$_3$-[Co(diNOchar)]Cl$_3$, 92216-18-7; Δ-*lel*$_3$-[Co(diNOchar)](CF$_3$SO$_3$)$_3$, 92281-95-3; Δ-*lel*$_3$-[Co(NOsemichar)]Cl$_3$, 92125-50-3; Δ-*lel*$_3$-[Co(NOsemichar)](CF$_3$SO$_3$)$_3$, 92216-87-0; Δ-*lel*$_3$-[Co(diNOchar)](ClO$_4$)$_2$, 92097-47-7; Λ-*lel*$_3$-[Co(diAMchar·H$_2$)]Cl$_5$, 92125-51-4; Λ-*lel*$_3$-[Co(diAMchar·H$_2$)](CF$_3$SO$_3$)$_5$, 92216-90-5; Δ-*lel*$_3$-[Co(diAMchar)]Cl$_2$, 92216-91-6; Δ-*lel*$_3$-[Co(diAMchar)](CF$_3$SO$_3$)$_2$, 92218-46-7; Λ-*lel*$_3$-[Co(diAMchar·H$_2$)]$^{5+}$, 92281-99-7; Δ-*lel*$_3$-[Co(diAMchar)]$^{2+}$, 92125-53-6; Δ-*lel*$_3$-[Co(diAMchar·H$_2$)]Cl$_5$, 92216-85-8; Δ-*lel*$_3$-[Co(diAMchar)]ZnCl$_4$, 92125-54-7; [Co(AMNOchar·H)]Cl$_4$, 92125-52-5; (*R*,*R*)$_3$-diNOchar, 92097-44-4; (*S*,*S*)$_3$-diNOchar, 92216-15-4; Li$_2$ZnCl$_4$, 61420-95-9; HCHO, 50-00-0; NO$_2$CH$_3$, 75-52-5.

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Communications to the Editor

Magnetic Effects on Chemical Reactions in the Absence of Magnets. Effects of Surfactant Vesicle Entrapped Magnetite Particles on Benzophenone Photochemistry

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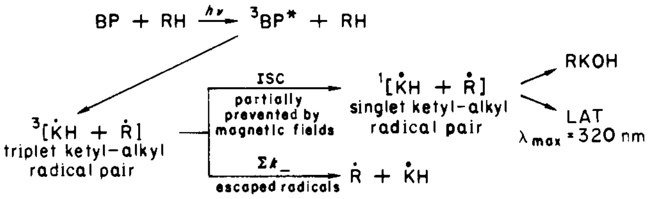
Received September 10, 1984

The paper reports the first observation of a substantial magnetic effect in the absence of an applied magnetic field: the dramatic alteration of benzophenone photochemistry by surfactant vesicle incorporated colloidal magnetite.

The influence of externally applied magnetic field on chemical reactions involving radical pairs is well documented.[2-6] A case in point is the photoreduction of benzophenone, BP, to an alcohol, RKOH (main product), and to light-absorbing coupling (minor) products, LAT.[7-10] Product formation has been rationalized in terms of the decay of photolytically generated benzophenone triplets, ^{3}BP*, in the presence of a hydrogen donor, RH, to a triplet ketyl radical pair, $^3[\dot{K}H + \dot{R}]$. The triplet ketyl radical pair undergoes, in turns, intersystem crossing to a singlet radical pair, $^1[\dot{K}H + \dot{R}]$, governed by ISC, competetively with the escape of radicals from their cages (governed by Σk_-). The observed decrease of LAT on photolyzing BP in the presence of an externally applied magnetic field substantiated the mechanism shown in Scheme I.[7] Incorporation of BP in aqueous micelles increased the amount of LAT formed on photolysis and amplified the magnetic effects.[7,8]

Dioctadecyldimethylammonium chloride (DODAC) surfactant vesicles[11] were utilized in the present work as media for benzophenone photoreactions.[12] Repetitive bursts (2 Hz) of 266 nm, ca. 1 mJ, laser pulses mediated the benzophenone photoreduction.[13] The progress of the reaction was monitored by a Hewlett-Packard 8450 A Diode Array Spectrophotometer. The amount of LAT formed in DODAC vesicles, just like in aqueous micelles,[7] is appreciably greater than that in a pure solvent (Figure 1). The increase in LAT yields is probably due to the solubilization of the ketyl radicals with the hydroxyl groups hydrogen bonded to water in the head-group region of DODAC vesicles. There they are likely to be arranged with their phenyl rings oriented toward the bilayers where the counterradicals are located, which then facilate the formaton of para-coupled products.[9] Incorporation of colloidal magnetite (Fe$_3$O$_4$) particles[14] dramatically decreased the LAT yields (Figure 1) by increasing the fraction of those escaped to those undergone intersystem crossing (Scheme I).

Scheme I



Effects of DODAC vesicle incorporated magnetite particles have been substantiated by laser flash photolysis.[16] Benzophenone

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[12] Stock solutions, 3.6 × 10^{-3} M (stoichiometric surfactant concentration), of DODAC vesicles were prepared by the ultrasonic dispersal of 53.7 mg of DODAC in 25 ml of distilled water at 70 °C for 15 min by the microtip of the Branson sonicator set at 70 W. Stock solutions were diluted tenfold by water for all photochemical experiments. Hydrodynamic diameters of the 3.6 × 10^{-4} M DODAC vesicles were determined to be 1100 ± 100 Å by dynamic light scattering. Recrystallized benzophenone was introduced by injection in MeOH to give a final concentration of 8.0 × 10^{-5} M.

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[14] Magnetite (Fe$_3$O$_4$) particles were prepared by adding 30% ammonium hydroxide to equal volumes of 0.9 M FeCl$_3$·6H$_2$O and 0.6 M FeCl$_2$·4H$_2$O.[15] Settling of the magnetic particles was facilitated by placing the solution in a beaker on a magnet. The precipitate was washed 6 times with 3% NH$_4$OH and stabilized by the addition of 10^{-3} M lauric acid. Cosonication of appropriate ratios of DODAC and lauric acid stabilized magnetites resulted in magnetic particle containing surfactant vesicles. Sizes of magnetite carrying DODAC vesicles were determined to be 1400 ± 100 Å. Vesicle incorporated magnetite particles remained stable at least a month. Saturation magnetization of 1.2 × 10^{-3} M Fe$_3$O$_4$ in 2 × 10^{-3} M DODAC vesicles was determined to be 0.25 G by means of a vibrationg magnetometer. Concentrations of Fe$_3$O$_4$ were determined by atomic absorption using a Perkin-Elmer Model 5000 spectrometer by dissolving Fe$_3$O$_4$ containing vesicles in concentrated HCl.

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