to water. The reaction of nucleophiles (X) with $(H–O–H··O–Cl)^-$ at chlorine to give $OH^- + (H–O–Cl–X)^-$ is an attractive alternative to the reaction at oxygen, and the rate constants would be expected to be much less than the direct reaction with HOCl. At present we are not able to distinguish between these two paths for OCl^-, but we believe there is overwhelming evidence for a Cl^+-transfer path for the HOCl reactions.

Conclusions

Contrary to a previous report,[15] the reactions between CN^- and OCl^-/HOCl are extremely rapid. The Cl^+-transfer reaction of HOCl with CN^- to give ClCN and OH^- ($k_4 = 1.22 \times 10^9$ M^{-1} s^{-1}) is even faster than H$^+$ transfer for the same reactants to give OCl^- and HCN ($k_{-5} = 6.6 \times 10^8$ M^{-1} s^{-1}). A typical concern about kinetic ambiguity[26,42] (or proton ambiguity) for the choice of either HOCl + CN^- or OCl^- + HCN as reactants is resolved in this case because only the HOCl path has the observed proton-transfer limitations. Hence, the usual statement that the two pathways are kinetically indistinguishable is no longer valid. The

HCN pathway can also be ruled out mechanistically, because HOCl is needed to give CNCl as the product.

For many years non-metal redox reactions of OCl^-/HOCl with a variety of reducing agents[43-47] have been thought to proceed by oxygen-atom-transfer mechanisms. The present work and other recent studies[18-21,37] show a strong preference for Cl^+-transfer mechanisms for the reactions of HOCl with a series of nucleophiles. An excellent correlation is found between the nucleophilicity of anions and log k values for their rate constants with HOCl. Attack at chlorine is extremely sensitive to nucleophilic strength.

(42) Weil, I.; Morris, J. C. *J. Am. Chem. Soc.* **1949**, *71*, 1664–1671.

(43) Halperin, J.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 375–380.
(44) Anbar, M.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 1073–1077.
(45) Chia, Y. T.; Connick, R. E. *J. Phys. Chem.* **1959**, *63*, 1518–1519.
(46) Lister, M. W.; Rosenblum, P. *Can. J. Chem.* **1963**, *41*, 3013–3020.
(47) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Freeman: New York, 1990; p 241.

Redox Behavior of Nitro Substituents of Cage Complexes[1]

Peter A. Lay*,† and Alan M. Sargeson*,‡

The redox behavior of nitro groups bonded in the apical (1,8) positions of sar (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) cage complexes is very diverse. Nitroso, hydroxylamine, amine, and nitro radical anions result as primary products from such reductions, depending on the type of reductant, pH, solvent, and the amount of reductant supplied. Secondary products also vary greatly according to the above parameters. The ultimate reduction products with Zn/HCl as the reductant contain amine substituents, whereas reductions with Sn^{2+}/HCl or $S_2O_4^{2-}$, or electrochemical reductions at a Hg-pool electrode, yield hydroxylamine-substituted cage complexes as the ultimate products. The behavior mirrors that normally associated with tertiary nitro groups in organic chemistry and allows the syntheses of a large variety of useful substituted cage complexes. The kinetic data on the reduction of nitro-substituted cage complexes by dithionite[11] have been reinterpreted in light of our studies in this area. No evidence has been found for nitro groups mediating the rate of electron transfer to the Co(III) center.

Introduction

The reduction of nitro substituents to amine substituents is a precursor to the synthesis of a large variety of cage complexes.[1-10] In addition to the reduction of the nitro groups to amines, hydroxylamine, nitroso, nitro radical ion derivatives, and their secondary reaction products were synthesized or implicated in the products.[1,6] An exclusive reduction of the nitro groups of [Co-$(NO_2)_2$–sar)]$^{3+}$ to the hydroxylamine derivative by the dithionite ion has also been reported.[11]

Further, it has been reported, on the basis of kinetic results with dithionite reductions,[11] that the nitro substituents of cage complexes mediate the rate of electron transfer to Co(III). In this paper, our earlier work on the reduction of the nitro groups is described in detail. This chemistry shows some parallels to reductions of tertiary nitro groups in organic chemistry and addresses the possibility of electron transfer being mediated by the nitro substituents.[12-18]

Experimental Section

Absorption spectra and molar absorptivities (ϵ, M^{-1} cm^{-1}) were recorded by using Cary 14 and 118C spectrophotometers. ^{1}H NMR spectra were recorded with a JEOL 100-MHz Minimar spectrometer using sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) or tetramethylsilane (TMS) as internal standards or with a Varian HA 100 spectrometer using TMS as a standard. Decoupled spectra were obtained from the Varian instrument. ^{1}H-decoupled ^{13}C NMR spectra were

obtained by using a JNM-FX 60 Fourier transform spectrometer with 1,4-dioxane as an internal standard. All chemical shifts (δ) are expressed

(1) Abstracted in part from: Lay, P. A. Ph.D. Thesis, The Australian National University, 1981.
(2) Geue, R. J.; Hambley, T. W.; Harrowfield, J. MacB.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478–5488.
(3) Gahan, L. R.; Hambley, T. W.; Sargeson, A. M.; Snow, M. R. *Inorg. Chem.* **1982**, *21*, 2699–2706.
(4) Hammershøi, A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 3554–3561.
(5) Petri, W.; Sargeson, A. M.; Snow, M. R. To be published.
(6) Bond, A. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010–2021.
(7) Boucher, H. A.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652–4661. Structure: Hagen, K. S.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1988**, *27*, 3424–3426.
(8) Harrowfield, J. MacB.; Herlt, A. J.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Mulac, W. A.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5503–5505.
(9) Gahan, L. R.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 4369–4376.
(10) Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 8282–8291.
(11) Balahura, R. J.; Ferguson, G.; Ruhl, B. L.; Wilkins, R. G. *Inorg. Chem.* **1983**, *22*, 3990–3992.
(12) Schröter, R.; Möller, F. In *Methoden der Organischen Chemie*, 4th ed.; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, FRG, 1957; Chapter 4.
(13) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970; Chapter 11.
(14) Boyer, J. H. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Wiley: New York, 1969; Part 1, Chapter 5.
(15) Rifi, M. R. In *Technique of Electroorganic Synthesis*; Weinberg, N. L., Ed.; Techniques of Chemistry, Vol. 5; Wiley: New York, 1975; Part 2, Chapter 8, pp 203–205.

† The University of Sydney.
‡ The Australian National University.

in ppm as positive, downfield shifts relative to these standards. Infrared spectra were recorded from KBr disks on a Perkin-Elmer 457 or 683 infrared spectrometer. For chromatography, SP-Sephadex C-25, Dowex 50W-X2 (Bio-Rad 200–400 mesh), and Dowex 1-X8 anion-exchange resins were used for separation of the complexes, desalting, and anion exchange, respectively. All column dimensions are given as length by diameter in centimeters. Evaporations were performed at reduced pressure with a Büchi rotary evaporator and a bath at 50 °C. Distilled water, acetone (Univar AR or Proanalys AR), and acetonitrile (Riedel-De Haën, AG or Univar AR) were used without further purification. DMF (Mallincrodt, AR) was dried over 4-Å molecular sieves and freshly distilled at reduced pressure prior to use. Butanenitrile (Ega, 98%) was used for low-temperature electrochemistry. $NaClO_4 \cdot H_2O$ (AR) and $HClO_4$ (70% w/w, AR) were used as supporting electrolytes in water, while $R_4NCF_3SO_3$[19] salts were used in nonaqueous solvents.

