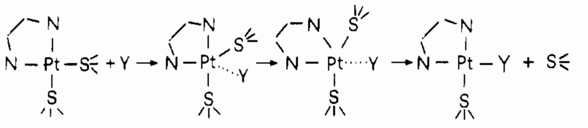
the high lability of the bis(sulfoxide) complex is due, in part at least, to stabilization of five-coordination relative to that of reagents and products together with a parallel lowering of the energies of the two transition states. The contribution made by the sulfoxide to this stabilization is thought to be due to its ability to act as a π-acceptor. This, however, is not enough to explain the peculiar mutual destabilization of a pair of cis sulfoxides. In the classical trigonal-bipyramidal intermediate, the originally cis ligands occupy axial positions and cannot contribute to the π interactions and so we would like to suggest that the usual intermediate undergoes a twist that places both sulfoxides in equatorial positions and that this twist occurs early in the bond making stage



otherwise the high lability could not be explained. Any steric effects which would be exacerbated by the increase of coordination number would be reduced again if both sulfoxides were in the trigonal plane, and this might serve as the driving force to the more π-bonded configuration. The idea of pseudorotation when the incoming group is still loosely bound can account for catalyzed isomerization[17] or substitution without retention of configuration. However, it must be more complicated than the Berry twist.

The extent to which classical steric effects contribute to the mutual labilization is not clear. There is no indication of any strong mutual repulsion between the two sulfoxides in the four-coordinate substrate.[6] Bond lengths and angles are not abnormal; the slightly enlarged S-Pt-S angle (93.8°) is probably due to the small bite of the chelate opposite it (N-Pt-N = 80.9°) since it is not observed in the other *cis*-bis(dimethyl sulfoxide) complexes whose structures have been determined, *cis*-$[Pt(Me_2SO)_2Cl_2]$[2] and *cis*-$[Pt(Me_2SO)_2(C_6H_5)_2]$,[18] the increase in the Pt-S bond length in the latter being ascribed to the trans influence of the phenyl group. In any case, steric acceleration of an A mechanism with a tight transition state seems paradoxical. If the ground state is destabilized by crowding, the associative transition state will be even more destabilized and the reactivity will be reduced (classical steric hindrance). However, if, as suggested above, some of this strain is relieved by an intramolecular twist that places both sulfoxides in equatorial positions, the steric hindrance can be used to facilitate the associative process.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the Ministry of Education and of the Italian CNR.

Registry No. $[Pt(en)(Me_2SO)_2](PF_6)_2$, 85664-82-0; $[Pt(en)(Me_2SO)(H_2O)]^{2+}$, 51542-85-9; Me_2SO, 67-68-5; NO_2^-, 14797-65-0; N_3^-, 14343-69-2; Cl, 22537-15-1; Br, 10097-32-2; I, 14362-44-8; SCN^-, 302-04-5; $SC(NH_2)_2$, 62-56-6.

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Electrochemistry of Macrobicyclic (Hexaamine)cobalt(III) Complexes. Metal-Centered and Substituent Reductions[1]

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Received October 26, 1982

The electrochemistry of a wide range of macrobicyclic hexaamine ("cage") and polyamine complexes of cobalt(III) is reported. All of the substituted $[Co(sar)]^{3+}$ and $[Co(absar)]^{3+}$ cage complexes exhibit chemically reversible Co(III)/Co(II) couples (sar = sarcophagene = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane, absar = 3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane). The Co(II) oxidation state for these complexes is substitutionally inert and undergoes irreversible reduction at very negative potentials in nonaqueous solvents ($\lesssim -2$ V). Quasi-reversible behavior is apparent with all the complexes under study in both aqueous (ClO_4^- and $CF_3SO_3^-$ media) and nonaqueous (acetone and acetonitrile, $CF_3SO_3^-$ media) solvents. However, in aqueous perchlorate media, at a mercury interface, these reductions are complicated by adsorption processes. The potential of the Co(III)/Co(II) couple is markedly dependent on the nature of substituents on the cage ligand and varies by ~0.6 V for the apically substituted $[Co(sar)]^{3+/2+}$ series. Other factors that influence the potential are preferred cavity size of the cage ligand and outer-sphere medium effects. For each series of structurally similar ligands with constant medium and electrode, the heterogeneous rate constants are the same within experimental error. In addition to the metal-centered electrochemistry, many of the complexes exhibit redox processes of electroactive organic substituents. These processes are utilized in selected electroorganic syntheses of new cage complexes. The pH dependence of the Co(III)/Co(II) couple is a useful probe to the acidity of various functional groups, and some applications in determining pK_a values are described.

