of N_2/Zr was produced during the reaction. Workup as for **7** yielded 0.29 g (81%) of colorless crystals. **8**-^{17}O was prepared analogously to method B from **6a**-^{17}O.

Preparation of $Cp^*_2ZrH(NH_2)$ (9a). Method A. A 0.24-g sample of $Cp^*_2ZrH_2$ (0.66 mmol) was dissolved in 15 mL of petroleum ether and the solution cooled to −78 °C. The solution was stirred, and 1.5 equiv of ammonia was condensed into the reaction vessel. The reaction mixture was warmed to room temperature, and then the solvent was removed under vacuum to yield 0.21 g (84%) of a colorless powder. A Toepler measurement indicated that 0.92 equiv of H_2/Zr was produced during the reaction. Anal. Calcd for $C_{20}H_{33}NZr$: C, 63.43; H, 8.78; N, 3.70. Found: C, 63.40; H, 8.70; N, 3.55. **Method B.** A 0.30-g sample of $[Cp^*_2Zr(N_2)]_2N_2$ was dissolved in 10 mL of toluene and placed in a sublimation apparatus. Two equivalents of NH_3 were condensed into the reaction vessel and the contents stirred at ambient temperature for 1 h during which time the solution changed from deep purple to blood red. The solvent was removed under vacuum and the residue sublimed (110 °C, 10^{-4} torr) to yield 0.13 g (46%) of colorless crystals.

Preparation of $Cp^*_2HfH(NH_2)$ (9b). Using a procedure similar to method A for **9a**, a 0.13-g sample of $Cp^*_2HfH_2$ was dissolved in 10 mL of petroleum ether and the solution stirred at ambient temperature with 2 equiv of NH_3 for 15 min. Removal of solvent under vacuum yielded 0.13 g (97%) of a colorless powder. Anal. Calcd for $C_{20}H_{33}NHf$: C, 51.55; H, 7.14; N, 3.01. Found: C, 51.61; H, 7.13; N, 3.08. **9b**-^{15}N was prepared analogously from $^{15}NH_3$.

Exchange Experiments. The exchange experiments previously described were effected on NMR tube scales. In a typical experiment, a 25-mg sample of $Cp^*_2Zr(OH)Cl$ was dissolved in 0.5 mL of C_6D_6 and placed, along with a sealed capillary of H_2O (5% ^{17}O) as a reference, in a 5-mm NMR tube with an open-faced cap with a septum. ^{17}O-enriched water was subsequently added through the septum via a microliter syringe, and the reaction was followed by ^{17}O NMR spectroscopy (i.e., the appearance and growth of the resonance corresponding to $Cp^*_2Zr(^{17}OH)Cl$).

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Registry No. 1a, 61396-34-7; **1b**, 81956-87-8; **2a**, 91294-89-2; **2a**-^{18}O, 91294-90-5; **2b**, 91294-91-6; **2b**-^{17}O, 91294-92-7; **3a**, 91294-93-8; **3a**-^{18}O, 91294-94-9; **3a**-^{17}O, 91294-95-0; **3b**, 91294-96-1; **3b**-^{17}O, 91294-97-2; **4**, 91294-98-3; **4**-^{17}O, 91294-99-4; **5a**, 77299-72-0; **5b**, 91295-01-1; **6a**, 91295-02-2; **6a**-^{17}O, 91295-03-3; **6b**, 91295-04-4; **6b**-^{17}O, 91295-05-5; **7**, 91295-06-6; **7**-^{17}O, 91295-07-7; **8**, 91295-08-8; **8**-^{17}O, 91295-09-9; **9a**, 91295-10-2; **9b**, 91295-11-3; **9b**-^{15}N, 91295-12-4; **10**, 54387-50-7; $Cp^*_2ZrCl_2$, 54039-38-2; H_2O, 7732-18-5; $^{18}OH_a$, 14314-42-2; $^{17}OH_2$, 13768-40-6; NH_3, 7664-41-7; $^{15}NH_3$, 13767-16-3.

Metal Ion Encapsulation: Cobalt Cages Derived from Polyamines, Formaldehyde, and Nitromethane

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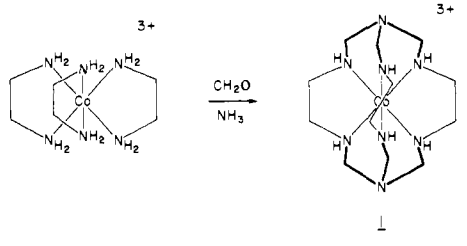
Abstract: The syntheses and characterization of a number of cage complexes derived from the products of the reactions between $Co(en)_3^{3+}$ (en = 1,2-ethanediamine) and $Co(sen)^{3+}$ (sen = 5-(4-amino-2-azabutyl)-5-methyl-3,7-diaza-1,9-nonanediamine) with formaldehyde and nitromethane in basic solution are described. The complexes can all be considered as derivatives of the hexaazamacrobicycle "sarcophagine" or 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane (sar). To confirm the cage structure of the ligands, the crystal structure of the deprotonated complex $[Co(diNOsar\text{-}H)]Cl_2\cdot 4H_2O$ is reported. Crystal data for $[Co^{III}(diNOsar\text{-}H)]Cl_2\cdot 4H_2O$ are the following: space group $P2_12_12_1$, a = 10.821 (5) Å, b = 15.929 (8) Å, c = 14.259 (10) Å, U = 2457.8 Å^3, D_{obsd} = 1.579 g cm^{-3}, D_{calcd} = 1.554 g cm^{-3}, Z = 4, 2423 nonzero structure factors ($I > 2.5\sigma I$), and R = 0.048. Reduction of the nitro-substituted sarcophagine complexes leads to amino-substituted derivatives which in turn may be diazotized to give a variety of new cages, and ultimately reductive elimination of the chloro derivative provides the "parent" complex $Co(sar)^{3+}$. Spectroscopic characterization of these complexes is also given, and the synthetic chemistry is analyzed in detail.

Cyclic, multidentate chelating ligands are the most potent yet often also the most selective of metal-coordinating agents, and in recent publications[1-6] we have described some of our efforts to synthesize macropolycyclic ligands especially suited to the binding of transition metals. The first-developed procedure, **1**,



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which led to the octaazamacrobicycle given the trivial name "sepulchrate",[1-4] seemed open to several obvious changes, one of which was to vary the central atoms of the ligand "caps" (shown as heavy lines in the above diagram). In sepulchrate, these atoms are nitrogen and are derived from ammonia formally acting as a tribasic acid under the preparative conditions. In principle, any other tribasic acid might therefore be expected to provide a substitute for ammonia and there are simple organic examples

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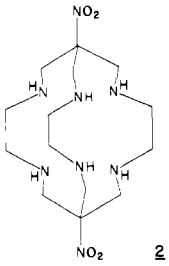
of this type of reaction, as seen for instance in the synthesis of phosphorus-substituted hexamethylenetetramines.[7] However, because a particular interest was to replace the cap nitrogen atoms of sepulchrate by carbon, our initial investigations centered on the substitution of nitromethane for ammonia. The present paper reports the basic results of this synthetic work, illustrating that even such a simple variation can lead to a considerable variety of encapsulating-ligand complexes.

To simplify the description of the complexes, we have used a trivial nomenclature in which the encapsulated metal ion, M^{n+}, is denoted by an abbreviated form of the parent hexaazamacrobicycle, "sarcophagine", as sar coupled with the substituents in the 1 and 8 positions, the tertiary carbon centers, i.e., $M(X,Ysar)^{n+}$. The abbreviations used for the trivial names of the ligands reflect the "cap" substituents, so that **2**, for example, will



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be referred to as "diNOsar" (for dinitrosarcophagine), ClMe = chloro, methyl, HO = hydroxy, AMME = amino, methyl, Clme = CH_2Cl, AMMEsarH = protonated amine group on the amino methyl sar. Clearly such a relatively obvious trivial nomenclature is required when the IUPAC names are so complex.

Experimental Section

Instrumentation. NMR spectra were obtained on JEOL "Minimar" MH100 (protons) and FX60 (^{13}C) spectrometers. Solution electronic spectra were obtained with a Cary-Varian 118C spectrophotometer, while infrared spectra were recorded by the KBr disk technique with a Perkin-Elmer Model 437 IR spectrophotometer. All evaporations were carried out under reduced pressure (<20 mmHg) with a Büchi rotary evaporator so that the temperature of the solution did not exceed 25 °C.

Syntheses. $[Co(en)_3]Cl_3$ was prepared and resolved by conventional procedures.[9]

$[Co(diNOsar)]Cl_3 \cdot H_2O$. Nitromethane (190 g) was added to a solution of $[Co(en)_3]Cl_3$ (163 g) in water (5 L) and the solution stirred until the CH_3NO_2 had completely dissolved. Aqueous HCHO solution (1300 g, 37%) and Na_2CO_3 (80 g) were then added and stirring was continued until the Na_2CO_3 had dissolved. The solution became warm and darkened in color. When the solution was left to stand at room temperature for 5 h, a copious precipitate of orange, needle-like crystals formed. This material, which appeared to be the chloride carbonate salt of the product, was collected, washed with a little ice-cold water, and dried in air. Vacuum desiccation or even washing with an organic solvent caused the solid to turn violet (due to a deprotonation reaction—see Discussion section), and it was convenient to convert it to the simple chloride salt by gradual addition to hot 3 M HCl (500 mL), mixing of the solution formed with ethanol (1500 mL), and cooling on ice. Yield: 156 g (69%). Anal. Calcd for $CoC_{14}H_{30}N_8O_4Cl_3 \cdot H_2O$: Co, 10.57; C, 30.15; H, 5.79; N, 20.09; Cl, 19.07. Found: Co, 10.57; C, 30.35; H, 5.61; N, 19.99; Cl, 19.10.

^1H NMR: In 36% DCl, δ 3.0–4.2 (relative to external Me_4Si) complex asymmetric pattern of at least 9 C-H resonances; δ 8.10, broad singlet (NH; integrated relative intensities 4:1 (24:6). In D_2O, after NH proton exchange (which was rapid), a pattern of CH resonances very similar to that observed for $Co(sep)^{3+}$, and crudely interpretable as two sets of partly superimposed AB doublet pairs, was obtained at δ 2.88, 2.97, 3.21, 3.35, 3.43, 3.51, 3.74, and 3.89 (relative to internal sodium trimethylsilylpropane sulfonate, DSS). Very much weaker resonances at δ 2.76 and 3.10 indicated that at least one spin system was more complicated than simply AB. ^{13}C NMR: Broad-band ^1H decoupled spectrum in D_2O, dioxane reference: δ +20.0, −10.8, and −14.4. IR: Strong absorptions characteristic of the NO_2 groups were apparent at 1555 and 1353 cm^{-1}. Electronic spectrum: λ_{max}, ϵ_{max} in 0.1 M HCl, 473.5 nm, 146 M^{-1} cm^{-1} and 343.5 nm, 124 M^{-1} cm^{-1}. Additional product (45 g) was precipitated by addition of $HClO_4$ (70%, 250 mL) to the filtrate from the chloride carbonate salt. This rather insoluble material was contaminated with small quantities of other reaction products, and 2 or 3 recrystallizations from hot water were required to give product of purity equivalent to that of the bulk chloride. $Co(diNOsar)^{3+}$ also precipitated as all possible chloride perchlorate salts, and to obtain the pure triperchlorate it was necessary to convert the chloride perchlorate to the acetate by anion exchange and then add $HClO_4$ to an aqueous solution of this very soluble acetate salt. Analogous procedures provided the pure nitrate and triflate salts. Starting with Λ-$(+)_{589}$-$Co(en)_3^{3+}$, all these materials were prepared in their chiral forms without significant alteration of the methods used with the racemate. Anal. Calcd for $[CoC_{14}H_{30}N_8O_4](CH_3CO_2)_3 \cdot 3H_2O$: Co, 8.87; C, 36.15; H, 6.83; N, 16.86. Found: Co, 8.54; C, 36.17; H, 6.00; N, 16.94. Calcd for $[CoC_{14}H_{30}N_8O_4](ClO_4)_3 \cdot H_2O$: Co, 7.86; C, 22.43; H, 4.30; N, 14.95; Cl, 14.19. Found: Co, 7.58; C, 22.25; H, 4.83; N, 14.61; Cl, 14.04. $[\alpha]_{589} = -204$, $[\alpha]_{465} = +742$ (10^{-3} M in H_2O) for material derived from Λ-$(+)_{589}Co(en)_3^{3+}$. Calcd for $[CoC_{14}H_{30}N_8O_4](NO_3)_3$: Co, 9.51; C, 27.15; H, 4.88; N, 24.88. Found: Co, 9.04; C, 27.00; H, 5.22; N, 24.53. Calcd for $[CoC_{14}H_{30}N_8O_4](CF_3SO_3)_3$: Co, 6.69; C, 23.19; H, 3.43; N, 12.72; F, 19.42. Found: Co, 6.56; C, 23.08; H, 3.48; N, 12.38; F, 20.06.