All electrochemical instrumentation and techniques used in this paper have been described elsewhere.[6] Spectroelectrochemical and ESR electrochemical techniques were performed with use of cells of our own design.[1,6,9] After controlled-potential electrolysis experiments, the complexes were reoxidized to Co(III) complexes and submitted to chromatography (as described later) or precipitated by the addition of R_4NX salts to the Co(II) solutions. Co(III) products obtained from these experiments were characterized by ^1H NMR, ^{13}C NMR, and infrared spectroscopy and compared with those complexes prepared by other means.[2]
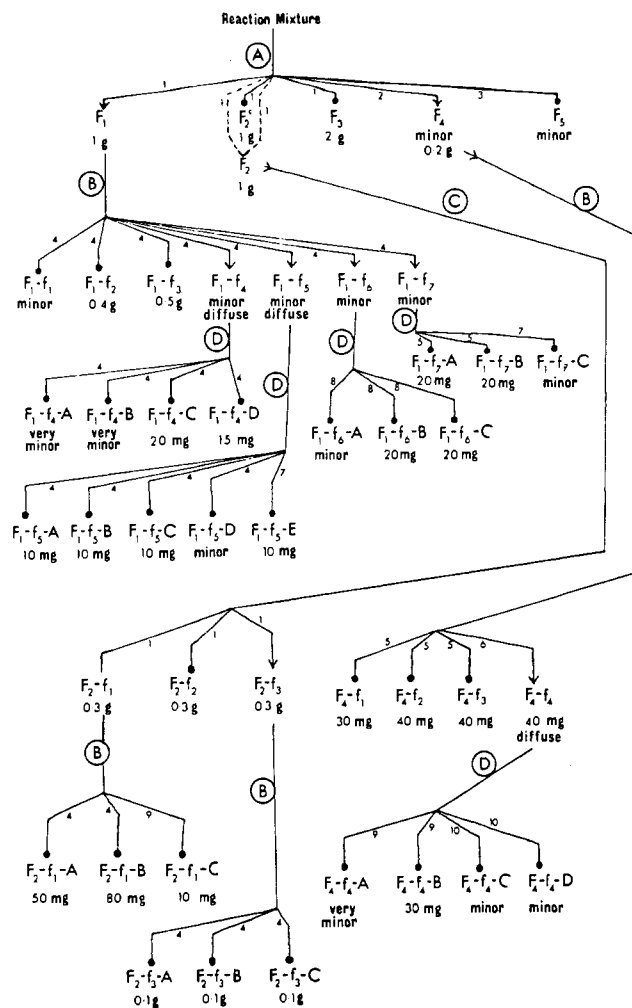
Syntheses. All chemicals were of AR grade unless otherwise described. $[Co((NO_2)_2-sar)]Cl_3 \cdot H_2O$, $[Co(CH_3,NO_2-sar)]Cl_3$, $[Co(Cl,-NO_2-sar)]Cl_3 \cdot H_2O$, $[Co((NH_3)_2-sar)]Cl_5 \cdot 1.5H_2O$, $[Co(NH_3,CH_3-sar)]Cl_4 \cdot H_2O$, $[Rh((NO_2)_2-sar)]Cl_3 \cdot H_2O$, and $[Pt((NO_2)_2-sar-H)]-Cl_3 \cdot 3H_2O$ were prepared by standard methods.[1,2,7,8] The cobalt complexes were converted to the acetate salts by anion-exchange chromatography using the acetate form of Dowex 1-X8,[20] followed by evaporation of eluant. Triflate salts were obtained by dissolving the chloride salt of the desired complex in distilled neat CF_3SO_3H (~0.1 g/mL).[21] The resultant solution was flushed with N_2 at 60 °C for 1 h to remove HCl; then diethyl ether (5 volumes) was added cautiously at 0 °C. The resultant precipitate was collected by filtration, washed with chloroform, and air-dried. The filtrate of ethereal CF_3SO_3H was converted to $NaCF_3SO_3$ as described previously.[22] The triflate salts were dehydrated, if required, by heating at 110 °C in a vacuum oven under reduced pressure.[23]

$[Co((NO_2)_2-sar)](CF_3SO_3)_3 \cdot H_2O$ was prepared as above. Anal. Calcd: C, 23.19; H, 3.43; N, 12.73; S, 10.92. Found: C, 22.9; H, 3.5; N, 12.4; S, 10.7. $[Co(CH_3,NO_2-sar)](CF_3SO_3)_3$ was prepared by a similar procedure.

$[Co((NO_2)_2-sar)](CF_3SO_3)_3 \cdot CF_3SO_3H \cdot H_2O$ was obtained by treating the carbonate salt[2] (1 g) with aqueous CF_3SO_3H (50% v/v, 10 mL). After cooling, the yellow precipitate was collected, air-dried, washed with diethyl ether (3 × 10 mL), and dried in vacuo over P_2O_5. Anal. Calcd for $[Co(C_{14}H_{30}N_8O_4)](CF_3SO_3)_3 \cdot CF_3SO_3H \cdot H_2O$: C, 20.75; H, 3.19; N, 10.76. Found: C, 20.8; H, 3.0; N, 10.8.

Reduction of $[Co((NO_2)_2-sar)]^{3+}$ by Zn/HCl. $[Co((NO_2)_2-sar)]-Cl_3 \cdot H_2O$ (4 g) was dissolved in water (200 mL), and the solution was deoxygenated with nitrogen. While a nitrogen blanket was maintained, Zn dust (3.5 g) was added, followed by the dropwise addition of concentrated HCl (20 mL) with stirring. After 3 h, the solution was filtered and 30% H_2O_2 solution (5 mL) was added (to oxidize Co(II) to Co(III)). The solution was diluted (2 L) and sorbed onto a column of SP-Sephadex C-25 (14 × 9). After being washed with water (1 L), the column was eluted with NaCl solution (0.25 M). Three orange bands separated (in a ratio of ~1:1:2), with the first (F_1) and the second (F_2) bands being more clearly separated than the second and third (F_3). A fourth narrow band appeared 4 cm down the column after F_1–F_3 were eluted. Further elution with NaCl solution (0.6 M) removed a fourth fraction (F_4), while a fifth fraction (F_5) remained stationary even with 2 M NaCl as eluant.

After separate collection of the bands (the central 50% of F_2 was

(16) Morrison, H. A. In ref 13; Chapter 4, pp 203–205.
(17) Timberlake, J. W.; Stowell, J. C. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: London, 1975; Part 1, Chapter 4, p 89.
(18) Drewer, R. J. In ref 27; Part 2, Chapter 20, p 281.
(19) Brownstein, S.; Bornais, J.; Latremouille, G. *Can. J. Chem.* **1978**, *56*, 1419–1422.
(20) The $CH_3CO_2^-$ form of Dowex 1-X8 is obtained by conversion of the Cl^- form to the CO_3^{2-} form by concentrated Na_2CO_3 followed by washing with water and then neutralization with glacial acetic acid.
(21) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1986**, *24*, 243–250.
(22) Dixon, N. E.; Jackson, W. G.; Lancaster, M. A.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470–476.
(23) Fujinaga, T.; Sakamoto, I. *Pure Appl. Chem.* **1980**, *52*, 1389–1396.

Figure 1. Chromatographic separations of products from Zn/HCl reduction of $[Co((NO_2)_2-sar)]^{3+}$. Conditions are given in Table I. Letters in circles indicate the size of the Sephadex column and the numerals, the eluants.
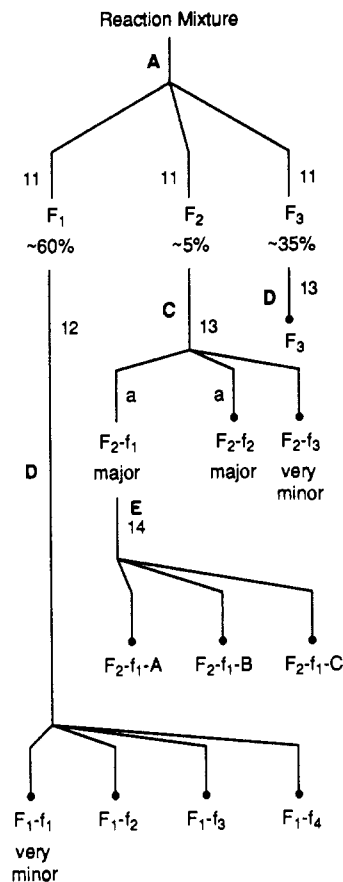
Table I. Conditions for the Chromatographic Separations in Figures 1 and 2[a]

(i) Column Dimensions

(a) Sephadex: (A) 14 × 9 cm; (B) 24 × 5 cm; (C) 18 × 3 cm; (D) 25 × 1 cm; (E) 30 × 5 cm

(b) Dowex (amount of complex used given in parentheses): (a) 7 × 2 cm (0.1–1 g); (b) 7 × 0.5 cm (<100 mg); (c) 3 × 5 cm (>1 g)

(ii) Eluants

(a) Sephadex: (1) 0.25 M NaCl; (2) 0.6 M NaCl; (3) unmoved by 2 M NaCl; (4) 0.135 M disodium (+)-tartrate; (5) 0.2 M disodium (+)-tartrate; (6) 0.5 M Na_2SO_4; (7) 0.3 M Na_2SO_4; (8) 0.17 M disodium (+)-tartrate; (9) 0.22 M disodium (+)-tartrate; (10) 0.26 M disodium (+)-tartrate; (11) 0.18 M NaCl; NaCl; (12) 0.07 M disodium (+)-tartrate; (13) 0.1 M disodium (+)-tartrate; (14) 0.2 M $(NH_4)_2CO_3$

(b) Dowex: (i) 3 M HCl (monomers, eluted from Sephadex by using conditions 1, 4, 11, 12, 13, or 14 above); (ii) 6 M HCl (dimers)

[a] The chromatographic separation conditions are marked on the arrows, and final separations are denoted by ●.

collected separately (F_2^c) from the leading and trailing ends (F_2^e)), each was resorbed onto Dowex 50W-X2 (7 × 2). The column was washed with water (500 mL) and 1 M HCl (500 mL), the complexes were eluted with 3 M HCl (f_1–f_3) or 5 M HCl (f_4), and the eluates were evaporated to dryness. Further separations of the fractions were continued as outlined in the flow chart (Figure 1 and Table I) until each fraction appeared pure spectroscopically or the band was too insignificant to be characterized. Compounds for elemental analysis were obtained by evaporation to near dryness followed by the slow addition of EtOH to

Reaction Mixture

Figure 2. Chromatographic separations of products from Zn/HCl reduction of [Co(CH$_3$,NO$_2$-sar)]$^{3+}$. Conditions are given in Table I.

turbidity. On cooling, the precipitate was collected, washed with EtOH and diethyl ether, and dried in vacuo over P$_2$O$_5$.