Introduction

Several syntheses of macropolycyclic molecules, commonly called cryptands, have been described.[4] These ligands can form inclusion complexes with cations, anions, and small molecules, denoted as cryptates. Recently, syntheses of a range of macrobicyclic (hexaamine)cobalt(III) complexes of the 20-membered [6.6.6]icosane structure (I) have been developed, based on organic syntheses with the inert $[Co(en)_3]^{3+}$ ion as a template (en = 1,2-ethanediamine).[5-10] In keeping with the

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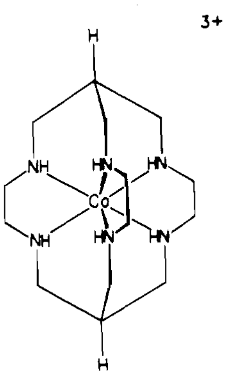

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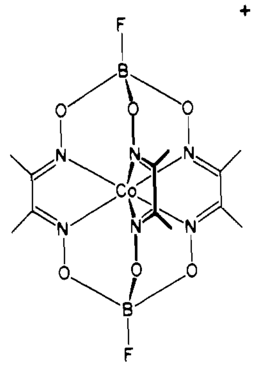
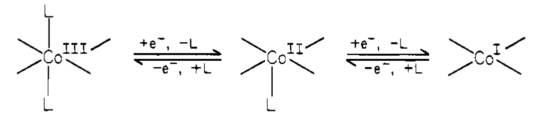


II

existing necrotic nomenclature for encapsulated complexes, these ligands have been given trivial names based on the parent structure sarcophagine (I), abbreviated sar.[7] The redox properties of these encapsulated metal ions or "cage" complexes, and of precursor and related multidentate ligand complexes, have now been subjected to an extensive electrochemical investigation.

Cobalt(III) amine complexes are kinetically inert (d^6, low spin) and undergo one-electron reductions to usually labile cobalt(II) complexes (d^7, high spin), which may or may not be reversible.[11-14] Reduction of $[\mathrm{Co(NH_3)_6}]^{3+}$ to cobalt(II) is irreversible in most solvents due to rapid ligand substitution,[11] which typically occurs on the μs time scale.[15] However, complexes with bi- or multidentate ligands such as $[\mathrm{Co(en)_3}]^{3+}$ or $[\mathrm{Co(dien)_2}]^{3+}$ (dien = 3-aza-1,5-pentanediamine), undergo reversible reductions under conditions where the cobalt(II) complexes retain their integrity on the voltammetric time scale.[12,13] These initial reductions are invariably followed by an irreversible two-electron reduction to cobalt metal at more negative potentials. Complexes of cobalt(III) with macromonocyclic,[16] Schiff base,[17] dimethylglyoximato,[18] or vitamin B_{12} ligands[19] apparently exhibit two one-electron steps to produce cobalt(II) and then cobalt(I) (d^8, square planar) complexes. Often, no further reduction to cobalt metal is observed at accessible potentials. Such reductions are accompanied by stereochemical change involving loss of axial ligands (eq 1).[16-19] Limited electrochemical studies of the macrobicyclic cobalt(II) ion (II) have been reported where the opportunity to lose one or two ligands no longer exist. In these instances, cobalt(III) and cobalt(I) species were observed,[20] comparable to the electrochemistry of $[\mathrm{Co(bpy)_3}]^{3+}$ (bpy = 2,2′-bipyridyl), which involves several reversible reductions (eq 2).[21]