Side Products of $Co(diNOsar)^{3+}$ Formation. Complete analysis of the products from the ~10% of $Co(en)_3^{3+}$ not converted to $Co(diNOsar)^{3+}$ under the above conditions proved exceedingly complex and necessitated laborious chromatographic separations. Some reduction to Co(II) had occurred, and some products had obviously, from their colors, been formed via en ligand hydrolysis reactions and so were not characterized. The major (~2%) side product and two minor species were, however, readily isolated, and their characterization provided useful information relating to the nature of the reactions occurring during $Co(diNOsar)^{3+}$ formation.

(a) 5-(4-Amino-2-azabutyl)-5-nitro-3,7-diaza-1,9-nonanediamine ($[Co(NOsen)]Cl_3$). (The trivial name "sen" has been used in the literature[10] to denote a sexidentate amine from which the present ligand can be considered to have been formed by formal replacement of a methyl group by a nitro group[8]). The solution obtained after filtering the $HClO_4$ acidified $Co(diNOsar)^{3+}$ reaction mixture was diluted to 10 L with water and passed through H^+ Dowex 50 WX2 cation exchange resin. The column was washed with water (1 L) and 1 M HCl (1 L), and the absorbed complexes were then eluted with 3 M HCl. The eluate was evaporated to dryness and the residue dissolved in water and absorbed on Na^+ Sephadex SP C25 cation exchange resin (5 cm diameter × 30 cm column). Elution with 0.3 M NaCl revealed a large number of pink to violet bands, but only one significant orange band was collected. The complexes present were recovered via absorption on H^+ Dowex 50 WX2, elution with 3 M HCl, and evaporation of the eluate to dryness. The residue was again chromatographed on Na^+ SP Sephadex C25 resin, this time with 0.1 M K_2SO_4 as eluant, producing a leading minor band which proved to be a trace of $Co(diNOsar)^{3+}$, followed by at least two diffuse and ill-separated bands. The second diffuse band was rechromatographed on Na^+ SP Sephadex C25 with 0.05 M trisodium citrate to reveal at least seven components, though the bulk of the material was contained in the third, fourth, and fifth bands. The complexes present in these fractions were isolated by absorbing the eluate on H^+ Dowex 50 WX2, washing with 1 M HCl, eluting with 3 M HCl, and taking these eluates to dryness under vacuum. The residue from the third band was crystallized from 1 M HCl by addition of ethanol to give yellow needles (~0.3 g). The same material was obtained in better overall yield when $Co(diNOsar^{3+}$ preparative mixtures were quenched by acidification at short reaction times. After only 30 min, for example, the reaction mixture contained comparable quantities of $Co(diNOsar)^{3+}$, $Co(NOsen)^{3+}$, and $Co(en)_3^{3+}$ (note that the fourth band above was found to contain $Co(en)_3^{3+}$, ~0.1 g). Anal. Calcd for $CoC_{10}H_{27}N_7O_2Cl_3$: Co, 13.31; C, 27.13; H, 6.15; N, 22.15; Cl, 24.03. Found: Co, 13.67; C, 27.34; H, 6.53; N, 21.77; Cl, 24.42.

^1H NMR: In 1 M DCl, broad resonances at δ 7.44 (3 NH) and 5.12 (3-NH_2) were apparent downfield of complex CH resonances (δ 2.4–4.0). On N deuteration, resolution of the CH resonances was increased, giving an apparent AB quartet (δ 3.24, 3.38, 3.76, 3.90) superimposed on a complex multiplet, δ 2.6–3.5. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, dioxane reference, δ +19.8, −9.6, −14.6, −22.4.

(b) (*N*-Methylene-1,2-ethanediamine)(bis(ethane-1,2-diamine))cobalt(III) iodide ($[Coen_2(enim)]I_3$). The complex residue from the fifth

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band (0.05 M $Na_3C_6H_5O_7$/SP Sephadex C25) was dissolved in water and NaI added to precipitate the complex as golden needles (~0.1 g). Anal. Calcd for $CoC_7H_{24}N_6I_3$: Co, 9.33; C, 13.30; H, 3.83; N, 13.30; I, 60.24. Found: Co, 9.18; C, 12.95; H, 3.86; N, 13.45; I, 59.20. ^1H NMR: In dilute DCl, δ 7.68 (2 H, br, N=CH_2), 4.92 (br, NH_2, exchangeable in D_2O), 3.84 (2 H, poorly resolved triplet, —CH_2N=), 2.71 (10 H, broad complex CH_2 resonance). This same material was independently detected as a product of reaction between $Co(en)_3^{3+}$, HCHO, and CO_3^{2-}.

(c) **[Co(N-MENOsen)]Cl_3.** The first diffuse band from 0.1 M K_2SO_4/SP Sephadex C25 chromatography of the $Co(diNOsar)^{3+}$ filtrate fraction was rerun on SP Sephadex C25 with use of 0.075 M Na_2HPO_4/0.075 M NaH_2PO_4 as eluant and found to give a leading band, containing by far the bulk of the material, followed by at least two weak bands. The material in the bulk band was recovered via H^+ Dowex 50 WX2 absorption, HCl elution, and evaporation to dryness under vacuum. It was then crystallized from 1 M HCl by addition of acetone (yield 4 g). Anal. Calcd for $CoC_{11}H_{29}N_7O_2Cl_3$: Co, 12.90; C, 28.93; H, 6.40; N, 21.47; Cl, 23.29. Found: Co, 13.43; C, 29.18; H, 6.91; N, 21.47; Cl, 23.78. ^1H NMR: The complicated spectrum of this material was very similar to that of $Co(NOsen)^{3+}$ except for the significant feature that the highest field resonance was a doublet, δ 2.29 and 2.34, which collapsed to a singlet on deuterium exchange of the N protons.

[Co(diNOsar-H)](ClO_4)$_2$. Aqueous NaOH (1.0 M, 2 mL) was added to a solution of [Co(diNOsar)](ClO_4)$_3$ (1.0 g) in water (25 °C, 300 mL). The pale yellow solution immediately turned a deep violet color and, on addition of a filtered, saturated solution of $NaClO_4$ (30 g) in water, lustrous, diamond-shaped, violet plates were precipitated. After cooling the mixture on ice for 5 min, the precipitate was collected and washed with ethanol and ether (yield 0.60 g). Anal. Calcd for $CoC_{14}H_{29}N_8Cl_2O_{12}$: Co, 9.34; C, 26.63; H, 4.63; N, 17.75; Cl, 11.23. Found: Co, 9.11; C, 26.77; H, 4.52; N, 17.72; Cl, 11.20. Visible spectrum in dimethyl sulfoxide—λ_{max}, ϵ_{max}: 528 nm, 514 M^{-1} cm^{-1}; 381 nm, 1180 M^{-1} cm^{-1}; 338 nm (shoulder), 1040 M^{-1} cm^{-1}. ^1H NMR in D_2O: Essentially three doublets at δ 2.61, 2.71, 3.11, 3.22, 3.57, and 3.69 with additional weak multiplets apparent between δ 2.8 and 3.0. The more soluble chloride and nitrate salts were obtained as violet needles and hexagonal tablets, respectively, by a similar procedure starting with concentrated solutions of the appropriate $Co(diNOsar)^{3+}$ salts. Preparations of the optically active materials were identical with those of the racemates. The tetrahydrate of the chloride salt of the complex derived from Λ-$(+)_{589}$-$Co(en)_3^{3+}$ was ultimately used in a crystal-structure determination. Anal. ($CoC_{14}H_{37}N_8O_8Cl_2$): Co, 10.45; C, 29.93; H, 5.67; N, 20.56; Cl, 12.58.

[Co(diNOsar)](ClO_4)$_2$. Although reduction of the metal center in $Co(diNOsar)^{3+}$ was readily achieved, it was complicated by subsequent reduction of the ligand nitro groups and successful isolation of the Co(II) complex demanded rapid manipulations. A slurry of [Co(diNOsar)](ClO_4)$_3$ (2 g) and Zn dust (5 g) in water (40 mL) was shaken vigorously under nitrogen for 60 s. Undissolved complex and excess Zn were filtered off rapidly and the filtrate mixed with an equal volume of deoxygenated, saturated $NaClO_4$ solution. Very pale greenish-white crystals were rapidly deposited and quickly collected from the pale orange supernatant. The solid complex appears to undergo internal redox reactions on prolonged storage. Anal. Calcd for $CoC_{14}H_{30}N_8Cl_2O_{12}$: Co, 9.32; C, 26.60; H, 4.78; N, 17.72; Cl, 11.21. Found: Co, 9.52; C, 26.29; H, 4.78; N, 17.27; Cl, 11.25.

[Co(diAMsar)]Cl_3·2HCl and [Co(diAMsarH_2)]Cl_5. [Co(diNOsar)]Cl_3 (40 g) was dissolved in water (2 L and the solution deoxygenated with nitrogen. Under vigorous stirring and maintenance of a nitrogen blanket, zinc dust (40 g) was added, followed by concentrated HCl (200 mL) drop by drop. Stirring was continued for 1 h after the acid addition was complete. The reduction was monitored by withdrawing a few drops of the green solution, adding a drop of 30% H_2O_2 (to oxidize the complex(es) to the Co(III) state), and separating the components by chromatography on a microcolumn of Na^+ SP Sephadex C25 with 0.3 M NaCl. When only a single, slowly eluted orange band was detectable, 30% H_2O_2 (50 mL) was added to the whole reaction mixture to reoxidise the cobalt(II) to cobalt(III). (Note: In some preparations up to 5 g of extra Zn was required to complete the nitro group reduction before the H_2O_2 addition). The now orange solution was warmed on the steam bath for 15 min and then absorbed on a 20 cm × 8 cm diameter column of H^+ Dowex 50 WX2 cation-exchange resin. The column was washed with water (2 L) and 1 M HCl (2 L, to remove Zn^{2+}) and the orange complex then eluted with 3 M HCl. The eluate volume was reduced under vacuum until crystallization commenced and deposition was completed by the addition of ethanol. The complex was recrystallized as large yellow-orange plates by dissolution in warm 1 M HCl, addition of ethanol to the point of turbidity, and slow cooling (yield 30 g). An identical procedure provided optically active complex from $(-)_{589}$-$Co(diNOsar)^{3+}$. Anal. Calcd for $CoC_{14}H_{36}N_8Cl_5$·H_2O: Co, 10.17; C, 29.01; H, 6.44; N, 19.33; Cl, 30.58. Found: Co, 10.15; C, 29.23; H, 6.67; N, 19.07; Cl, 30.22. ^1H NMR: The spectrum of this complex was strongly concentration and pH dependent. At 55 mg mL^{-1} in D_2O (after N deuteration, which was complete on dissolution), strong resonances were detectable at δ 2.79, 2.84, 2.94, 3.43, and 3.53, though each showed evidence of fine structure. In 36% DCl, a single, symmetrical NH resonance appeared at δ 7.8. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O/DCl, dioxane reference, δ −10.3 (weak), −11.5, −15.6 (these shifts are those for the fully protonated, 5+ cation). Visible spectrum—λ_{max}, ϵ_{max} in 0.1 HCl: 475 nm, 149 M^{-1} cm^{-1}, 344.5 nm, 130 M^{-1} cm^{-1}. IR bands characteristic of the NO_2 groups of $Co(diNOsar)^{3+}$ were obviously absent whereas a new broad absorption near 3050 cm^{-1}, characteristic of NH_3^+, was apparent.