Reduction of [Co(CH$_3$,NO$_2$-sar)]$^{3+}$ by Zn/HCl. This reduction was performed in an analogous fashion to that of [Co((NO$_2$)$_2$-sar)]Cl$_3$ using [Co(CH$_3$,NO$_2$-sar)]Cl$_3$ (4 g), Zn dust (1.2 g), and HCl (20 mL) in water (200 mL). The products were separated by chromatography according to the flow chart of Figure 2 and Table I.

Reduction of [Co(Cl,NO$_2$-sar)]Cl$_3$ by Zn/HCl. To [Co(Cl,NO$_2$-sar)]Cl$_3$·H$_2$O (0.75 g) in water (20 mL) under N$_2$ was added Zn dust (1.5 g, 2 molar excess) while the solution was vigorously stirred. Concentrated HCl (36%, 2 mL) was added dropwise to the solution while a N$_2$ atmosphere was maintained. After the addition of further concentrated HCl (3 × 2 mL) at intervals during the next 3 h, the N$_2$ flow was stopped, H$_2$O$_2$ solution (30%, 2 mL) was added, and the solution was left overnight. An orange precipitate of the mixed [ZnCl$_4$]Cl$_2$ salt of the product was collected, washed with acetone and diethyl ether, and air-dried (0.85 g).

The remaining solution was diluted to 500 mL and absorbed onto a Dowex 50W-X2 column (4 × 1). After being washed with water (300 mL) and 1 M HCl (300 mL), the complexes were eluted with 4 M HCl. The solid obtained by evaporation was dissolved in water (200 mL), sorbed onto SP-Sephadex C-25 (21 × 3.5), and eluted with 0.28 M NaCl. Two very minor leading bands were observed, F$_1$ and F$_2$, followed by a major band (F$_3$). All fractions were sorbed onto Dowex 50W-X2 and treated as above. A very minor fourth band remained at the top of the column.

[Co(NH$_3$,Cl-sar)]Cl$_4$·4H$_2$O·^{1}/$_2$H$_3$OCl (F$_3$) was obtained by evaporation of the eluate from Dowex 50W-X2 to near dryness (to the onset of precipitation) and by precipitating the remainder with the slow addition of ethanol (0.045 g). When the reduction was performed with less zinc dust (~0.5 g), the [Co(Cl,NH$_2$OH-sar)]Cl$_4$ complex was obtained as a major fraction (F$_2$) and unreacted [Co(Cl,NO$_2$-sar)]$^{3+}$ was also obtained (F$_1$).

Reductions of Nitro-Containing Complexes by Sn^{2+}/HCl. [Co-((NO$_2$)$_2$-sar)]Cl$_3$·H$_2$O (2.5 g) was dissolved in water (200 mL), and the solution was purged with N$_2$. A suspension of SnCl$_2$·H$_2$O (8.5 g) in 6 M HCl (50 mL) was added, and the suspension was stirred under nitrogen for 30 h at 40 °C. The mixture was diluted 10-fold and absorbed onto a column of SP-Sephadex C-25, and the products were separated, as before.

Reduction of [Co(CH$_3$,NO$_2$-sar)]Cl$_3$ (0.5 g) with SnCl$_2$·2H$_2$O (0.85 g) was performed in essentially the same manner, while the reduction of [Pt((NO$_2$)$_2$-sar-H)]Cl$_3$·3H$_2$O was performed as reported previously.[7]

Reductions of Nitro-Containing Complexes by S$_2$O$_4$$^{2-}$. These reductions were performed essentially as described by Balahura et al.[11] using Cr^{2+}-scrubbed N$_2$. Reactions were performed at pH 6.3 (MES buffer) with a 10:1 molar ratio of dithionite to nitro group for the complexes [Co((NO$_2$)$_2$-sar)]$^{3+}$, [Co(CH$_3$,NO$_2$-sar)]$^{3+}$, and [Co(Cl,NO$_2$-sar)]$^{3+}$. All subsequent separations of products were performed as described previously.

Controlled-Potential Reductions of Nitro Groups to Hydroxylamine Groups at a Mercury-Pool Electrode. [Co((NO$_2$)$_2$-sar)]$^{3+}$, [Co-(CH$_3$,NO$_2$-sar)]$^{3+}$, and [Co(Cl,NO$_2$-sar)]$^{3+}$ were reduced electrochemically to the corresponding hydroxylamine complexes by the following procedure. Controlled-potential electrolysis was performed at 0.2 V more negative than $E_{1/2}$ for the –NO$_2$ to –NH$_2$OH$^+$ reduction wave.[6] At both neutral (CH$_3$CO$_2$H buffer) and acidic (0.1 M HCl) pH values, 4.0 ± 0.2 electrons were transferred per nitro group (after taking into account the reduction of Co(III) to Co(II)). The chromatographic separations, performed as before, indicated ~90% yields of the desired hydroxylamine complexes with minor impurities of the amine, nitro, and dimeric species.

Controlled-Potential Reductions of Nitro Complexes in Nonaqueous Solvents. [Co(CH$_3$,NO$_2$-sar)](CF$_3$SO$_3$)$_3$ and [Co((NO$_2$)$_2$-sar)]-(CF$_3$SO$_3$)$_3$ were reduced to the cobalt(II) complexes in both acetone and acetonitrile at a mercury-pool electrode. In each instance 1.0 ± 0.1 electron was consumed, and the color decreased dramatically, in keeping with a reduction at the Co(III) center. The reduction was also examined by using the spectroelectrochemical cell described previously.[1,6] The Co(II) complexes were precipitated as chloride salts by the addition of Et$_4$NCl under Ar and were moderately stable to aerial oxidation in the solid state.

Tollen's Reagent. In addition to the spectroscopic characterization of the hydroxylamine complexes, the presence of this functional group was identified further by the use of Tollen's reagent ([Ag(NH$_3$)$_2$]OH),[24] a precipitation of Ag being a positive test for hydroxylamine, hydrazo, or hydrazine groups.[24]

Stoichiometric Reductions of Nitro Complexes by Na$_2$S$_2$O$_4$. The stoichiometric experiments were performed under argon at pH 6.3 (MES buffer, μ = 0.50 M). Final Co(III) concentrations were typically 2 mM after the reactants were mixed. All manipulations were carried out with 50-mL bubble flasks and standard argon-line techniques.

Results

Reduction of Nitro Groups by Zn/HCl. The partial reduction of the nitro groups of [Co((NO$_2$)$_2$-sar)]$^{3+}$ with insufficient Zn dust resulted in a mixture of mononuclear cage complexes containing nitro, hydroxylamine, and amine groups. In addition, a variety of dimers, trimers, and polymers were obtained, but not in sufficient amounts to enable complete characterization. The reduction of [Co(CH$_3$,NO$_2$-sar)]$^{3+}$ differed in that only monomers were obtained. [Co(Cl,NO$_2$-sar)]$^{3+}$ was also reduced to [Co-(NH$_3$,Cl-sar)]$^{4+}$ in >90% yield by Zn/HCl without measurable reductive dechlorination, and [Co(Cl,NH$_2$OH-sar)]$^{4+}$ was obtained as an intermediate. Analytical data are given in Table II, NMR spectroscopic data are listed in Table III, and the data relating to vis/UV and IR spectroscopy and sensitivity to Tollen's reagent are collected in Table IV.

All initial separations of the reaction mixtures were performed on SP-Sephadex C-25 cation-exchange resin (Na$^+$ form) with 0.25 M NaCl as eluant. This tended to separate the higher charged, protonated amine and hydroxylamine complexes from the other complexes. Secondary separations were performed by using disodium (+)-tartrate as the eluant. This has been documented previously[25] as one of the best eluants for separating complexes with related structures.

Reductions with Sn^{2+}/HCl. Reaction of the nitro-containing cobalt cage complexes with excess Sn^{2+} resulted in a mixture of products. Chromatographic separations and ^{1}H-decoupled ^{13}C NMR spectroscopy showed that the hydroxylamine-substituted cage complexes were the predominant products (>50%). This was also consistent with their reaction with Tollen's reagent. Reexamination of the major reduction product from the [Pt-

(24) Vogel, A. I. *A Text-book of Practical Organic Chemistry, Including Qualitative Organic Analysis*, 3rd ed.; Longmans: London, 1966; p 1074.

(25) Yoshikawa, Y.; Yamasaki, K. *Coord. Chem. Rev.* **1979**, *28*, 205–209.