(1)

$$[\mathrm{Co(bpy)_3}]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Co(bpy)_3}]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Co(bpy)_3}]^{+} \xrightarrow{2e^-} [\text{products}] \quad (2)$$

The cobalt(III) macrobicyclic cage complexes I are constrained to be six-coordinate upon reduction unless the cage ruptures. Preliminary studies have established that the cobalt(II) oxidation state is unusually substitution inert and retains an octahedral geometry in these hexaamine cage complexes.[5,9,10] No exchange with ^{60}Co was observed within 17 h at room temperature, and the cobalt(III) species were regenerated completely, even with full retention of chirality. It was of interest, therefore, to examine whether these cage complexes more closely resembled the simple amine complexes or those species capable of stabilizing cobalt(I).

Another aspect for study was the electrochemistry of electroactive substituent groups, which was expected to parallel the extensive functional-group electrochemistry in organic molecules where substituents are located on quaternary carbons. The effects of substituents and ligand cavity size on the redox potential of the Co(III)/Co(II) couple have been probed.

Experimental Section

Syntheses of the precursor, macrobicyclic, and multidentate ligand complexes have been described or are being prepared for publication.[5-10,22] When required, complexes were converted into trifluoromethanesulfonate ($\mathrm{CF_3SO_3^-}$, triflate) salts by dissolution of the chloride salt of a complex in distilled anhydrous $\mathrm{CF_3SO_3H}$ (~0.1 g/mL). The resultant solution was warmed at ~50 °C while N_2 was passed through the solution for 0.5 h to remove HCl gas, and diethyl ether (5 volumes) was added after cooling in an icebath. *Caution! The reaction is vigorous.* The precipitate was collected by filtration, washed with ether, and air-dried.

Supporting electrolytes were $\mathrm{NaClO_4{\cdot}H_2O}$ (AR) or $\mathrm{NaCF_3SO_3{\cdot}H_2O}$ in water and $\mathrm{NaCF_3SO_3}$ or $\mathrm{R_4NCF_3SO_3}$ salts (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$) in nonaqueous solvents acetone (p.A., AR), acetonitrile (Riedel-DeHaen, AG), dimethylformamide (Mallinckrodt, AR) or, for low-temperature electrochemistry, butanenitrile (Ega, 98%). Standard purification methods were used when required. $\mathrm{(CH_3)_4NCF_3SO_3}$ and $\mathrm{(C_2H_5)_4NCF_3SO_3}$ were prepared by a method analogous to that previously described,[23] involving neutralization of aqueous $\mathrm{R_4NOH}$ with neat $\mathrm{CF_3SO_3H}$. Purity of the electrolytes was evaluated by microanalysis and by the absence of extraneous waves in dc polarograms of acetonitrile solutions of each compound.

The accessible potentials in aqueous media are restricted by oxidation or reduction of water or electrolytes and are dependent on the pH and working electrode.[24] Useful potential ranges are greatly increased in nonaqueous solvent systems. The use of $\mathrm{R_4NCF_3SO_3}$ salts as supporting electrolytes resulted in potential ranges similar to those obtainable with perchlorate salts.[25] Ranges of >4 V were readily accessible, and the triflate salts of complexes generally were much more soluble (in triflate media) than the corresponding perchlorates (in perchlorate media). Furthermore, the triflate salts were readily and safely dehydrated at 110 °C in a vacuum oven without complex decomposition. Triflate supporting electrolytes and triflate salts of complexes were used routinely in all nonaqueous work and in water where solubility problems with perchlorate systems arose.