Products of Nitrosation of Co(diAMsar)Cl_3. The original hope was that the preparation below would provide $Co(diCLsar)^{3+}$ and then, via reductive dehalogenation, $Co(sar)^{3+}$ itself. Though this was realized, nitrosation of $Co(diAMsar)^{3+}$ in Cl^--containing media provided at least nine products in addition to $Co(diCLsar)^{3+}$, and extensive chromatographic separations were necessary. A solution of [Cl(diAMsarH_2)]Cl_5 (20 g) and LiCl (50 g) in water (250 L) was cooled on ice to a temperature below 5 °C. $NaNO_2$ (20 g) was added and the mixture swirled until all the solid had dissolved. A slight effervescence occurred, and the solution was left to stand on ice for 30 min. Concentrated HCl (10 mL) was then added and cooling continued for another 30 min, during which period considerable precipitation of a yellow solid occurred. Finally, more concentrated HCl (20 mL) was added and the mixture allowed to warm to room temperature over 30 min. (Note: In other preparations conducted entirely at room temperature and above, no difference in product distributions was noted but in some cases unreacted $Co(diAMsar)^{3+}$ was detected.) After dilution to ~2 L with water, the reaction mixture solution was absorbed on a 30 cm × 9 cm diameter column of H^+ Dowex 50 WX2 cation exchange resin. The column was washed with water (2 L) and 1 M HCl (1 L) and the complexes then eluted with 3 M HCl. On such a heavily laden column only two bands were seen, the leading orange band being by far the major component and the trailing bright yellow material being very difficult to see against the background color of the resin, so that its elution was monitored visually through the color of the effluent. These "orange" and "yellow" fractions were separately taken to dryness under vacuum and the residues crystallized from the minimum volumes of water by the addition of several volumes of acetone to each. Approximate quantities in the two residues were 15 and 2.5 g, respectively. The mixtures within them were separated by chromatography on Na^+ SP Sephadex C25 cation exchange resin with 0.1 M Na_2HPO_4 as eluant. A loading of not more than 0.5 g for a 30 cm × 5 cm diameter column was necessary to achieve the separations described.

"Orange" Complexes. The chromatography revealed six components, with only the first being readily separated so that fractions 2–6 were independently rerun under the same conditions to achieve clear final separations. The complexes were recovered by absorbing the pure eluates on H^+ Dowex 50 WX2 resin, eluting with 3 M HCl, evaporating the HCl eluate to dryness under vacuum, and crystallizing the residue from 1 M HCl by the slow addition of acetone. Weighing the crystalline products enabled a crude estimate of their distribution to be made, although with some of the minor components appreciable mechanical losses probably occurred during the multiple manipulations.

Fraction 1 [Co(diNOsar)]Cl_3 (3%). This fraction was identified by comparison of its ^1H NMR spectrum and solubility characteristics with those of authentic material (see above).

Fraction 2 [Co(CLNOsar)]Cl_3 (18%). Anal. Calcd for $CoC_{14}H_{30}N_7Cl_4O_2$: Co, 11.14; C, 31.78; H, 5.71; N, 18.53; Cl, 26.80. Found: Co, 11.10; C, 31.20; H, 5.52; N, 18.28; Cl, 26.77. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 474 nm, 148 M^{-1} cm^{-1}; 344.5 nm, 123 M^{-1} cm^{-1}. IR spectrum: NO_2 absorptions at 1340 and 1560 cm^{-1}. ^1H NMR: In 36% DCl an NH resonance considerably broader than that in $Co(diNOsar)^{3+}$ was detected at δ 8.02. CH resonances between δ 3.0 and 4.5 were complex. In D_2O (after N deuteration), sharp CH resonances appeared at δ 2.74, 2.86, 3.16, 3.34, 3.45, 3.56, 3.73, 3.86, though with evidence of further structure. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, δ +19.9 −4.7, −10.8, and −14.4. (The complex was run as its acetate salt in order to form a concentrated solution and acetate carbon resonances are not reported.)

Fraction 3 [Co(HONOsar)]Cl_3 (7.5%). Anal. Calcd for $CoC_{14}H_{31}N_7Cl_3O_3$·$^1/_2H_2O$: Co, 11.34; C, 32.36; H, 6.20; N, 18.87; Cl, 20.47. Found: Co, 11.11; C, 32.42; H, 6.43; N, 18.77; Cl 20.35. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 474 nm, 148 M^{-1} cm^{-1}; 344.5 nm, 127 M^{-1} cm^{-1}. IR spectrum: NO_2 absorption at 1353 and 1560 cm^{-1}. ^1H NMR: In 36% DCl, the NH resonance appeared as a doublet, δ 7.68 and 7.92, CH resonances again being a complex pattern between δ 2.6 and 4.2. In D_2O after N deuteration the CH resonances remained very complex, with principal peaks at δ 2.44, 2.57, 2.78, 2.83, 2.87, 3.09, 3.22,

3.32, 3.36, 3.73, and 3.96. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, δ +19.7, +6.0, −10.9, −11.8, −14.7.

Fraction 4 [Co(diCLsar)]Cl$_3$ (44%). Anal. Calcd for $CoC_{14}H_{30}N_6Cl_5$: Co, 11.36; C, 32.42; H, 5.83; N, 16.20; Cl, 34.18. Found: Co, 10.99; C, 32.63; H, 5.99; N, 16.12; Cl, 33.99. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 473.5 nm, 143 M^{-1} cm^{-1}; 344.5 nm, 121 M^{-1} cm^{-1}. ^{1}H NMR: In 36% DCl (in which the complex is far less soluble than are the others) a single NH resonance appears at δ 7.73 (CH resonances δ 2.8–4.0). In D_2O, principal resonances occur at δ 2.70, 2.81, 2.97, 3.31, 3.39, 3.46, and 3.58. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ −4.7, −10.8, −11.1.

Fraction 5 [Co(CLHOsar)]Cl$_3$ (26%). Anal. Calcd for $CoC_{14}H_{31}N_6Cl_4O{\cdot}H_2O$: Co, 11.37; C, 32.45; H, 6.42; N, 16.22; Cl, 27.37. Found: Co, 11.53; C, 32.73; H, 6.22; N, 16.28; Cl 27.68. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 474 nm, 148 M^{-1} cm^{-1}; 344.5 nm, 127 M^{-1} cm^{-1}. ^{1}H NMR: In 36% DCl, a single NH resonance appears at δ 7.56 (CH resonances δ 2.6–4.0). In D_2O, principal resonances appear at δ 2.43, 2.56, 2.70, 2.84, 2.97, 3.10, 3.30, 3.37, 3.45, and 3.57. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ +5.0, −4.6, −10.7, and −11.5.

Fraction 6 [Co(diHOsar)]Cl$_3$ (1.5%). Anal. Calcd. for $CoC_{14}H_{32}N_6Cl_3O_2{\cdot}{}^1/_2H_2O$: Co, 12.01; C, 34.27; H, 6.78; N, 17.15; Cl, 21.68. Found: Co, 12.19; C, 34.09; H, 6.38; N, 16.86; Cl, 21.73. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 474 nm, 146 M^{-1} cm^{-1}; 344 nm, 129 M^{-1} cm^{-1}. ^{1}H NMR: In 36% DCl, a single NH resonance appears at δ 7.5 (CH resonances δ 2.6–3.8). In D_2O, principal resonances appeared at δ 2.44, 2.57, 2.66, 2.74, 3.11, 3.23, 3.28, 3.37. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ +6.1, −10.7, and −11.8. (Note that any "yellow" material not clearly separated out in the initial Dowex 50 WX2 chromatography appeared as a seventh band trailing well behind the "orange" materials on SP Sephadex.)

"Yellow" Complexes. As the spectroscopic properties of the yellow complexes suggested (see discussion) that they were products of molecular rearrangements, leading to a change in the cap structure of the cage ligands, we have used the trivial basic name "absar" to describe the new cage produced, i.e., 3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane.

Chromatography under exactly the same conditions as used for the orange complexes provided four components, though the second and third were only efficiently separated with the use of a considerably larger column. To avoid this more extensive chromatography, however, it proved simpler to take the second and third bands as one fraction from SP Sephadex and to rechromatograph this material on H^+ Dowex 50 WX2 with 3 M HCl eluant. This produced a rapid and effective separation, though the order of elution was inverted from that on SP Sephadex/0.1 M Na_2HPO_4. Again, the crystalline materials finally obtained were weighed to provide a crude estimate of the product distribution.

Fraction 1 [Co((Clme)NOabsar)]Cl$_3$ (~20%). The complex was crystallized from water by addition of acetone as thin, golden flakes. Anal. Calcd for $CoC_{14}H_{30}N_7Cl_4O_2{.}2.5H_2O$: Co, 10.27; C, 29.29; H, 6.14; N, 17.08; Cl, 24.70. Found: Co, 10.52; C, 29.34; H, 5.52; N, 16.80; Cl, 24.85. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 459 nm, 189 M^{-1} cm^{-1}; 335 nm, 179 M^{-1} cm^{-1}. ^{1}H NMR: In 36% DCl, four NH resonances of relative area 1:3:1:1 were observed at δ 6.6, 6.9, 7.4, and 8.0, respectively. CH resonances between δ 2.9 and 4.4 were poorly resolved except for a sharp peak at δ 4.10. In D_2O after N deuteration a well-resolved but complex pattern of CH resonances was observed, a very sharp, strong peak at δ 3.79 in this medium being the most obvious feature. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ +19.6, +5.5, −6.4, −7.0, −8.6, −11.2, −13.3, −14.28, −14.5, −14.7, −15.8, −20.80, −24.6.

Fraction 2 [Co((Clme)Clabsar)]$^{3+}$ (~60%). The chloride salt was crystallized as clusters of broad yellow needles by addition of acetone to its aqueous solution. Golden needles of the nitrate salt were readily deposited by addition of HNO_3 to a solution of the chloride, and this relatively low solubility of the nitrate distinguished this "yellow" complex from the others. Anal. Calcd for $CoC_{14}H_{30}N_6Cl_5{\cdot}2H_2O$: Co, 10.63; C, 30.32; H, 6.18; N, 15.15; Cl, 31.96. Found: Co, 10.67; C, 30.68; H, 5.79; N, 15.24; Cl, 32.59. Calcd for $CoC_{14}H_{30}N_9Cl_2O_9$: Co, 9.85; C, 28.11; H, 5.05; N, 18.73. Found: Co, 9.49; C, 28.95; H, 5.34; N, 19.20. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 458 nm, 185 M^{-1} cm^{-1}; 335 nm, 176 M^{-1} cm^{-1}. ^{1}H NMR: In 36% DCl, four NH resonances, relative areas 1:3:1:1, were seen at δ 6.4, 7.0, 7.3, and 8.0, respectively. Again, the most prominent feature of the CH resonances was a strong, sharp peak at δ 4.06 in DCl and 3.78 in D_2O. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ +5.6, −5.2, −6.1, −7.0, −7.8, −8.3, −8.52, −10.5, −13.6, −13.8, −14.8, −15.3, −21.2, −24.5.

Fraction 3 [Co((Clme)HOabsar)]Cl$_3$ (~17%). The complex was crystallized as clusters of thin, golden needles by addition of acetone to its aqueous solution. Anal. Calcd for $CoC_{14}H_{31}N_6Cl_4O.2.5H_2O$: Co, 10.81; C, 30.84; H, 6.66; N, 15.41; Cl, 26.01. Found: Co, 10.86; C, 31.00; H, 6.80; N, 15.44; Cl, 26.46. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 459 nm, 191 M^{-1} cm^{-1}; 335.5 nm, 179 M^{-1} cm^{-1}. ^{1}H NMR: In 36% DCl, four NH resonances appeared at δ 6.4, 6.7, 7.2, and 7.9 and again a very strong sharp CH resonance stood out at δ 4.07 (3.83 in D_2O). ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ +6.4, +5.2, −6.4, −7.0, −8.3, −8.5, −8.7, −11.3, −13.5, −14.3, −14.7, −15.7, −21.1, −24.5.