Table II. Analyses of the Reduction Products of Nitro-Containing Cage Complexes

compd	fraction	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
(a) Analyses of Products from HCl/Zn Reduction of [Co((NO$_2$)$_2$–sar)]$^{3+}$							
[Co((NO$_2$)$_2$–sar)]Cl$_3$·H$_2$O^a	F$_1$–f$_1$						
[Co(NH$_2$OH,NO$_2$–sar)]Cl$_4$·2H$_2$O	F$_1$–f$_2$	29.67	29.9	6.59	6.9	19.79	19.8
[Co(NH$_3$,NO$_2$–sar)]Cl$_4$·2.5H$_2$O	F$_2$–f$_1$	28.93	28.4	6.48	6.9	18.96	18.8
[Co((NH$_2$OH)$_2$–sar)]Cl$_5$·H$_2$O	F$_1$–f$_3$	27.89	28.3	6.35	6.4	18.59	18.4
[Co(NH$_3$,NH$_2$OH–sar)]Cl$_5$·3H$_2$O·0.5H$_3$OCl	F$_2$^{c}, F$_2$–f$_2$	25.86	25.8	6.75	6.2	17.24	17.1^b
[Co((NH$_3$)$_2$–sar)]Cl$_5$^{a}	F$_2$–f$_3$, F$_3$						
(b) Analyses of Products from HCl/Zn Reduction of [Co(CH$_3$,NO$_2$–sar)]$^{3+}$							
[Co(CH$_3$,NO$_2$–sar)]Cl$_3$^{a}	F$_1$						
[Co(NH$_2$OH,CH$_3$–sar)]Cl$_4$·H$_2$O	F$_3$–f$_1$	32.97	33.4	7.01	7.2	17.95	17.8
[Co(NH$_3$,CH$_3$–sar)]Cl$_4$^{a}	F$_3$–f$_2$						
(c) Analyses of Products from HCl/Zn Reduction of [Co(Cl,NO$_2$–sar)]$^{3+}$							
[Co(Cl,NO$_2$–sar)]Cl$_3$^{a}	F$_1$						
[Co(Cl,NH$_2$OH–sar)]Cl$_4$^{c}	F$_2$						
[Co(NH$_3$,Cl–sar)]Cl$_4$·4H$_2$O·0.5H$_3$OCl	F$_3$	26.48	26.5	6.75	6.4	15.44	15.4^d
[Co(NH$_3$,Cl–sar)]ZnCl$_4$·Cl$_2$·3H$_2$O	F$_3$	23.16	23.3	5.41	5.1	13.51	13.3^e

^{a}Spectroscopic identification from ref 2. ^{b}Anal. Calcd: Cl, 30.00; Co, 9.06. Found: Cl, 29.8; Co, 9.6. ^{c}Characterized from chromatographic behavior and Tollen's test for hydroxylamine. ^{d}Anal. Calcd: Cl, 30.73. Found: Cl, 30.9. ^{e}Anal. Calcd: Cl, 34.18; Co, 8,12; Zn, 9.08. Found: Cl, 34.0; Co, 8.0; Zn, 9.4.

((NO$_2$)$_2$–sar–H)]Cl$_3$/Sn^{2+} reaction confirmed this was the [Pt-((NHOH)$_2$–sar)]$^{4+}$ ion and not [Pt((NH$_2$)$_2$–sar)]$^{4+}$ as initially described.[7] Its reaction with Tollen's reagent and arguments based on ^{13}C NMR spectral data were consistent with this assignment (see Discussion).

Reductions with S$_2$O$_4$$^{2-}$. These results confirmed the work of Balahura et al.,[11] with the major product of the reduction of [Co((NO$_2$)$_2$–sar)]$^{3+}$ being [Co((NHOH)$_2$–sar)]$^{3+}$ after aerial oxidation. However, contrary to the previous reports,[11] the products were Co(II) complexes, if sufficient time and anaerobic conditions were used. Similarly, the hydroxylamine species [Co(Cl,NHOH–sar)]$^{3+}$ and [Co(NHOH,CH$_3$–sar)]$^{3+}$ were the chief products (after aerial oxidation) from reduction of the nitro groups of [Co(Cl,NO$_2$–sar)]$^{3+}$ and [Co(CH$_3$,NO$_2$–sar)]$^{3+}$, respectively.

Reductions at a Mercury-Pool Electrode. Controlled-potential electrolyses were performed in both aqueous and nonaqueous solvents. In all solvents, [Co^{II}((NO$_2$)$_2$–sar)]$^{2+}$ was obtained as the initial product, although it undergoes further slow reduction in aqueous media (neutral pH) presumably of the nitro groups. The electronic spectra obtained for the Co(II) complexes were typical of other Co(II) complexes,[26,27] and the presence of the –NO$_2$ group was confirmed from the IR spectra.

In dry nonaqueous solvents, the reduction of the nitro groups resulted in a total change amounting to 1.0–2.0 electrons per nitro group, often yielding an intensely red-violet solution. The color indicates that a secondary amine site has been deprotonated and the proton transferred to the reduction site. Examination of the final orange-yellow products indicated that one minor final product was the proton-capped species (^{13}C NMR) with other as yet unidentified products. Electrochemical EPR experiments (–80 °C, acetone) indicated the presence of radical signals (g ~ 2) that were not due to either background impurities or the broad signal of the Co(II) complexes. However, the resolution and reproducibility of these signals were not such that the species giving rise to them could be identified. When the Co(II) complexes containing –NO$_2$ substituents are dissolved in degassed aqueous medium, the Co(III) color reappeared after a period of time. This behavior was a function of pH, Co(II) concentration, and the potential of the Co(III)/Co(II) couple. The interpretation of these results awaits more detailed investigations. In aqueous media (pH ≤ 7), the nitro groups were reduced in a 4-electron step per nitro

group to hydroxylamine groups (≥90%), while 1-electron to 2-electron steps were observed in nonaqueous media at more negative potentials. In nonaqueous media containing limited protons, the number of electrons consumed per nitro group decreased with decreasing access to H$^+$. Detailed analyses of the products have not as yet been performed, but the indications are that dinuclear azoxy species are among the products formed.[6]

Stoichiometric Reductions with S$_2$O$_4$$^{2-}$. When S$_2O_4$$^{2-}$ was added in a 1:2 ([S$_2$O$_4$$^{2-}$]:[Co]) stoichiometric ratio to solutions of either [Co((NO$_2$)$_2$–sar)]$^{3+}$ or [Co((NH$_2$)$_2$–sar)]$^{3+}$ (at pH 6.3 under Ar), the intensity of the yellow color of Co(III) decreased and changed to pale green or red. Co(II) complexes were isolated by standard procedures.[2,10] The loss of the yellow color typical of Co(III) was rapid for [Co((NO$_2$)$_2$–sar)]$^{3+}$ but appreciably slower for [Co((NH$_2$)$_2$–sar)]$^{3+}$. Similar experiments with [Co(CH$_3$,NO$_2$–sar)]$^{3+}$ did not result in a diminution of the color over a similar time scale. Spectrophotometric examination for the presence of S$_2$O$_4$$^{2-}$ showed that essentially all the S$_2$O$_4$$^{2-}$ had been consumed on the time scale of the experiment.

The reductions were performed with 2:1 or 4:1 stoichiometric ratios of S$_2$O$_4$$^{2-}$:[Co((NO$_2$)$_2$–sar)]$^{3+}$, and the yellow color of Co(III) reappeared after the initial rapid reduction of Co(III). The yellow color was retained even after all the S$_2$O$_4$$^{2-}$ was consumed. When reductions were performed with a 2:1 stoichiometric ratio of S$_2$O$_4$$^{2-}$:[Co(CH$_3$,NO$_2$–sar)]$^{3+}$, again the yellow color typical of Co(III) was retained.

When excess dithionate was added to either [Co((NO$_2$)$_2$–sar)]$^{3+}$ (≥4.5:1 ratio for [S$_2$O$_4$$^{2-}$]:[[Co((NO$_2$)$_2$–sar)]$^{3+}$]) or [Co-(CH$_3$,NO$_2$–sar)]$^{3+}$ (≥2.5:1 ratio for [S$_2$O$_4$$^{2-}$]:[[Co(CH$_3$,NO$_2$–sar)]$^{3+}$]), the yellow color of the Co(III) hydroxylamine-substituted complexes slowly disappeared after the initial rapid reductions.

Product Identification

NMR Spectroscopy. The ^{1}H NMR spectra of all the products were complex in the methylene region, as a result of the rigidity of the cage ligand. The cap methylene groups for the D_3 cage complexes exhibited an AB quartet while an AA'BB' pattern was observed for the 1,2-ethanediamine moieties in D$_2$O. In favorable instances, these were clearly separated (e.g. [Co((NO$_2$)$_2$–sar)]$^{3+}$,[2] in Figure 3) and the chemical shifts of the four resonances were readily obtained.[2] However, the multiplets generally overlapped, especially where the cage complex was unsymmetrically substituted. The ^{1}H resonances of coordinated NH were not observed in D$_2$O due to rapid exchange of the protons but were observed in nonaqueous solvents or 12 M DCl/D$_2$O. Under these conditions the NH protons were seen to be coupled with the CH$_2$ protons, which further complicated the signals of methylene region. Unsymmetrically 1,8-substituted cage complexes generally ex-

(26) 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*, 3181–3182.

(27) 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*, 6016–6025.