Fraction 4 [Co(AM(Clme)absarH)]Cl$_4$ (<3%). The complex was crystallized as thin, yellow flakes by addition of acetone to its aqueous solution. Insufficient material was obtained for complete spectroscopic characterization. Anal. Calcd for $CoC_{14}H_{33}N_7Cl_5{\cdot}2H_2O$: Co, 10.31; C, 29.11; H, 6.52; N, 17.15; Cl, 31.81. Found: Co, 10.41; C, 30.34; H, 6.46; N, 16.19; Cl, 29.84. ^{1}H NMR: In D_2O, after N deuteration, a well-resolved complex set of CH resonances appeared in the range δ 2.6–4.0, with two very strong, sharp resonances at δ 2.64 and 3.84 standing out. Although accurate separate integration of these two peaks was not possible, the δ 2.64 resonance did appear considerably stronger than that at δ 3.84. ^{13}C NMR: The spectrum was recorded in D_2O, pH 6, corresponding to conditions where the deprotonated, 3+ complex was present, since the resonances were then better separated; relative to dioxane, δ +5.3, −5.7, −6.9, −7.4, −9.1, −10.5, −10.7, −14.3, −14.6, −15.5, −16.9, −22.3, −26.0, −39.2.

Dechlorination of Co(diCLsar)$^{3+}$. Various procedures were examined as a means of converting Co(diCLsar)$^{3+}$ to the "parent" encapsulated complex Co(sar)$^{3+}$. Treatment with Zn dust was found to be most effective, though use of a large excess was necessary as the Zn appeared to lose activity during the reaction. The procedure was also not highly efficient and chromatographic separation of reaction products was essential. Zn dust (5 g) was added to a solution of [Co(diCLsar)]Cl$_3$ (0.5 g) in water (50 mL) and the mixture boiled under N_2 for 30 min. The excess Zn was filtered off and the filtrate treated with H_2O_2 (100 vol, 0.5 mL) and HCl (12 M, 1 mL) to reconvert the complexes to their Co(III) forms. The solution was diluted and absorbed on H^+ Dowex 50 WX2 cation exchange resin and the yellow Co(III) complexes recovered by elution with 3 M HCl. The eluate was taken to dryness under vacuum and the residue chromatographed on Na^+ SP Sephadex C25 with 0.1 M Na_2HPO_4. Three principal orange bands were seen and the complexes in them were recovered and characterized. Fraction 1 proved to be unreacted Co(diCLsar)$^{3+}$.

Fraction 2 [Co(CLsar)]Cl$_3$. The complex crystallized as orange plates on addition of acetone to its aqueous solution (yield 0.15 g). Anal. Calcd for $CoC_{14}H_{31}N_6Cl_4{\cdot}2H_2O$: Co, 11.33; C, 32.32; H, 6.01; N, 16.15; Cl, 27.26. Found: Co, 11.94; C, 32.30; H, 6.39; N, 15.83; Cl, 27.55. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 472 nm, 137 M^{-1} cm^{-1}; 345 nm, 121 M^{-1} cm^{-1}. ^{1}H NMR: In 1 M DCl, two barely resolved NH resonances at δ 6.95 and 7.18 were apparent. In D_2O, the N-deuterated complex showed a pattern of at least 14 sharp CH resonances between δ 2.4 and 3.7. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ −5.0, −11.0 (on expanded scale this peak showed evidence of splitting near the limit of instrumental resolution), −16.6, −27.6. In the off-resonance ^{1}H-decoupled spectrum, the δ −27.6 peak became a doublet and the −5.0 peak was unaffected. The δ −11.0 and −16.6 peaks both became triplets.

Fraction 3 [Co(sar)]Cl$_3$. The complex crystallized as orange-yellow needles on addition of acetone to its aqueous solution (yield 0.15 g). Anal. Calcd for $CoC_{14}H_{32}N_6Cl_3{\cdot}1.5H_2O$: Co, 12.36; C, 35.27; H, 7.40; N, 17.63; Cl, 22.31. Found: Co, 12.80; C, 35.62; H, 6.84; N, 17.35; Cl, 22.62 Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 471 nm, 135 M^{-1} cm^{-1}; 343 nm, 108 M^{-1} cm^{-1}. ^{1}H NMR: In 1 M DCl, a symmetrical single NH resonance appeared at δ 6.68. In D_2O, the N-deuterated complex showed resonances at δ 2.52, 2.59, 2.70, 2.80 (weak), 3.14, and 3.26. ^{13}C NMR: Broad-band ^{1}H-decoupled spectrum in D_2O, dioxane reference, δ −11.0, −16.3, −27.7. In the off-resonance ^{1}H-decoupled spectrum, the δ −11.0 and −16.3 peaks became triplets and the δ −27.7 peak a doublet.

[Co(MENOsar)]Cl$_3$. A solution of [Co(sen)]Cl$_3$ ("sen" = $CH_3C(CH_2NHCH_2CH_2NH_2)_3$) (1.0 g), CH_3NO_2 (1.5 g), 37% HCHo solution (10 g), and Na_2CO_3 (0.5 g) in water (50 mL) was left standing at room temperature for 2 h. Monitoring of the progress of the reaction by chromatography on a microcolumn of SP Sephadex C25 (Na^+ form), with 0.05 M sodium citrate as eluant, showed that in this time all the reactant complex had been converted into a new yellow species plus a trace of Co^{2+}. Hence, reaction was quenched by addition of CH_3CO_2H and the solution diluted and absorbed on H^+ Dowex 50 WX2. The column was washed with water and then eluted with 1 M HCl to remove Co^{2+}. The yellow product was rapidly removed with 3 M HCl and the eluate taken to dryness under vacuum. The residue was crystallized from water by addition of acetone to give fine, yellow needles (0.9 g). Anal. Calcd for $CoC_{15}H_{33}N_7O_2Cl_3$: Co, 11.61; C, 35.48; H, 6.55; N, 19.31; Cl, 20.95. Found: Co, 11.52; C, 35.46; H, 6.61; N, 18.65; Cl. 20.79.

Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 472 nm, 135 M^{-1} cm^{-1}; 344 nm, 117 M^{-1} cm^{-1}. ^1H NMR: In 1 M DCl, an unsymmetrical NH resonance appeared at δ 7.1. In D_2O, CH resonances between δ 2.2 and 4.0 were again complex though well resolved. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, dioxane reference, δ +19.8, −10.9, −11.3, −14.5, −22.5, −44.6.

[Co(AMMEsarH)]Cl_4. The conversion of [Co(MENOsar)]Cl_3 to [Co(AMMEsarH)]Cl_4 was achieved in a manner completely analogous to that used to convert [Co(diNOsar)]Cl_3 to [Co(diMAsarH$_2$)]Cl_5. The product complex was crystallized from 1 M HCl by addition of ethanol as thin golden needles. Anal. Calcd for $CoC_{15}H_{36}N_7Cl_4 \cdot {}^1/_2H_2O$: Co, 11.24; C, 34.37; H, 7.11; N, 18.70; Cl, 27.05. Found: Co, 10.96; C, 34.36; H, 6.89; N, 18.65; Cl, 26.91. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 472 nm, 139 M^{-1} cm^{-1}; 345 nm, 123 M^{-1} cm^{-1}. ^1H NMR: In 1 M DCl, a single NH resonance appeared at δ 6.88. In D_2O (after N deuteration) a complex and concentration dependent but well-resolved pattern of C–H resonances appeared at δ 2.2–3.8 along with a sharp CH_3 resonance at δ 0.98. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, dioxane reference, δ −9.7, −10.8 −11.6, −14.5, −22.6, −44.7.

Nitrosation of Co(AMMEsar)$^{3+}$. This experiment was conducted under conditions identical with of used for the Co(diAMsar)$^{3+}$ nitrosation and gave closely similar, though simpler results. Thus, chromatography of the whole nitrosation products on Na^+ SP Sephadex C25 with 0.1 M Na_2HPO_2 eluant revealed three "orange" bands trailed by a single "yellow" band. The first orange band, present as a very minor component, proved to be Co(MENOsar)$^{3+}$, but the remaining bands contained new species.

Fraction 2 (Orange) [Co(CLMEsar)]Cl_3 (~70% of Product). The complex was crystallized from water by addition of acetone to give lustrous, yellow plates which effloresced on being washed with acetone and ether at the filter. Anal. Calcd for $CoC_{15}H_{33}N_6Cl_4 \cdot H_2O$: Co, 11.42; C, 34.90; H, 6.83; N, 16.28; Cl, 27.47. Found: Co, 11.12; C, 34.63; H, 6.89; M, 15.89; Cl, 27.27. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 472 nm, 143 M^{-1} cm^{-1}; 344 nm, 122 M^{-1} cm^{-1}. ^1H NMR: In 1 M DCl, an unsymmetrical NH resonance appeared at δ 6.0. In D_2O, the CH resonances were again well resolved but complex. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, dioxane reference, δ −5.0, −11.5, −12.2, −24.0, −47.3.

Fraction 3 (Orange) [Co(HOMEsar)]Cl_3 (~20%). The complex was crystallized from water by addition of acetone to give shiny, yellow flakes. Anal. Calcd for $CoC_{15}H_{34}N_6OCl_3 \cdot H_2O$: Co, 11.84; C, 36.19; H, 7.29; N, 16.88; Cl, 21.37. Found: Co, 11.83; C, 36.05; H, 6.72; N, 16.59; Cl, 21.77. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 472 nm, 143 M^{-1} cm^{-1}; 344 nm, 124 M^{-1} cm^{-1}. ^1H NMR: In 1 M DCl, a single NH resonance appeared at δ 6.9. In D_2O, the CH resonances were complex but the complex was characterized by a very sharp, strong singlet at 2.74. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, dioxane reference, δ 6.3, −11.6, −11.9, −12.1, −12.4, −24.2, −47.5.

Fraction 4 (Yellow) [Co((Clme)MEabsar)]Cl_3 (~10%). The complex was crystallized from water by addition of acetone to give bright yellow, thin plates. Anal. Calcd for $CoC_{15}H_{33}N_6Cl_4 \cdot 2H_2O$: Co, 11.03; C, 33.71; H, 6.98; N, 15.72; Cl, 26.53. Found: Co, 10.80; C, 34.10; H, 7.03; N, 15.62; Cl, 26.32. Visible spectrum—λ_{max}, ϵ_{max} in 0.1 M HCl: 458 nm, 164 M^{-1} cm^{-1}; 334 nm, 170 M^{-1} cm^{-1}. ^1H NMR: In 1 M DCl, two NH resonances appeared at δ 6.22 and 6.56. As with the "yellow" complexes derived from Co(diAmsar)$^{3+}$ a strong resonance at δ 3.78 stood out from the multiple CH peaks. ^{13}C NMR: Broad-band ^1H-decoupled spectrum in D_2O, dioxane reference, δ +5.3, −6.8, −7.5, −8.4, −8.7, −9.1, −12.1, −14.4, −15.1, −15.6, −16.5, −22.5, −23.9, −25.9, −46.9.

Results and Discussion

Structure of the Complexes. Direct evidence of the encapsulated form of the complexes was obtained from the crystal structure of the N-deprotonated species [Co(diNOsar-H)]Cl_2. This complex was chosen for structural investigation not only to establish whether or not encapsulation had been achieved but also to characterize for the first time an N-deprotonated Co(III) amine complex, such species being, of course, considered intermediates in base-catalyzed ligand loss from all Co(III) acido primary or secondary amine complexes.[11]

Crystal Data. Crystals of [Co^{III}(diNOsar-H)]$Cl_2 \cdot 4H_2O$ were grown by diffusion of ethanol into an aqueous solution of the complex adjusted to a pH above 10. The crystals were orthorhombic blocks elongated along c and showing the forms (110). Precession photographs defined the space group uniquely as $P2_12_12_1$. A crystal with dimensions 0.08 × 0.16 × 0.4 mm was mounted about c and lightly coated with epoxy resin. The cell constants at 20 °C were obtained from axial reflections by ω-(h00,0k0) and μ(00l) scans on a Stoe Weissenberg diffractometer using Mo Kα radiation and a graphite monochromator. The cell constants are a = 10.821 (5) Å, b = 15.929 (8) Å, and c = 14.259 (10) Å, and U = 2457.8 Å^3. The observed density is 1.579 g cm^{-3}, and the calculated value for four water molecules (Z = 4) is 1.554. Intensity data were collected for the levels $hk0$ to $hk11$ in the range 3° < 2θ < 50° with use of the ω-scan technique. Corrections were applied for Lorentz and polarization effects, but not for absorption (μ = 9.6 cm^{-1}), to give 2423 nonzero structure factors with $I > 2.5\sigma I$ and 488 with $I < 2.5\sigma I$.

Solution and Refinement.[12] The structure was solved by Patterson methods and refined by blocked full-matrix least-squares methods. Scale factors for the individual data levels were adjusted during the isotropic phase of the refinement which incorporated the cation hydrogen atoms at their calculated positions. In the anisotropic phase of the refinement, the positional parameters and the thermal parameters were refined alternately. The positions of all the water hydrogens were located and included, but their parameters were not refined. Unit weights were employed throughout, and this scheme was checked by plotting $(|F_o| - |F_c|)^2$ averaged in ranges of $|F_o|$ vs. $|F_c|$. It was evident that the very weak and very strong reflections had received weights that were relatively too large; the range of ΔF^2 values was 1.5–4.0 except for the two terminal ranges. The error in an observation of unit weight was 1.38 from the final coordinate refinement block. The final R factor was 0.048 for 2423 nonzero reflections. The absolute configuration was checked by reversing the signs of the $\Delta f''$ terms and repeating the final refinement sequence to give the significantly higher R value of 0.056. The final difference map shows no peaks larger than 0.5 e/Å^3 which is the height of a typical hydrogen peak in the earlier difference maps.

The Co^+ scattering factor and those for O, N, and C were taken from International Tables[13] while for Cl^- the values of Doyle and Turner[14] were used. For hydrogen the values of Stewart et al.[15] were taken. Values of the anomalous components $\Delta f'$ and $\Delta f''$ in the scattering factors of Co (0.299 and 0.973) and Cl (0.132 and 0.159) were acquired from Cromer and Liberman.[16] Table I contains the final non-hydrogen atomic parameters, and Table II has the crystal geometry.

Description of the Structure. Figures 1 and 2 show sideways and end-on views of the structure. The complex is similar to that of [Co(sepulchrate)]$^{3+}$,[1] which differs from the present structure by having only N instead of C-NO_2 caps. Figure 2 shows that the conformations of the ethylenediamine rings are "ob" rather than "lel" as found in the [Co(sep)]$^{3+}$ complex.[1] This conformational difference is predicted by molecular mechanics and discussed in the next section. With respect to the disposition of the en-derived chelate rings about Co(III), the absolute configuration is Λ, showing that, as with Co(sep)$^{3+}$, the configuration about Co is retained in the synthesis from Co(en)$_3^{3+}$.

Table II shows that deprotonation of N(6) has a significant shortening effect on the Co–N(6) bond to 1.946 (7) Å and a concomitant lengthening of the *trans*-Co–N(1) bond to 2.016 (7) Å. These distances are respectively 0.042 Å shorter and 0.028 Å longer than the mean of the four other distances, 1.974 Å, itself close to the value of 1.990 (3) Å for [Co^{III}(sep)]$Cl_3 \cdot H_2O$.[1,4] The other bond distances to N(6), C(10)–N(6) = 1.468(12) Å and

(11) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; 2nd ed.; Wiley: New York, 1967; pp 182–192.

(12) In addition to local programs for the University of Adelaide CDC6400, the following programs or modifications were used: Zalkin's FORDAP Fourier program; FUORFLS, a modification by Taylor of Busing, Martin, and Levy's ORFLS program; ORFEE, a function and error program by Busing, Martin, and Levy; Blount's geometry program BLANDA; Johnson's ORTEP, a thermal ellipsoid plot program.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III.

(14) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390–397.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3186.

(16) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

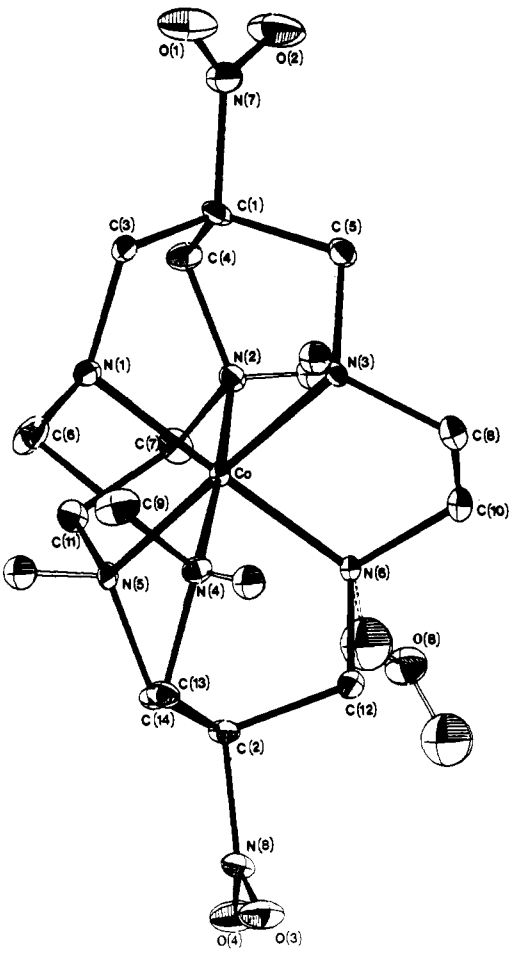


Figure 1. The complex ion $[Co^{III}(diNOsar\text{-}H)]^{2+}$ and its hydrogen bonded atoms. Hydrogens omitted from ORTEP plot with 50% probability ellipsoids.

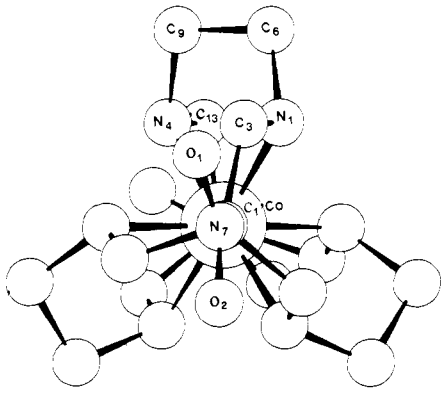


Figure 2. The complex ion $[Co^{III}(diNOsar\text{-}H)]^{2+}$ viewed end on.

C(12)–N(6) = 1.465(10) Å, are also shortened compared to the mean, 1.496 Å, of the other C–N bonds in this structure. A deprotonated amine nitrogen of this kind might be expected to flatten if not constrained by the cage structure. The bond angles at N(6) remain close to tetrahedral values, however, and are slightly smaller than the values at the other nitrogens. The nitrogen is involved in a hydrogen bond to the water molecule at O(8). The bond length for this $N^{-}\cdots H\text{--}OH$ system at 2.816 Å is a little shorter than a typical $N\text{--}H\cdots OH_2$ system in this (e.g. $O(7)\cdots N(2)$, 2.883 Å) structure and comparable to $N\text{--}H\cdots O^{-}\text{--}$ systems near 2.85 Å.[17] The hydrogen atom in this hydrogen bond was located giving $N(6)\cdots H$ = 1.88 Å and N(6)--H--O(8) = 156°.

Molecular Mechanics Calculations. The potential conformational isomerism of $[Co(diNOsar)]^{3+}$ arises from two sources: the relative orientations of the two $NO_2\text{–}C(CH_2\text{–})_3$ caps and the orientations of the C–C vectors of the "en" rings. By analogy with $[Co(sep)]^{3+}$, three possible conformations are designated D_3lel$_3$, C_3lel$_3$, and D_3ob$_3$[1,4] where the first term refers to the overall symmetry of the complex excluding the NO_2 group and the second to the orientation of the C–C vector parallel to (lel) or oblique to (ob) the cap-to-cap axis of the complex. While the nitro groups of the diNOsar ligand prevent the attainment of strict D_3 or C_3 symmetries, the same basic cage conformations are expected irrespective of the substituent.

In the two structures of $[Co(sep)]^{3+}$ which have been reported[1,4,18] the D_3lel$_3$ conformation has been observed while in the present structure the geometry approximates D_3ob$_3$. In order to seek an explanation for this difference, all three conformers of $[Co(diNOsar)]^{3+}$ were subjected to energy minimization analysis. The method and force field used have been described previously[19] and have been successfully used in the study of a number of systems.[17,20,21] Additions to the force field necessary for the modeling of the nitro groups were developed for the present study and have been tested by application to a similar complex [Co(NOsartacn)]$^{3+}$.[22] The energy minimized is $U_{total} = \sum E_b + \sum E_{nb} + \sum E_\theta + \sum E_\phi$ where these sums are the bond-length, nonbonded, valence angle, and torsion angle deformation energies, respectively.

Each of the three conformers refined easily to a true potential energy minimum; and the final strain energy terms are listed in Table III. From these values it can be seen that the most stable conformer is the D_3ob$_3$, in accord with the observation of this geometry in the present structure. The relative stabilization of

Table I. Positional Parameters[a] for $[Co^{III}(diNOsar\text{-}H)]Cl_2\cdot 4H_2O$

atom	*x*	*y*	*z*
Co	5431 (9)	2137 (6)	6718 (9)
Cl(1)	3383 (3)	1240 (2)	2880 (2)
Cl(2)	2136 (2)	1445 (2)	−2144 (2)
N(1)	1618 (6)	588 (4)	−57 (6)
N(2)	−982 (6)	−378 (4)	281 (6)
N(3)	686 (6)	−493 (4)	180 (5)
N(4)	2099 (6)	799 (4)	981 (5)
N(5)	388 (6)	936 (4)	−443 (5)
N(6)	−470 (6)	975 (4)	1412 (5)
N(7)	72 (8)	−2584 (5)	739 (7)
N(8)	909 (7)	2998 (4)	762 (7)
C(1)	230 (7)	−1631 (4)	664 (8)
C(2)	833 (7)	2040 (4)	681 (8)
C(3)	1557 (8)	−1466 (5)	309 (7)
C(4)	−751 (8)	−1267 (5)	5 (8)
C(5)	37 (9)	−1322 (5)	1681 (7)
C(6)	289 (8)	−231 (7)	−124 (9)
C(7)	−1609 (7)	138 (6)	−477 (7)
C(8)	2200 (9)	18 (6)	2644 (8)
C(9)	3163 (7)	277 (6)	698 (10)
C(10)	−838 (8)	557 (6)	2286 (8)
C(11)	−624 (9)	561 (5)	−1065 (7)
C(12)	180 (8)	1765 (5)	1593 (8)
C(13)	2153 (7)	1682 (5)	641 (8)
C(14)	74 (8)	1826 (5)	−193 (7)
O(1)	982 (8)	−3016 (4)	768 (8)
O(2)	−953 (8)	−2847 (4)	851 (8)
O(3)	1734 (7)	3301 (4)	1239 (6)
O(4)	91 (7)	3404 (4)	410 (6)
O(5)	−149 (9)	2089 (5)	−3500 (9)
O(6)	−923 (8)	−694 (6)	−2958 (9)
O(7)	−1876 (8)	775 (6)	−3601 (9)
O(8)	−2708 (6)	1816 (4)	1049 (6)

[a] All $\times 10^4$.