Table III. ^1H and ^{13}C NMR (^1H-Decoupled) Spectral Data for Reduction Products of Nitro-Containing Cage Complexes

compd	^{13}C NMR[a,b] C (quax)	CH$_2$ (cap)	CH$_2$ (en)	other	^1H NMR (36% DCl)[a,c] NH	CH$_2$ (cage)	other	^1H NMR (D$_2$O)[a,d] CH$_2$ (cap) + CH$_2$ (en)	other
$[Co((NO_2)_2\text{-sar})]^{3+}$	+21.3	−15.7	−11.3		7.93	2.8–4.2	e	3.82, 3.28 (9 Hz)	2.88–3.51
$[Co(NH_2OH,NO_2\text{-sar})]^{4+}$	+21.2 (NO$_2$); −1.6 (NH$_2^+$OH)	−15.3; −15.6	−12.0		7.88	2.8–4.2	e	e	e
$[Co(NH_3,NO_2\text{-sar})]^{4+}$	+21.2 (NO$_2$); −10.4 (NH$_3^+$)	−15.3; −15.6	−11.7		f	f	e		e
$[Co((NH_2OH)_2\text{-sar})]^{5+}$	−2.1	−16.2	−12.7		7.60	2.8–4.0	e	e	e
$[Co(NH_3,NH_2OH\text{-sar})]^{5+}$	−1.8 (NH$_2^+$OH); −10.5 (NH$_3^+$)	−15.6 (NH$_3^+$); −16.6 (NH$_2^+$OH)	−12.2		7.82		e	e	e
$[Co(NH_3)_2\text{-sar})]^{5+}$	−10.3	−15.6	−11.7		7.92	2.8–4.0	e	e	e
$[Co(NHOH,NO_2\text{-sar})]^{3+}$	+21.2 (NO$_2$); −1.7 (NHOH)	−15.7; −15.6 (NHOH)	−11.4	e	7.90	2.8–4.0	e	2.8–3.8	e
$[Co(NH_2,NHOH\text{-sar})]^{3+}$	−1.8 (NHOH); −10.1 (NH$_2$)	−15.6 (NHOH); −11.8 (NH$_2$)	−11.8	e	e	e	e	2.8–3.5	
$[Co((NH_2)_2\text{-sar})]^{3+}$	−10.3	−11.6	−11.6		e	e	e	2.6–3.6	
$[Co(CH_3,NO_2\text{-sar})]^{3+}$	+21.1 (NO$_2$); −23.9 (CH$_3$)	−15.3 (NO$_2$); −12.1 (CH$_3$)	−11.6	−47.3 (CH$_3$)	7.68 (NO$_2$); 7.30 (CH$_3$)	3.9–4.2 (CH$_2$, cap); 2.5–3.8 (en + CH$_2$, cap)	0.96 (CH$_3$)	2.2–4.0	0.99 (CH$_3$)
$[Co(CH_3,NO\text{-sar})]^{3+}$[g]	−5.3 (NO); −23.9 (CH$_3$)	−15.1 (NO); −12.2 (CH$_3$)	−11.6	−47.3 (CH$_3$)	7.55 (NO); 7.32 (CH$_3$)	2.5–4.0	0.96 (CH$_3$)	f	
$[Co(NH_2OH,CH_3\text{-sar})]^{4+}$	−2.2 (NH$_2^+$OH); −24.2 (CH$_3$)	−17.0 (NH$_2^+$OH); −12.2 (CH$_3$)	−11.8	−47.3 (CH$_3$)	7.67 (NH$_2^+$OH); 7.29 (CH$_3$)	2.1–4.1	0.97 (CH$_3$)	e	0.98 (CH$_3$)
$[Co(NH_2,CH_3\text{-sar})]^{3+}$	−10.2 (NH$_2$); −24.5 (CH$_3$)	−11.6	−11.6	−47.0 (CH$_3$)	e	e	0.90 (CH$_3$)	2.2–3.8	
$[Co(NH_3,CH_3\text{-sar})]^{4+}$	−10.4 (NH$_3^+$); −24.0 (CH$_3$)	−15.5 (NH$_3^+$); −11.7 (CH$_3$)	−11.7	−47.3 (CH$_3$)	7.65 (NH$_3^+$); 7.26 (CH$_3$)	2.1–3.9	0.96 (CH$_3$)	e	e
$[Co(Cl,NO_2\text{-sar})]^{3+}$	+21.3 (NO$_2$); −4.8 (Cl)	−15.2 (NO$_2$); −11.3 (Cl)	−11.3	e	7.81	2.7–4.1	e	2.7–3.9	e
$[Co(Cl,NH_2OH\text{-sar})]^{4+}$	f	f	f	e	7.91 (NH$_2^+$OH); 7.62 (Cl)	2.8–4.0	e	f	f
$[Co(NH_2,Cl\text{-sar})]^{3+}$	−4.8 (Cl); −10.1 (NH$_2$)	−11.6	−11.6	e	e	e	e	2.7–3.9	f
$[Co(NH_3,Cl\text{-sar})]^{4+}$	−5.1 (Cl); −10.1 (NH$_3^+$)	−11.8 (Cl); −15.2 (NH$_3^+$)	−11.6	e	7.60 (Cl); 7.84 (NH$_3^+$)	2.8–4.0	e	e	f

[a] ppm; adjacent functional group is indicated in parentheses. [b] Positive downfield shifts vs 1,4-dioxane as an internal reference; ^1H decoupled. [c] Shifts vs NaTPS as an internal reference. [d] Shifts vs NaTPS as internal reference. [e] Not measured; NH protons deuterated. [f] Not applicable. [g] Only obtained in a very small amount; characterization is uncertain.

Table IV. UV/Vis and IR Spectral Data and Sensitivity to Tollen's Reagent of the Reduction Products of Nitro-Substituted Cage Complexes

compd	IR $\nu(NO_2)^a$	UV/vis λ $(\epsilon)^b$	Tollen's reagent test for NHOH
[Co((NO$_2$)$_2$-sar)]Cl$_3$·H$_2$O^c	1555, 1353^c	473.5 (146) 343.5 (124),^{c} 246 (17 700)^c	no
[Co(NH$_2$OH,NO$_2$-sar)]Cl$_4$	1557, 1347	475 (153), 344 (127)	yes
[Co(NH$_3$,NO$_2$-sar)]Cl$_4$	d	475 (155), 343 (129)	no
[Co((NH$_2$OH)$_2$-sar)]Cl$_5$	no	471 (139)^e	yes
[Co(NH$_3$,NH$_2$OH-sar)]Cl$_5$	no	475 (150), 343 (130)	yes
[Co((NH$_3$)$_2$-sar)]Cl$_5$	no	475 (149), 344.5 (130),^{c} 222, 240 sh	no
[Co(CH$_3$,NO$_2$-sar)]Cl$_3$	1556	472 (135), 344 (117)^c	no
[Co(NH$_2$OH,CH$_3$-sar)]Cl$_4$	no	d	yes
[Co(NH$_3$,CH$_3$-sar)]Cl$_4$	no	472 (139), 345 (123)^c	no
[Co(Cl,NO$_2$-sar)]Cl$_3$	1560, 1340^c	474 (148), 344.5 (123)^c	no
[Co(Cl,NH$_2$OH-sar)]Cl$_4$	no	d	yes
[Co(NH$_3$,Cl-sar)]Cl$_4$	no	d	no

$^a\nu$ in cm^{-1}; KBr disks. $^b\lambda$ in nm, ϵ in M^{-1} cm^{-1}; 0.1 M HCl; the first two bands are d–d transitions, and the third is the ligand to metal charge-transfer band. ^{c}Reference 2. ^{d}Not measured. ^{e}Reference 11.

Table V. Characteristic ^{13}C NMR Chemical Shifts for the Apical and Cap Methylene Carbon Atoms of Cobalt Cage Complexes

substituent	δ(apical)^a	δ(CH$_2$)^a
–NO$_2$	+21.2 ± 0.1	–15.5 ± 0.3
–NHOH	–1.8	–15.6
–NH$_2$	–10.2	–11.7
–NH$_2$OH^{+b}	–1.9 ± 0.3	–16.4 ± 0.6
–NH$^+_3$^{b}	–10.3 ± 0.2	–15.4 ± 0.3
–CH$_3$	–23.3 ± 0.4	–14.5 ± 2.9
–Cl	–5.0 ± 0.3	–11.6 ± 0.3

^{a}Downfield shifts in ppm versus 1,4-dioxane. ^{b}0.1 M DCl/D$_2$O.

hibited two distinct NH resonances of equal intensity (3 protons each) attributed to the coordinated NH groups. This pattern was used to determine whether different functional groups were bound to the caps of the various products and to aid in determining structure.[28]

The substituent NH$_3^+$ or NHR'R''$^+$ proton resonances were not observed even in 12 M DCl/D$_2$O. Therefore, these protons were presumed to have exchanged prior to measuring the spectrum, even under the strongly acidic conditions. However, such resonances were observed in DMSO-d_6, CDCl$_3$, or other deuterated nonaqueous solvents, but their chemical shifts were very dependent on the solvent and the anion.

By far, the best method for determining the nature of the substituents on a cage complex was ^{13}C NMR spectroscopy. Typical spectra are shown in Figure 3 (Table V). For symmetrically substituted (D_3) complexes, the proton-decoupled ^{13}C NMR spectra of the cage ligands consist of two singlets of equal intensities, corresponding to the methylenes of the cap and 1,2-ethanediamine moieties, and a third resonance of much weaker, but variable, intensity (depending on the complex), due to the quaternary carbons of the caps. The 1,2-ethanediamine carbons have ^{13}C NMR resonances that are relatively insensitive to the nature of the substituents (δ(CH$_2$ (en)) $\sim$ –11.7 ± 0.8) (Table III), which is not surprising, given their distance from the substituents. However, the cap methylenes, and especially the quaternary carbons, are particularly sensitive to the variations in functional groups (Table III). Each functional group appears to have a characteristic position for both of these resonances, as indicated in Table V. The utility of this technique for product identification is illustrated by Figure 3, which depicts the ^{1}H and ^{1}H-decoupled ^{13}C NMR spectra of the symmetrically substituted products of the Zn/HCl reduction of [Co((NO$_2$)$_2$-sar)]$^{3+}$. It can be seen that ^{1}H NMR spectroscopy is not definitive for product identification in this instance, whereas ^{13}C NMR spectroscopy is.