(17) Hambley, T. W.; Hawkins, C. J.; Martin, J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 2505–2523.
(18) Dubicki, L.; Ferguson, J.; Geue, R. J.; Sargeson, A. M. *Chem. Phys. Lett.* **1980**, *74*, 393–397.
(19) Hambley, T. W.; Hawkins, C. J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 45–56.
(20) Hambley, T. W.; Hawkins, C. J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 2525–2542.
(21) Hambley, T. W.; Searle, G. H.; Snow, M. R. *Aust. J. Chem.*, in press.
(22) Hambley, T. W.; Snow, M. R.; Taylor, S. G., unpublished results, NOsartacn = 1,4,7,11,14,19-hexaaza-9-nitrotricyclo[7.7.4.2^{4,14}]docosane.

Table II. Interatomic Distances (Å) and Angles (deg) for $[Co^{III}(diNOsar\text{-}H)]Cl_2\cdot 4H_2O$

(a) Bond Lengths			
Co–N(1)	2.016 (7)	N(1)–C(6)	1.493 (11)
Co–N(2)	1.980 (7)	N(2)–C(7)	1.519 (11)
Co–N(3)	1.967 (7)	N(3)–C(8)	1.510 (13)
Co–N(4)	1.975 (7)	N(4)–C(9)	1.477 (11)
Co–N(5)	1.975 (7)	N(5)–C(11)	1.492 (11)
Co–N(6)	1.946 (7)	N(6)–C(10)	1.468 (12)
C(1)–C(3)	1.546 (12)	C(6)–C(9)	1.455 (16)
C(1)–C(4)	1.535 (12)	C(7)–C(11)	1.514 (13)
C(1)–C(5)	1.545 (15)	C(1)–N(7)	1.530 (10)
C(2)–C(12)	1.544 (14)	N(7)–O(1)	1.203 (10)
C(2)–C(13)	1.540 (10)	N(7)–O(2)	1.200 (10)
C(2)–C(14)	1.532 (14)	N(8)–O(3)	1.221 (10)
N(1)–C(3)	1.494 (10)	N(8)–O(4)	1.205 (10)
N(2)–C(4)	1.491 (10)	N(8)–C(2)	1.533 (9)
N(3)–C(5)	1.506 (10)		
N(4)–C(13)	1.487 (10)		
N(5)–C(14)	1.490 (9)		
N(6)–C(12)	1.465 (10)		
(b) Bond Angles			
O(1)–N(7)–O(2)	123.6 (8)	C(3)–N(8)–O(4)	123.8 (7)
O(1)–N(7)–C(1)	118.6 (8)	C(2)–N(8)–O(3)	118.3 (8)
O(1)–N(7)–C(1)	117.4 (8)	C(2)–N(8)–O(4)	117.6 (8)
N(7)–C(1)–C(3)	107.2 (7)	C(12)–C(2)–C(13)	110.5 (8)
N(7)–C(1)–C(4)	109.9 (7)	C(12)–C(2)–C(14)	112.1 (6)
N(7)–C(1)–C(5)	103.6 (8)	C(14)–C(2)–C(13)	112.6 (8)
C(5)–C(1)–C(3)	112.2 (8)	C(13)–C(2)–N(8)	108.8 (6)
C(4)–C(1)–C(5)	111.2 (8)	C(14)–C(2)–N(8)	108.2 (7)
C(4)–C(1)–C(3)	112.2 (8)	C(12)–C(2)–N(8)	104.1 (8)
C(1)–C(3)–N(1)	108.4 (6)	C(2)–C(13)–N(4)	107.6 (6)
C(1)–C(4)–N(2)	108.2 (7)	C(2)–C(14)–N(5)	107.7 (6)
C(1)–C(5)–N(3)	108.8 (7)	C(2)–C(12)–N(6)	108.4 (7)
C(5)–N(3)–C(8)	111.9 (7)	C(9)–N(4)–C(13)	114.4 (7)
C(4)–N(2)–C(7)	113.6 (7)	C(11)–N(5)–C(14)	112.9 (7)
C(3)–N(1)–C(6)	114.8 (7)	C(10)–N(6)–C(12)	111.7 (5)
N(1)–C(6)–C(9)	110.3 (8)	C(6)–C(9)–N(4)	112.1 (8)
N(2)–C(7)–C(11)	108.7 (7)	C(7)–C(11)–N(5)	110.3 (7)
N(3)–C(8)–C(10)	106.2 (7)	C(8)–C(10)–N(6)	110.1 (7)
C(3)–N(1)–Co	112.8 (6)	C(13)–N(4)–Co	114.0 (5)
C(4)–N(2)–Co	112.8 (5)	C(14)–N(5)–Co	112.5 (6)
C(5)–N(3)–Co	112.0 (6)	C(12)–N(6)–Co	111.1 (5)
N(1)–Co–N(4)	85.6 (4)	C(10)–N(6)–Co	109.3 (5)
N(2)–Co–N(5)	87.4 (4)		
N(3)–Co–N(6)	87.3 (4)		
(c) Hydrogen Bonds			
Cl(1)····N(4)	3.122	O(8)····O(6)[d]	2.720
Cl(1)····N(1)[a]	3.120	O(7)····N(12)[e]	2.883
Cl(1)····O(6)[a]	3.120	O(5)····O(7)	2.810
Cl(1)····O(5)[b]	3.223	O(6)····O(7)	2.717
Cl(2)····N(3)[a]	3.183	N(6)····O(8)	2.816
Cl(2)····N(5)	3.213	O(3)····O(8)[f]	3.323
Cl(2)····O(5)	3.303	O(4)····O(8)[f]	3.182
Cl(2)····O(8)[c]	3.183		

[a-f] Atomic transforms: (a) $^1/_2 - x, -y, -^1/_2 + z$; (b) $-^1/_2 + x, ^1/_2 - y, -z$; (c) $^1/_2 + x, ^1/_2 - y, -z$; (d) $-^1/_2 - x, -y, ^1/_2 + z$; (e) $-^1/_2 - x, -y, -^1/_2 + z$; (f) $-^1/_2 + x, ^1/_2 - y, -z$.

Table III. Minimized Strain Energies of the $[Co(diNOsar)]^{3+}$ Conformers (kJ mol^{-1})

	E_b	E_{nb}	E_θ	E_ϕ	U_{total}	relative U
D_3lel_3	19.4	60.2	23.9	37.7	141.5	3.9
C_3lel_3	19.7	59.9	23.9	37.7	141.2	3.6
D_3ob_3	15.4	61.2	18.5	42.5	137.6	0

the D_3ob_3 geometry arises from increased valence angle deformation terms in the lel_3 conformations, and these are primarily due to distortions in the C–N–C angles. These results are in contrast to some obtained for $[Co(sep)]^{3+}$ which can show[23] a reversed stability order arising from a reversal in the relative contributions of the valence angle deformation terms (again associated with the C–N–C angles). Thus, the observation of the D_3ob_3 conformation in the present structure is explicable in terms of steric causes.

(23) Hambley, T. W.; Snow, M. R., unpublished results.

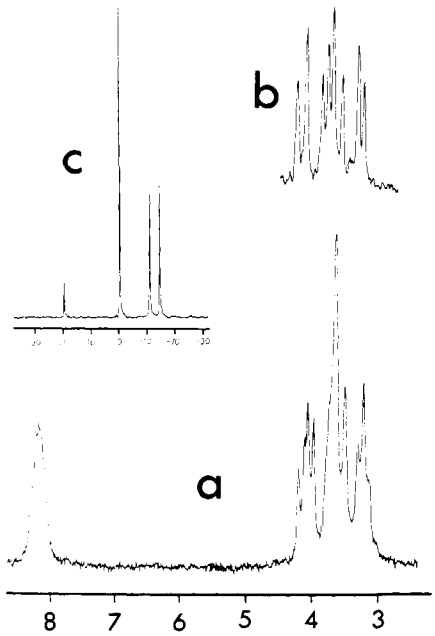


Figure 3. Nuclear magnetic resonance spectra of $Co(diNOsar)^{3+}$: (a) ^1H spectrum in 36% DCl; (b) ^1H spectrum in D_2O after N deuteration; and (c) broad-band proton-decoupled ^{13}C spectrum in D_2O, dioxane reference (0 ppm).

Since this work was completed, the structure of $[Co(diNOsar)]Cl_3\cdot 2H_2O$ has been determined by L. M. Engelhardt and A. H. White (private communication). They have found the D_3lel_3 configuration in contradiction to the prediction here. However, the lattice also contains an extensive H-bonding network, and the D_3lel_3 configuration better accommodates the three pairs of N–H atoms hydrogen bonded to the three Cl^- ions than does the D_3ob_3 configuration.

General Spectroscopic Characteristics. Since most of the presently described complexes are derived chemically from $Co(diNOsar)^{3+}$ and those which are not were prepared by methods essentially identical with those used to prepare $Co(diNOsar)^{3+}$ and its derivatives, all are assumed to be encapsulated species. This conclusion is, however, very strongly supported by both the spectroscopic and chemical properties of all. In particular, ^1H and ^{13}C nuclear magnetic resonance spectra clearly define the complex ion symmetry in most cases. The ^1H NMR spectrum of N-deuterated $Co(diNOsar)^{3+}$ (Figure 3) is very similar to that of $Co(sep)^{3+}$, and this and the simple three-resonance $^{13}C\{^1H\}$ spectrum is consistent with D_3 symmetry for the complex in solution, as expected for the encapsulated structure. The single NH resonance observed for the complex in acid solution is also consistent with D_3 symmetry, though this resonance is, of course, rather broad, and other evidence (see below) suggests that NH resonances are not always specially sensitive to changes in complex ion symmetry.

Aside from chemical shift differences, the nuclear magnetic resonance spectra of $Co(sar)^{3+}$ and all its 1,8 symmetrical derivatives $Co(X_2sar)$ are closely similar, though the ^1H spectrum of $Co(sar)^{3+}$ would be expected to differ from those of its derivatives due to the presence of its two "terminal" protons, and it is possible that a higher resolution spectrum would show such differences more clearly. Certainly the >CH groups of $Co(sar)^{3+}$ are clearly revealed in the off-resonance $^{13}C\{^1H\}$ spectrum by the appearance of a high-field double (Figure 4). ^{13}C spectra also enable $Co(sar)^{3+}$ and its symmetrical derivatives to be clearly distinguished from the "orange" complexes taken to be unsymmetrical $Co(sar)^{3+}$ derivatives, $Co(X,Ysar)^{3+}$. Although in no case were the six resonances expected for C_3 symmetry of $Co(X,Ysar)^{3+}$ observed, certainly at least four were found for all. Further, observed peak widths and intensities were consistent with

Table IV. ^{13}C NMR Chemical Shifts Relative to 1,4-Dioxane for X– Co –Y^{n+} Complexes

X	Y	X–C (a)	Y–C (a)	CH2–CH2 (b)	X–C(CH2)3 (c)	Y–C(CH2)3 (c)	CH3–C
H	H		−27.7	−11.0		−16.3	
H	Cl	−27.6	−5.0	−11.0	−16.6	−11.0	
CH_3	NO_2	−22.5	+19.8	−10.9	−11.3	−14.5	−44.6
CH_3	NH_3^+	−22.6	−9.7	−10.8	−11.5	−14.5	−44.7
NO_2	NO_2		+20.0	−10.8		−14.4	
NH_3^+	NH_3^+		−10.3	−11.5		−15.6	
OH	OH		+6.1	−10.7		−11.8	
Cl	Cl		−4.7	−10.8		−11.1	
Cl	NO_2	−4.7	+19.9	−10.8	−10.8	−14.4	
Cl	OH	−4.6	+6.0	−10.7	−10.7	−11.5	
OH	NO_2	+6.0	+19.7	−10.9	−11.8	−14.7	

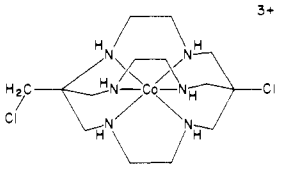
[a] Quaternary carbons and the tertiary carbons of (1) and (2) were identified through off-resonance $^{13}C\{^1H\}$ spectra. Assignments for the unsymmetrical complexes were made on the basis of "characteristic" chemical shifts observed in the symmetrical species. [b] Assignments are based on the essential constancy of chemical shift and the fact that in two unsymmetrical complexes (3 and 11) the peak was considerably more intense than any other. [c] Assignments depend on the correctness of footnote *b* and the assumption that chemical shifts would be characteristic of X and Y.

Table V. Quaternary Carbon Resonances in $Co(X(Clme)absar)^{n+}$ Complexes

X	(X)	(Cl)
NO_2	+20.9	+6.0
Cl	−5.2	+5.6
OH	+6.8	+5.5
$^+NH_3$	−9.1	+6.8
NH_2	−10.5	+5.4

the assumption that the C atoms most distant from X and Y (the en derived carbons) were least differentiated and hence accidentally degenerate in all cases as well as being close to degenerate with one set of "cap" methylene carbons. ^1H spectra were also more obviously complex for Co(X,Ysar) species, though only in $Co(HONOsar)^{3+}$ were two resolved NH resonances seen. A summary of ^{13}C NMR data for $Co(sar)^{3+}$ and its derivatives is given in Table IV.

Table IV shows that the chemical shift of the central "cap" carbon is sensitive to the nature of the terminal substituent but is apparently not greatly affected by other features of the molecular structure, since it is possible to assign resonances in the unsymmetrical complexes' spectra simply by assuming superposition of the spectra of the appropriate symmetrical species. If this is accepted, it is possible to simplify analysis of the spectra of the "yellow" complexes obtained in nitrosation of $Co(diAMsar)^{3+}$. Their ^{13}C spectra clearly show the complete asymmetry of these complexes. A well-resolved resonance is seen for every carbon, and in ^1H spectra this is also evidenced in the complexity of both NH and CH resonances. Since such spectra do not in general reflect the full consequences of the loss in symmetry in conversion of X_2sar to Co(X,Ysar) (see above), it would appear that a fairly drastic change in molecular structure has occurred in generating the "yellow" complexes. This, of course, is also consistent with the ~15-nm shift to shorter wavelengths in the first absorption maximum (of $^1A_{1g} \rightarrow {}^1T_{1g}$ parentage) of the complexes. However, the ^{13}C spectra of the yellow species show (through off-resonance experiments) that two quaternary carbons are present in each and that one may be identified with a "normal" quaternary carbon as found in $Co(X_2sar)$compounds (Table V). This is interpreted as indicating that any structural change involves only one of the molecular "caps", and since for the five forms of the four complexes[24] five different quaternary carbon resonances are seen while the other resonance is essentially constant, the analytical data are taken as indicating that chloride is selectively incorporated in producing a new type of quaternary carbon. If this chloride is directly bound to the new quaternary carbon, however, the ^{13}C chemical shift is well downfield of $Cl-C(CH_2-)_3$ and it implies another electronegative atom, logically N, is also bound. The problem has been resolved by a crystallographic analysis of the $[Co((Clme)Clabsar)](NO_3)_3$ salt which shows that a strained system of type **3** is obtained:



3

The structural details of these complexes along with those of other related systems will be published in a subsequent communication.

The NMR data also imply that chloromethyl derivatives with apical substituents of OH and NO_2 are also generated. The fact that ^1H NMR spectra show NH resonances which can be interpreted as three distinct single-proton peaks plus one (unsymmetrical) three-proton peak is consistent with the rather different environments for the three NH groups of the rearranged cap and the similar environments of the unrearranged cap groups. For the yellow complexes, the sharp resonances in their ^1H NMR spectra near δ 3.8 are logically assigned to the freely rotating CH_2Cl group. These signals may well be characteristic of such rearranged cages.

Syntheses. The synthetic procedure described for $Co(diNOsar)^{3+}$ and $Co(MENOsar)^{3+}$ is an obvious extension of that developed for $Co(sep)^{3+}$,[1,4] with trisubstitution at the reactive carbon of nitromethane occurring instead of that at the nucleophilic N of NH_3. These syntheses were, of course, developed on the basis of an understanding of a macrocycle formation reaction involving Co(III) amine complexes and formaldehyde in aqueous solution.[25] The pathway to $Co(sep)^{3+}$ and the presently described species therefore bears a remarkable parallel with the development of the syntheses of the first-known encapsulated Co(III) complexes.[26-28] A greater variety of chemistry is possible with the sarcophagine systems, however, both because the complexes themselves are in general more stable toward disruption of the cage and because

(24) The fourth "yellow" complex may be obtained readily in both its protonated ($-NH_3^+$) and unprotonated ($-NH_2$) forms. Note that this complex was first taken to be a doubly rearranged species but was subsequently shown to contain an amino group which had not undergone diazotization: Lay, P. A. Ph.D. Thesis, The Australian National University, 1981. The reasons for its presence are obscure.

(25) Geue, R. J.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J.; Taylor, D. J. *J. Chem. Soc., Chem. Commun.* **1976**, 285–287.

(26) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1968**, *90*, 6859–6860.

(27) Jackels, S. C.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1232–1237. See also: Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3500–3502; *Inorg. Chem.* **1971**, *10*, 2472–2478.

(28) As pointed out by the authors in ref 26, their work was partly based on a macrocycle formation reaction reported by: Schrauzer, G. N. *Chem. Ber.* **1962**, *95*, 1438–1445.

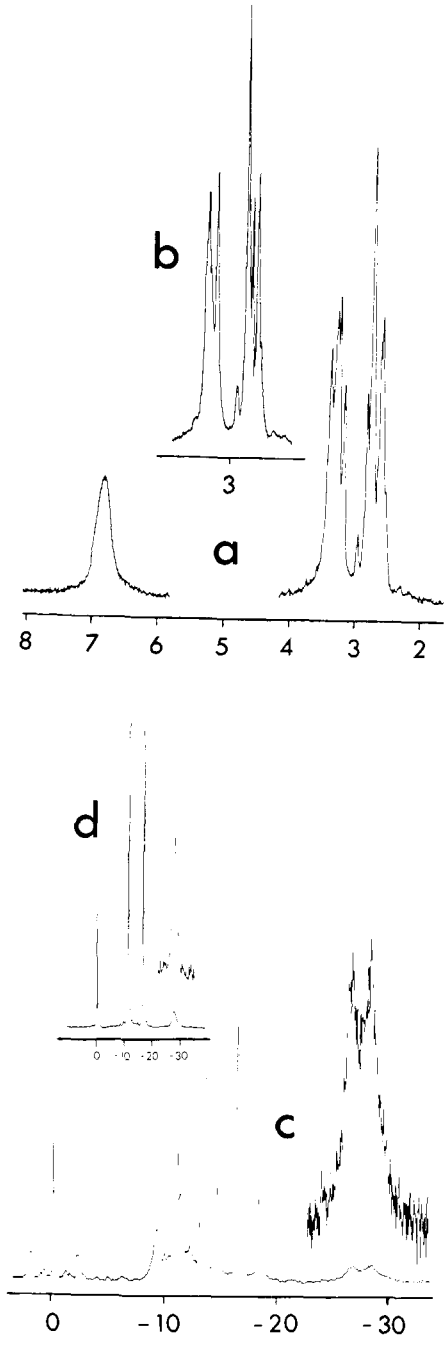


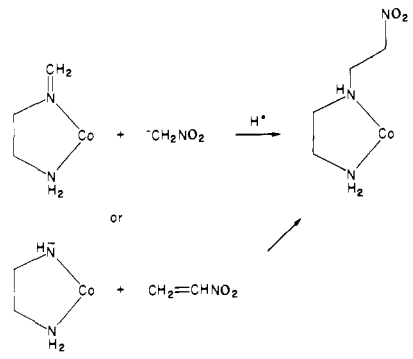
Figure 4. Nuclear magnetic resonance spectra of $Co(sar)^{3+}$: (a) ^1H spectrum in 1 M DCl (HOD peak at δ 5 not shown); (b) (inset) ^1H spectrum in D_2O after N deuteration; (c) off-resonance proton-decoupled ^{13}C spectrum in D_2O, dioxane reference (0 ppm); and (d) broad-band proton-decoupled ^{13}C spectrum.

functional groups with a wide range of properties may be attached to the (exposed) terminal positions on the cage and the "ethylenediamine" links.

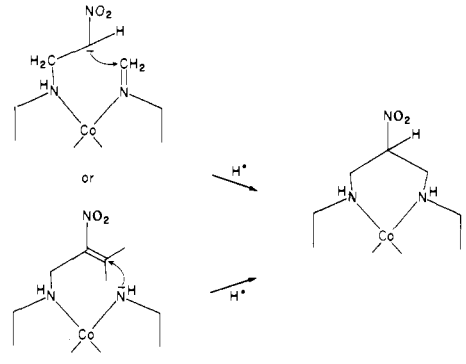
As with $Co(sep)^{3+}$, two simple reaction pathways can be envisaged for at least the first two steps of "cap" formation on $Co(en)_3^{3+}$ leading to $Co(diNOsar)^{3+}$. Thus, in the first step free nitromethane anion might add to a coordinated methyleneimine or free nitroethylene, formed from base-catalyzed condensation between CH_3NO_2 and HCHO, might be attacked by a deprotonated coordinate amine.

The second step would necessarily be intramolecular, Scheme II, but again two possibilities arise. The third reaction step leading to completion of the cap must, however, involve carbanion addition to a coordinated imine since an activated olefin can no longer be formed at the now tertiary (ultimately bridgehead) carbon, Scheme III.

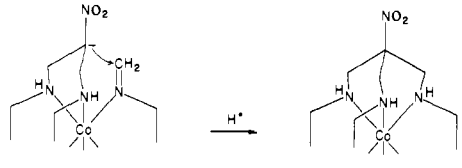
Scheme I



Scheme II



Scheme III



For simplicity, therefore, we prefer to postulate formation of $Co(diNOsar)^{3+}$ through a series of carbanion additions to coordinated imines, though evidence to exclude more complex processes is not conclusive. Certainly, inter- and intramolecular additions of coordinated deprotonated amines to unsaturated carbon are well-known[29-32] (and must, of course, be the first step in formation of a coordinated imine from $Co(en)_3^{3+}$ and aqueous formaldehyde, for example), but so also are carbanion and other nucleophile additions to coordinated imines.[30,33] Isolation of the tris chelate $Coen_2(NH_2CH_2CH_2N{=}CH_2)^{3+}$ and of the crossed Cannizzarro reaction product, Co(N—Me—NOsen)$^{3+}$ (arising from reduction of the monomethyleneimine of $Co(NOsen)^{3+}$ by HCHO) from the $Co(diNOsar)^{3+}$ reaction mixture also supports the mechanism proposed.

Regardless of mechanism, the formation of $Co(diNOsar)^{3+}$ and $Co(MENOsar)^{3+}$ is remarkable for its simplicity and efficiency. The fact that yields of these complexes and of $Co(sep)^{3+}$ are ≥80% in a reaction mixture from which a multitude of alternative products are possible suggests that such high symmetry encapsulated complexes must be extraordinarily kinetically favored. There are, of course, a number of purely organic analogues of these reactions, perhaps the best known being the formation of "hexamethylenetetramine" from formaldehyde and ammonia.[7,34] Undoubtedly, however, metal-dependent factors may strongly

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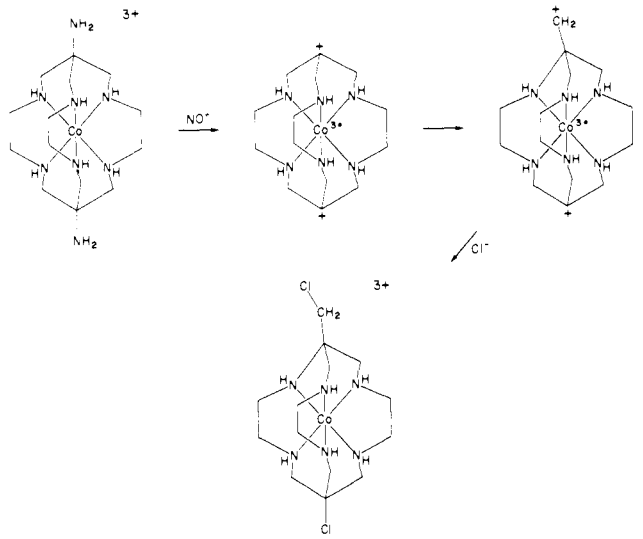
Scheme IV



influence the reactions, since so far only Rh(III), Ir(III), and Pt(IV)[35] are known to react under conditions similar to those used for the Co(III) complexes to give good yields of their encapsulated derivatives. Loss of an ethylenediamine chelate appears to lead to a multitude of products and little, if any, cage complex.