The factors governing the effect of the substituents on the ^{1}H, ^{13}C, and ^{59}Co NMR chemical shifts are discussed in detail elsewhere.[28]

Infrared Spectroscopy. Infrared spectroscopy was useful for the identification of the nitro group ($\sim$1560 and 1350 cm^{-1}).[29]
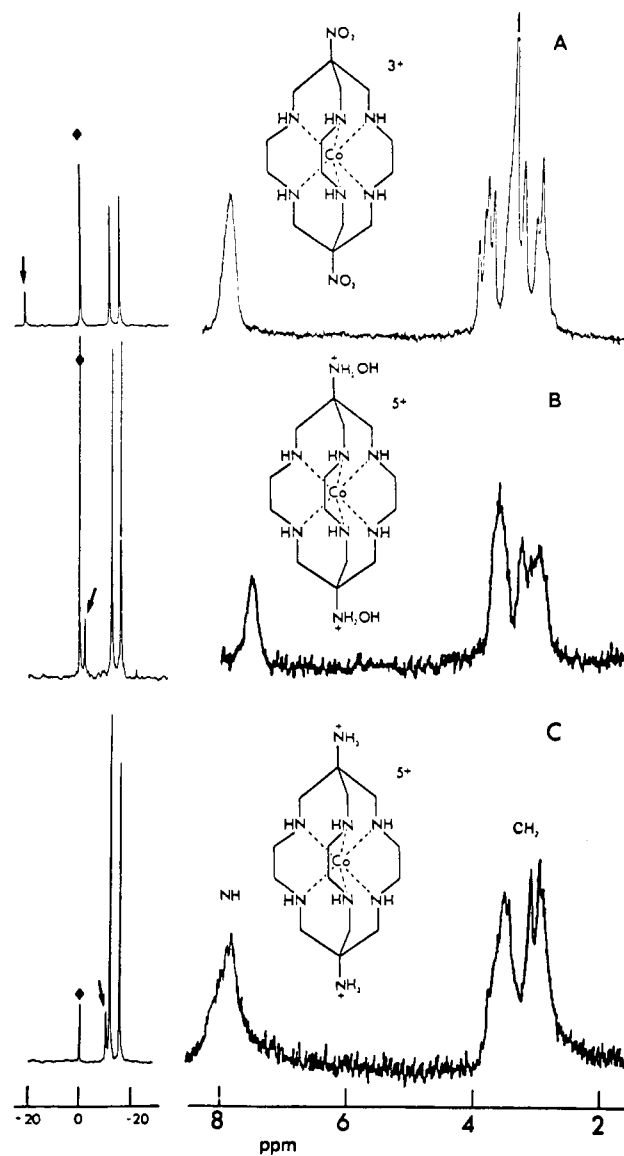
Figure 3. ^{1}H (36% DCl) and ^{13}C NMR (^{1}H decoupled, 0.1 M DCl/D$_2$O) spectra of [Co((NO$_2$)$_2$-sar)]$^{3+}$ (A), [Co((NH$_2$OH)$_2$-sar)]$^{5+}$ (B), and [Co((NH$_3$)$_2$-sar)]$^{5+}$ (C). (Quaternary C atoms are arrowed in ^{13}C NMR Spectra. Dioxane reference peak is denoted by ♦.)

Both the N–H and C–H stretching modes (2800–3400 cm^{-1}) were very prominent and formed a characteristic pattern indicative of the cage complexes, with two broad peaks of equal intensity at

(28) Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.*, submitted for publication.

(29) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974; Chapter 3.

~ 2900 and ~ 3100 cm^{-1}, which are attributed to C–H and N–H stretching modes, respectively.

Electronic Spectra. The positions of the d–d bands in the electronic spectra of the cage complexes were fairly independent of the nature of the substituents with two d–d transitions at ~ 474 nm ($\epsilon \sim 150$ M^{-1} cm^{-1}) and 344 nm ($\epsilon \sim 130$ M^{-1} cm^{-1}).[2,6] Such spectra are typical of other *lel*$_3$ hexaamine cobalt(III) complexes[10,30] (e.g. [Co(en)$_3$]$^{3+}$), except that the intensities were generally higher. Greater variations were noted in the positions of the charge-transfer bands (20 nm).

Tollen's Reagent Test for Hydroxylamine. The presence of hydroxylamine groups in products from the Zn/HCl reductions of nitro groups was readily ascertained by the deposition of silver on treatment with Tollen's reagent, according to the reaction[24]
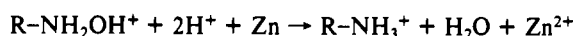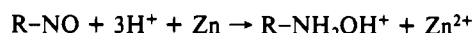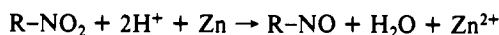
$$RNHOH + 2[Ag(NH_3)_2]OH \rightarrow$$
$$RNO + 2Ag + 4NH_3 + 2H_2O$$

Hydrazine substituents should also give a similar response.

Discussion

Synthesis. Reductions of Nitro Groups by Zn/HCl. The reduction of nitro groups to amines by Zn/HCl is well-known in organic chemistry.[12] For tertiary nitro groups, these reductions proceed in three 2-electron steps as shown in Scheme I.[13] The
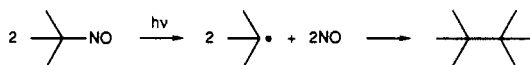
Scheme I

$$R{-}NO_2 + 2H^+ + Zn \rightarrow R{-}NO + H_2O + Zn^{2+}$$

$$R{-}NO + 3H^+ + Zn \rightarrow R{-}NH_2OH^+ + Zn^{2+}$$

$$R{-}NH_2OH^+ + 2H^+ + Zn \rightarrow R{-}NH_3{}^+ + H_2O + Zn^{2+}$$
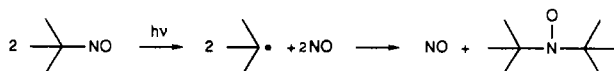
first 2-electron step produces the nitroso intermediate, which is reduced further in successive 2-electron reduction steps to the hydroxylamine and finally to the amine, provided protons are available. The expectation that the intermediates might be isolated after partial reduction of [Co((NO$_2$)$_2$–sar)]$^{3+}$ was not fully realized. All combinations containing nitro, hydroxylamine, and amine groups were isolated, but none containing nitroso groups. A small amount ($\sim 10\%$) of a mixture of dimeric and polymeric species was evident during the elution of the complexes from the cation-exchange columns, and it became apparent that these complexes arose from reactions involving the intermediate nitroso-substituted complexes. These highly charged complexes have not yet been characterized, but they presumably arise from known nitroso chemistry of the following kind: (i) dimerization of the nitrosyl groups[14]
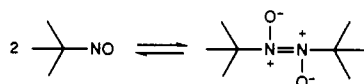
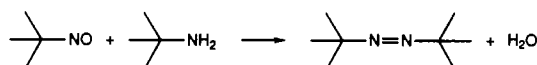(ii) photochemical cleavage and dimerization[15]

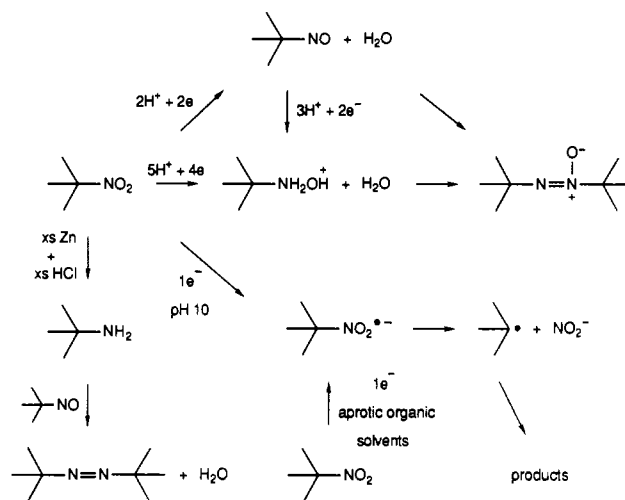(iii) photochemical cleavage, followed by reaction with a second nitroso group[16]

(iv) condensation with a hydroxylamine[17,18]

(v) condensation with an amine[31]

(30) Geue, R. J.; Hendry, A. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1646–1647. Hendry, A. J. Ph.D. Thesis, The Australian National University, 1986.

Scheme II

Although NMR spectroscopic analysis was performed on some of these dimeric complexes, they only relvealed that the products were unsymmetrical, which is to be expected. There were insufficient amounts to allow for a more positive identification of the nature of the bridge. The products from reactions iv and/or v are favored for the following reasons. A clean separation was observed, without dimers, when [Co(CH$_3$,NO$_2$–sar)]$^{3+}$ was reduced. Apparently, the trace of nitroso complex [Co(CH$_3$,NO–sar)]$^{3+}$ generated separated from [Co(NH$_2$,CH$_3$–sar)]$^{3+}$ and [Co(NHOH,CH$_3$–sar)]$^{3+}$ before the pH was increased sufficiently (pH 2 $\rightarrow$ 6) during the chromatography. This condition would obviate the condensations. Clearly, the dimeric products and the reactions leading to them require further characterization.

One of the best methods for the preparations of specific complexes was electroorganic synthesis. By use of this technique, the reductions to hydroxylamine complexes could be performed cleanly. The differences between the Zn and electrolytic reductions or those using dithionite are not surprising (despite claims to the contrary[11]) and are well understood in terms of known redox behavior of nitro groups.[6,12–18,21,32] This aspect has been elaborated elsewhere,[6] and the chemistry is summarized by Scheme II.

When similar reductions were performed with Sn^{2+}/HCl, a variety of products were obtained, even after long reaction times. It was apparent that the major component of such reactions was the hydroxylamine derivative. This prompted us to reinvestigate similar reductions involving [Pt((NO$_2$)$_2$–sar–H)]$^{3+}$, which were thought to give the [Pt((NH$_2$)$_2$–sar)]$^{4+}$ complex.[7] The positive test for hydroxylamine (Tollen's test) initially indicated that the complex might be [Pt((NHOH)$_2$–sar)]$^{4+}$, so the ^{13}C NMR spectral data were examined more closely. The single peak observed at +6.1 ppm for the apical carbon seemed too positive for an amine-capped species by comparison with the cobalt cage complexes. Furthermore, the chemical shift difference between the apical carbons with nitro substituents and those with amine substituents remained constant at ~ 31–34 ppm for Co(III) (Table V), Rh(III),[8] and Ir(III).[8] The 24 ppm difference observed for [Pt((NO$_2$)$_2$–sar)]$^{4+}$ and its reduction product is close to the difference observed between [Co((NO$_2$)$_2$–sar)]$^{3+}$ and [Co-((NHOH)$_2$–sar)]$^{3+}$ (23 ppm). In addition, the microanalysis for the supposed [Pt((NH$_2$)$_2$–sar)]$^{4+}$ complex allowed for at least two waters of crystallization[7] and, therefore, the microanalytical data were equally consistent with a [Pt((NHOH)$_2$–sar)]$^{4+}$ formulation. All these factors pointed to the bis(hydroxylamine) complex as the product of the Sn^{2+}/HCl reduction and not to the diamine-substituted complex, and that conclusion has now been substantiated by an X-ray crystallographic study.[7]
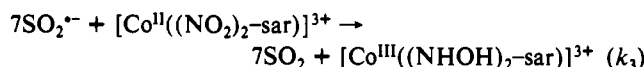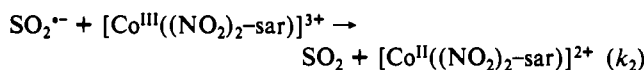
(31) Reference 17; p 278.
(32) Tomilov, A. P.; Mairanovskii, S. G.; Fioshin, M. Ya. Smirnov, V. A. *Electrochemistry of Organic Compounds* (English translation); Schmorak, J., Translator; Halsted Press: New York, 1972; Chapter 5.

Mechanisms of Reductions of Co(III) Complexes and Nitro Functional Groups. Recently, it was suggested that the comparatively fast reduction of $[Co((NO_2)_2-sar)]^{3+}$ as compared to $[Co(sep)]^{3+}$, $[Co((NH_2)_2-sar)]^{3+}$, and $[Co((NHOH)_2-sar)]^{3+}$ was due to channeling of electrons through the nitro groups to the cobalt center.[11] Reported in detail here are some of the results of earlier work, to clear up this and several other misconceptions within the kinetic paper.[11]

The self-exchange rate for the Co(III)/Co(II) couple of $[Co((NO_2)_2-sar)]^{3+}$ has been established to be approximately the same as other cage complexes from heterogeneous electron-transfer experiments, which mitigates the involvement of the nitro groups in affecting the rate of electron transfer.[1,6] Furthermore, the Co(II) complex may be produced electrochemically at the pH values mentioned previously for dithionite reductions,[11] and any intramolecular reductions of the nitro groups are slow, as shown by isolation of their Co(II) complexes, following controlled-potential electrolyses in solution. Certainly, the intramolecular $R-NO_2^-$ reduction of Co(III) cannot be on a time scale required to produce the overall second-order rate constant (3.5×10^5 M^{-1} s^{-1})[11] for reduction of Co(III) to Co(II). In the discussions of the rate of this second-order reduction, the authors[11] make no mention of the fast self-exchange rate of cage complexes in comparison to other Co(III)/Co(II) couples.[26,27,33-35] This more than compensates for differences in thermodynamic driving forces. Furthermore, the observation that no reduction of $[Co(sep)]^{3+}$, $[Co((NH_2)_2-sar)]^{3+}$, or $[Co((NHOH)_2-sar)]^{3+}$ was observed over a similar time scale is not compelling, since the more negative reduction potentials of these cage complexes ($\sim$-0.3 V vs [Co-$((NO_2)_2-sar)]^{3+/2+})$[6] means that the reduction by dithionite is >2 orders of magnitude slower than for $[Co((NO_2)_2-sar)]^{2+}$. Further, the reaction of the Co(II) complexes with dioxygen is >2 orders of magnitude faster than for $[Co((NO_2)_2-sar)]^{2+}$. Oxygen contamination is, therefore, a possible explanation for this discrepancy, especially in light of the experiments reported here, which clearly show that $[Co((NH_2)_2-sar)]^{3+}$ is reduced quantitatively by $S_2O_4^{2-}$ over a time scale of minutes.

Another claim made in the paper[11] was that it was surprising that the final product of the reduction was the Co(III) bis(hydroxylamine) cage complex $[Co((NHOH)_2-sar)]^{3+}$ (Scheme III).

Scheme III

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^{\bullet-} \qquad (K_1)$$

$$SO_2^{\bullet-} + [Co^{III}((NO_2)_2-sar)]^{3+} \rightarrow$$
$$SO_2 + [Co^{II}((NO_2)_2-sar)]^{2+} \quad (k_2)$$

$$7SO_2^{\bullet-} + [Co^{II}((NO_2)_2-sar)]^{3+} \rightarrow$$
$$7SO_2 + [Co^{III}((NHOH)_2-sar)]^{3+} \quad (k_3)$$

Again, from general thermodynamic considerations, the reduction of $[Co^{III}((NHOH)_2-sar)]^{3+}$ by $SO_2^{\bullet-}$ should be $\geq$20-fold slower than the reduction of the nitro groups ($\sim$300-fold slower than reduction of the $[Co((NO_2)_2-sar)]^{3+}$ complex). It is, therefore, unlikely that this reaction rate was determined in the kinetic measurements. Finally, the inter- or intramolecular oxidation of the Co(II) complex initially formed is to be expected. It is well-known in organic chemistry that nitroso groups are more readily reduced than aliphatic tertiary nitro groups,[12-18,31,32] and our work confirms that only small amounts of nitroso groups are obtained in partial reductions. The bulk of complexes isolated contain $-NO_2$, $-NHOH$, or $-NH_2$ derivatives, confirming the high susceptibility of nitroso intermediates to rapid subsequent reductions. Given the greater thermodynamic driving force for the intramolecular (or intermolecular) reduction by Co(II) of the nitroso group as compared to the nitro group, it is expected that the Co(II) oxidation state would be oxidized rapidly by nitroso

Scheme IV
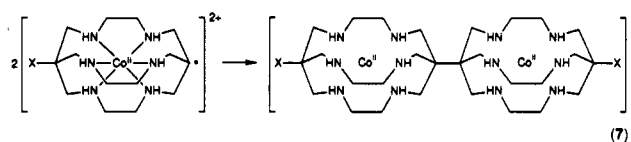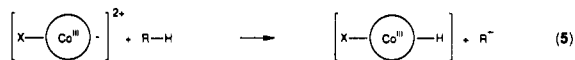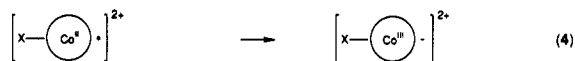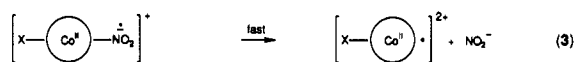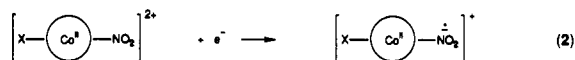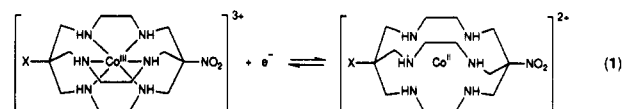
intermediates. Also, the observation of hydroxylamine substituents in the final reduction product is to be expected at the high pH values, in light of well-known organic chemistry.