Conversions of $Co(diNOsar)^{3+}$ to the other encapsulated complexes described in this work illustrate conventional organic chemistry which does not appear to be greatly modified by its occurrence on a tripositive metal ion center. The hydrolytic stability of $Co(diCLsar)^{3+}$ toward conversion to $Co(diHOsar)^{3+}$, for example, is consistent with that of analogues such as 1-chloroadamantane,[36] where the difficult of forming a carbocation at a nonplanar bridgehead position is postulated as the reason for its low reactivity. However, an unusual rearrangement occurs in the nitrosation of $Co(diAMsar)^{3+}$ in a way which is not commonly observed in organic systems. The surprising feature is the apparent formation of a carbocationic methylene moiety, Scheme IV. The general organic chemistry would indicate that the rearrangement should have occurred in the opposite direction.[37] One rationalization of the rearrangement is that the positive charge on the cobalt ion and that on the nearby bridgehead cation are too close for comfort.[38] The Coulombic effect is relieved by the rearrangement to separate the charges. Another is that the carbocationic ligand is strained when bound to the Co(III) ion and that strain is relieved partly by the bridgehead rearrangement. Some evidence for such a proposal might be adduced from the bridgehead strain observed in the $[Co^{III}sepulchrate]^{3+}$ ion.[1]

The numbers of products observed in both $Co(diAMsar)^{3+}$ and $Co(AMMEsar)^{3+}$ nitrosation are nicely consistent with the assumption that nitrosation without rearrangement involves competition for all nucleophiles in solution while nitrosation with rearrangement appears to involve selective Cl^- entry. Thus, with three nucleophiles (NO_2^-, Cl^- and H_2O) present $Co(diAMsar)^{3+}$ could be expected to give six $[Co(X,Ysar)]^{3+}$ (including X = Y) species and three $[Co(XCH_2,CLabsar)]^{3+}$ species. However, the yellow species are produced in low yield and Cl^- is the most effective nucelophile in the non-rearrangement path, so that it is quite likely that other yellow species were simply present in concentrations too low to be detected. (It is possible that doubly rearranged species might also have been present in as yet undetectable concentrations.) Nonetheless, these rearranged materials provide a new series of encapsulated complexes in which a significant change in the electronic structure of the metal ion, as evidenced in the shift of ligand field bands and redox potentials,[35] has been engendered.

Properties and Utility. The unique properties of encapsulated metal ion complexes have been discussed previously.[1-4,39] Many of the presently described species are, however, of even greater robustness than $Co(sep)^{3+}$[1,3,4] and may ultimately be of greater utility. The substitutional inertness engendered by the bicyclic ligands is well illustrated by the fact that $Co^{II}(diAMsar)^{2+}$ may be boiled in 3 M HCl for at least 24 h without appreciable release of free Co(II). The rather crude procedure used to convert $Co(diCLsar)^{3+}$ to $Co(sar)^{3+}$ would, of course, lead to the complete decomposition of any unencapsulated Co(III)-saturated amine complex. The NH acidity of $Co(sar)^{3+}$ ($pK_a > 14$) and its derivatives is not surprising in view of trends in the properties of Co(III) amine complexes in general, but a deprotonated species such as $Co(diNOsar\text{-}H)^{2+}$ (pK_a 8.85, 25 °C, $\mu = 10^{-2}$ M) has not previously been isolated and fully characterized. The structure of this molecule does not answer all questions that relate to the possible involvement of deprotonated intermediates in Co(III)-substitution reactions, but it certainly shows that N-deprotonation can have a significant effect on the bonding of other donor atoms and therefore may rationalize the labilizing effect of this reaction. If this is accepted, the implication in the structural result is that the group trans to the deprotonated N center is the one most likely to be lost.

The six nitrogen donor atoms of sarcophagine stabilize Co(III) effectively and, as with $Co(sep)^{2+}$, $Co(sar)^{2+}$ and its derivatives are good reducing agents. Their reducing properties do, however, depend on the terminal groups, thus giving rise to a number of chiral reducing agents with a useful range of reducing powers. Their electron-exchange properties (for Co(II)/Co(III) reaction) also vary and allow thereby a subtle study of the factors influencing such reactions. An extensive study of the electrochemistry of these encapsulated complexes has been described elsewhere.[8]

The syntheses presently described show that a reaction at Co(III) first observed in the synthesis of $Co(sep)^{3+}$ can be logically extended to provide a considerable variety of encapsulated complexes. A number of other variations of the procedure in sexidentate or in the tris chelate reactants are obvious and are presently under investigation. A limitation does appear to be, however, that an inert metal ion species such as $Co(en)_3^{3+}$ or $Rh(en)_3^{3+}$ is necessary to obtain high yields of encapsulated complexes. Attempts to carry out reactions, similar to those presently observed, with complexes such as $Ni(en)_3^{2+}$, $Cu(en)_3^{2+}$, or $Zn(en)_3^{2+}$ have not given reasonable yields of the cages, although it appears monocapped complexes and various macrocycles can be made in this way.[40] However, a small yield (<1%) of $[Nisepulchrate]^{2+}$ has been reported along with a mono-aza-capped product and other quadridentates.[41] Even $Cr(en)_3^{3+}$ does not react efficiently, a rather unexpected discovery made in examining its reactions being that in the presence of HCHO and base $Cr(en)_3^{3+}$ very rapidly loses its en ligands. A general procedure for encapsulation therefore remains to be discovered. One obvious method would be to remove sarcophagine or its derivatives from Co, but as described above, the encapsulating ligands do not dissociate readily even from Co(II). However, several procedures for achieving ligand removal have been developed by using vigorous conditions, and a variety of metal complexes have been synthesized. This work will be described in subsequent publications. The encapsulated transition-metal ions could provide reagents of great utility as innocent oxidants and reductants and as efficient catalysts for a number of simple reactions.[2]

Acknowledgment. Support from the Australian Research Grants Scheme (to T.W.H. and M.R.S.) is gratefully acknowledged and also the assistance of D. Bogsanyi for the pK_a mea-

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surements and the Microanalytical Service Unit, ANU.

Registry No. [Co(diNOsar)]Cl_3, 71935-78-9; [Co(diNOsar)]-$(CH_3CO_2)_3$, 91192-19-7; [Co(diNOsar)]$(ClO_4)_3$, 91002-73-2; [Co(diNOsar)]$(NO_3)_3$, 91002-74-3; [Co(diNOsar)]$(CF_3SO_3)_3$, 91002-75-4; [Co(NOsen)]Cl_3, 91002-76-5; [$Coen_2$(enim)]I_3, 91002-77-6; [Co(NMeNOsen)]Cl_3, 91032-16-5; [Co(diNOsar-H)]$Cl_2 \cdot 4H_2O$, 91032-17-6; [Co(diNOsar-H)]$(ClO_4)_2$, 91002-79-8; [Co(diNOsar)]$(ClO_4)_2$, 71935-81-4; [Co(diAMsar)]Cl_3, 91002-80-1; [Co(diAMsarH_2)]Cl_5, 71935-72-3; [Co(CLNOsar)]Cl_3, 91002-81-2; [Co(HONOsar)]Cl_3, 91002-82-3; [Co(diCLsar)]Cl_3, 91002-83-4; [Co(CLHOsar)]Cl_3, 91002-84-5; [Co(diHOsar)]Cl_3, 91002-85-6; [Co((ClMe)NOabsar)]Cl_3, 91109-32-9; [Co((ClMe)Clabsar)]Cl_3, 91109-33-0; [Co((Clme)HOabsar)]Cl_3, 91109-34-1; [Co(AM(Clme)absarH)]Cl_4, 91032-18-7; [Co(sar)]Cl_3, 71935-73-4; [Co(MENOsar)]Cl_3, 91002-87-8; [Co(AMMEsarH)]Cl_4, 91002-88-9; [Co(CLMEsar)]Cl_3, 91002-89-0; [Co(HOMEsar)]Cl_3, 91002-90-3; [Co(Clmeabsar)]Cl_3, 91032-19-8; [Co(en)$_3$]Cl_3, 13408-73-6; [Co(sen)]Cl_3, 82796-46-1; HCHO, 50-00-0; CH_3NO_2, 75-52-5; diNOsar, 87655-55-8; diAMsar, 91002-72-1; AMMEsar, 91002-71-0.

Supplementary Material Available: A listing of positional and thermal parameters, hydrogen atom coordinates, and the observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

Cadmium-113 Shielding Tensors of Oxo Cadmium Compounds. 2. Single-Crystal Studies on Cadmium Calcium Tetraacetate Hexahydrate, Cadmium Maleate Dihydrate, Cadmium Formate Dihydrate, Cadmium Diammonium Disulfate Hexahydrate, and Cadmium Diacetate Dihydrate

Robert S. Honkonen and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received December 8, 1983*

Abstract: Crystals of the title compounds have been investigated by single-crystal oriented ^{113}Cd NMR. The orientation of six distinct ^{113}Cd shielding tensors in the respective molecular reference frames has been determined. In each case, the tensor configuration was found to comply with the cadmium site symmetry. Tensor–lattice site orientations for cadmium calcium tetraacetate and cadmium maleate were unambiguously determined via NMR and crystallographic data. The ^{113}Cd NMR of cadmium formate, cadmium diammonium disulfate, and cadmium acetate crystals gave rise to symmetry-related tensors. A qualitative method for making symmetry-related tensor–lattice site assignments is introduced and was employed for these cadmium salts. The magnitude and orientation of the principal elements of the ^{113}Cd shielding tensor are discussed in terms of the structural features of the corresponding oxo cadmium reference frame and tensor element–structure correlations are proposed.

The importance of ^{1}H and ^{13}C NMR in organic and organometallic structure determination may be second only to X-ray crystallography. The utility of these nuclei as structural probes rests largely upon well-established isotropic chemical shift–structure correlations. Now, the demonstration of at least partial retention of activity for cadmium-substituted metalloproteins[1] coupled with the observation of ^{113}Cd resonances from cadmium-substituted metal-containing proteins[2-8] indicated that ^{113}Cd NMR and protein crystallography might enjoy a similar relationship with respect to the structure of the metal site in proteins. Specifically, native Ca^{2+} and Zn^{2+} could be replaced with NMR-favorable $^{113}Cd^{2+}$ and the metal coordination sphere configuration (the number and type of ligands) determined via comparison of the observed chemical shift with well-established shift–structure correlations. Unfortunately, the interpretation of isotropic shifts of spin $^1/_2$ metal nuclides in terms of structural parameters has not been straightforward.

Chemical shift data, solution and solid state, have demonstrated that specific regions within the nearly 1000-ppm ^{113}Cd shift range are dominated by particular ligand types.[8a,c] The overlap of these regions and the lack of intraregion relationships between σ_{iso} and the number of ligands, the cadmium–ligand distances, or the ligand type result in ambiguous shift–structure correlations. Hence, at the present time, cadmium thiolates[9] can be readily distinguished from oxo cadmium compounds; however, it is not possible to discriminate 6-, 7-, and 8-coordinate oxo complexes by employing only isotropic ^{113}Cd-shift data.[10] This deficiency clearly limits the utility of cadmium NMR as a structural tool.

Because of our present work in the application of ^{113}Cd NMR spectroscopy as a probe for calcium sites in troponin C[8d] we have been interested in a detailed understanding of the structural factors responsible for the shielding of the ^{113}Cd nucleus.[11] The sin-

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