It is also worth pointing out that the reductions of $[Co((NO_2)_2-sar)]^{3+}$, $[Co(CH_3,NO_2-sar)]^{3+}$, and $[Co(Cl,NO_2-sar)]^{3+}$ by the excited state of $[Ru(bpy)_3]^{2+}$ ($[Ru^*(bpy)_3]^{2+}$) show no abnormal behavior and have quenching constants commensurate with their Co(III)/Co(II) redox potentials.[36-38] This again supports the notion that redox reactions occur initially by reduction of the metal ion and not of the nitro substituents.

Another puzzling feature of the previous kinetic study[11] is that it was reported that pseudo-first-order kinetics were found for both k_2 and k_3 when the initial concentrations of $[Co((NO_2)_2-sar)]^{3+}$ and $S_2O_4^{2-}$ were the same. It is difficult to reconcile how this could be the case.

The different behavior observed in the reductions by $S_2O_4^{2-}$ of $[Co((NO_2)_2-sar)]^{3+}$ and $[Co(CH_3,NO_2-sar)]^{3+}$ is probably due to the differences in their Co(III)/(II) redox potentials. $[Co-((NO_2)_2-sar)]^{3+}$ has a Co(III)/Co(II) redox potential which is 230 mV more positive than that of $[Co(CH_3,NO_2-sar)]^{3+}$. This will lead to the rate constant for the reduction of $[Co-(CH_3,NO_2-sar)]^{3+}$ at the cobalt center being 2 orders of magnitude smaller than the rate constant for the reduction of $[Co-((NO_2)_2-sar)]^{3+}$ to the Co(II) complex. Therefore, the reduction of the nitro group of $[Co(CH_3,NO_2-sar)]^{2+}$ is more rapid than the reduction of the cobalt center and the diminution of the yellow color due to Co(III) only occurs after the nitro group has been reduced to the hydroxylamine group.

The reduction of the nitro complexes in nonaqueous media poses some further interesting problems. It appears that intramolecular electron transfer between the bridgehead radical species and Co(II) is much faster than that between the nitro radical anions and Co(II). In the absence of a proton source, the redox chemistry may be best described by Scheme IV. Step 3 is well-known in

(33) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23-27.

(34) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022-4029.

(35) Dubs, R. V.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2523-2527.

(36) Creaser, I. I.; Gahan, L. R.; Geue, R. J.; Launikonis, A.; Lay, P. A.; Lydon, J. D.; McCarthy, M. G.; Mau, A. W.-H.; Sargeson, A. M.; Sasse, W. H. F. *Inorg. Chem.* **1985**, *24*, 2671-2680.

(37) Launikonis, A.; Lay, P. A.; Mau, A. W.-H.; Sargeson, A. M.; Sasse, W. H. F. *Aust. J. Chem.* **1986**, *24*, 243-250.

(38) Creaser, I. I.; Launikonis, A.; Lay, P. A.; Sargeson, A. M.; Sasse, W. H. F. To be submitted for publication.
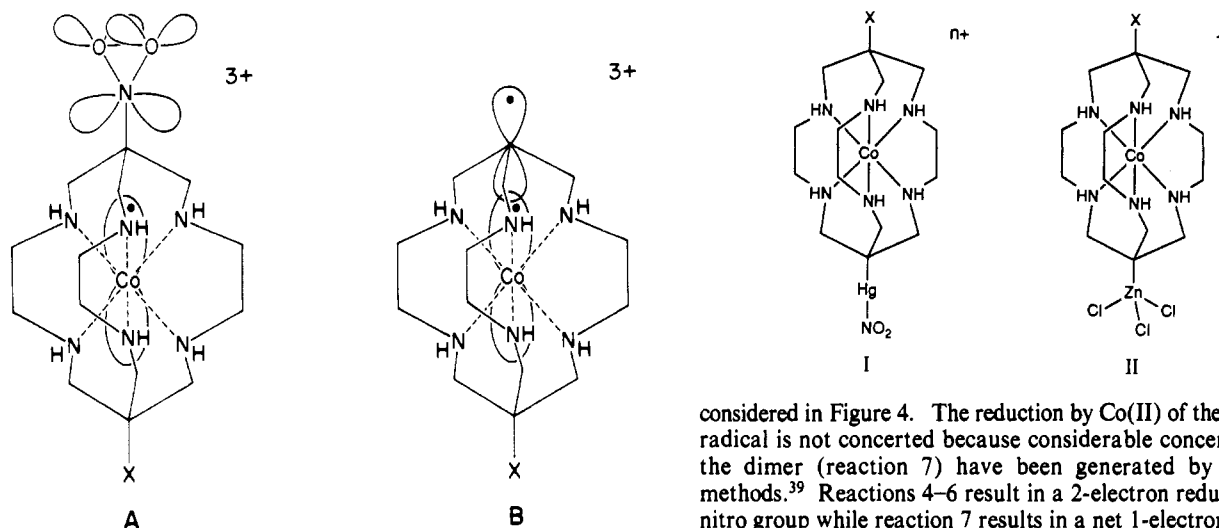
Figure 4. Overlap between the $\pi^*(NO_2)$ orbital and a Co(II) t_2 orbital (A) and between a bridgehead radical p_z orbital and a t_2 orbital of Co(II) (B).

organic chemistry, and the intramolecular redox process (4) has been detected during photochemical production of the radical species.[39] The exact role of the electrode in these reductions is uncertain but organomercury complexes of the type shown in I could be intermediates by analogy with the well-characterized and stable zinc species II.[40] Unlike the reduction of the nitro groups, the reduction of radical species via an intramolecular route is expected and observed to be very facile. Such an expectation arises from a consideration of the geometric overlap of orbitals, as

(39) Lydon, J. D.; Sargeson, A. M.; Snow, M. R. Manuscript in preparation. See also: Sargeson, A. M. *Pure Appl. Chem.* **1984**, *56*, 1603–1619.
(40) Creaser, I. I.; Lydon, J. D.; Sargeson, A. M.; Horn, E.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5729–5731.

considered in Figure 4. The reduction by Co(II) of the bridgehead radical is not concerted because considerable concentrations of the dimer (reaction 7) have been generated by alternative methods.[39] Reactions 4–6 result in a 2-electron reduction of the nitro group while reaction 7 results in a net 1-electron reduction. The competition between these two pathways may explain the variation in electron counts between 1 and 2 electrons for coulometric reductions performed in aprotic solvents. Some of the above facets are currently being investigated further.

Conclusions

By control of reductions it is seen that the products from the reduction of nitro functional groups of cage complexes may be controlled, in part, to give desired products. Further details are needed of work involved in the synthesis of azoxy-bridged cage complexes. It is apparent that the above chemistry leaves open many potential areas of interest.

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^{77}Se NMR Spectroscopic Study of Fluxional Selenium Sulfide 1,2,3,4,5-Se$_5$S$_2$

Pentti Pekonen,[1a] Yrjö Hiltunen,[1b] Risto S. Laitinen,*,[1a] and Tapani A. Pakkanen[1c]

The ^{77}Se NMR spectrum has been recorded for the fluxional heterocyclic selenium sulfide 1,2,3,4,5-Se$_5$S$_2$, which has been prepared from the ^{77}Se-enriched [Ti(C$_5$H$_5$)$_2$Se$_5$] (enrichment 94%) and from S$_2$Cl$_2$. The spectrum shows three second-order multiplets at 1087.1, 1025.0, and 978.9 ppm (relative to Me$_2$Se) corresponding to a five-spin [AMM'XX'] system. A simulation enables the complete assignment of all transitions to be made and yields the refined values of all ^{77}Se–^{77}Se coupling constants. The number of NMR signals, their coupling pattern, and the values of the spin–spin coupling constants are consistent with the concept of facile pseudorotation in the seven-membered chalcogen-containing ring molecules.

^{77}Se NMR spectroscopy is a useful tool for the identification and characterization of individual heterocyclic selenium sulfides, which are generally produced as a complicated mixture of different molecular species (for a recent review, see ref 2). The spectral analysis has been based on the combined information obtained from the ^{77}Se NMR spectra of the samples containing natural-abundance selenium and from those of the ^{77}Se-enriched samples of the same chemical composition.[3,4]

Bis(cyclopentadienyl)titanium sulfides and selenides of the types [Ti(C$_5$H$_5$)$_2$E$_5$] and [Ti(C$_5$H$_5$)$_2$(μ-E$_2$)$_2$Ti(C$_5$H$_5$)$_2$] (E = S, Se) have successfully been applied in the preparation of stoichiometrically pure selenium sulfides with ring sizes of six, seven, and eight.[5]

(1) (a) Department of Chemistry, University of Oulu. (b) Department of Physics, University of Oulu. (c) University of Joensuu.
(2) Laitinen, R. S. *Acta Chem. Scand., Ser. A* **1987**, *41*, 361.
(3) Because of the low natural abundance of the ^{77}Se isotope, the ^{77}Se–^{77}Se coupling effects can only be seen as small satellites that are often lost in the background. Isotope enrichment leads to complete information on the coupling when the enrichment is sufficiently high.
(4) (a) Laitinen, R. S.; Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1381. (b) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598. (c) Laitinen, R. S.; Pekonen, P.; Hiltunen, Y.; Pakkanen, T. A. *Acta Chem. Scand.* **1989**, *43*, 436.