Standard electrochemical measurements were performed with either a PAR Model 174A polarographic analyzer coupled with a Houston Instruments Ominigraphic 2000 recorder or a PAR Model 170

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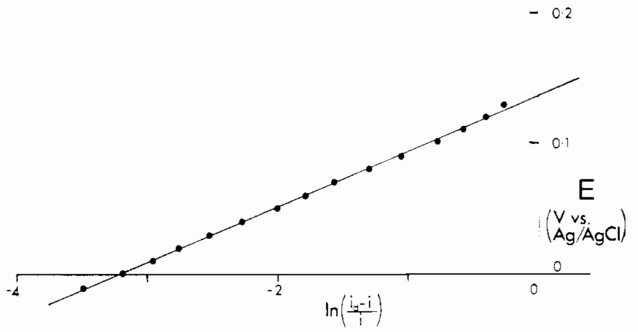

Figure 1. Heyrovsky–Ilkovic plot from the dc polarogram of a 2×10^{-3} M solution of $[Co(diNOsar)](CF_3SO_3)_3$ in a 0.1 M $Me_4NCF_3SO_3$ acetone solution at the DME.

electrochemistry system. Rapid-scan cyclic voltammograms (>500 mV/s) were obtained as photographs on a Tektronix C-70 oscilloscope camera attached to a Tektonix 5031 dual-beam storage oscilloscope coupled with the PAR 170 system. Coulometric measurements were achieved with a PAR Model 173 potentiostat–galvanostat with a Model 179 digital coulometer or an Amel Model 731 digital integrator in conjunction with an Amel Model 551 potentiostat. PAR coulometry cell systems, Models 9800 or 377A, or coulometry cells of our own design, were used in such measurements, with a mercury pool or platinum basket as working electrode.

In all experiments the conventional three-electrode system was used, with positive feedback *iR* compensation in voltammetric experiments. The auxiliary electrode was platinum wire (or gauze, for coulometry), and the reference electrode was saturated calomel (SCE) or Ag/AgCl/LiCl (saturated in acetone) for aqueous or nonaqueous solutions, respectively. A salt bridge containing the solvent and electrolyte used in the working compartment separated the reference electrode from the solution in that compartment. For voltammetry, the working electrode was a PAR Model 172A dropping mercury electrode (DME), platinum or gold wire, or a Beckmann rotating Pt disk. Certain experiments were performed with a PAR Model 303 static dropping mercury electrode (SMDE) interfaced with the PAR Model 170 with a Ag/AgCl/saturated KCl reference electrode (water); this electrode has the capacity to operate as a hanging mercury drop electrode (HMDE). All solutions were degassed with N_2 or Ar that had been presaturated with the solvent used in the working compartment of the cell.

Diffusion coefficients (*D*) were evaluated by using the Ilkovic equation for the maximum diffusion current from dc polarograms obtained at the DME.[26] Values of the reduction potentials ($E_{1/2}$) were obtained from the intercepts of plots of log $[(\bar{i}_d - \bar{i})/\bar{i}]$ vs. potential (*E*), as illustrated in Figure 1. In addition, the number of electrons involved in the reversible electrode process were estimated from the slopes of such plots of the Heyrovsky–Ilkovic equation:

$$E = E_{1/2} + \frac{RT}{nF} \ln [(\bar{i}_d - \bar{i})/\bar{i}] \qquad (3)$$

Charge-transfer coefficients (α) were evaluated by using the equation

$$[E_{dc}]_p - E_{1/2}{}^r = \frac{RT}{nF} \ln [(1 - \alpha)/\alpha] \qquad (4)$$

for ac polarograms at the DME.[27,28] Plots of the ac peak current, $[I(\omega t)]_p$, vs. $\omega^{1/2}$ (ω = frequency),[28,29] or alternatively, dc cyclic voltammetry at variable scan speeds were used to evaluate the heterogeneous electron-transfer rate constant (k_s), at Hg, Au, and Pt electrodes.[30-32]

Electronic absorption spectra of electrochemically reduced species were recorded in situ with a short (2 mm) path length spectroelectrochemical cell incorporating a gold minigrid working electrode, a Pt auxiliary electrode, and an SCE or Ag/AgCl reference electrode.[33] Values of the molar absorptivities (ϵ) were determined from the concentration of the Co(III) precursor complexes.

Electron paramagnetic resonance (EPR) spectra of species generated in situ at low temperature under an inert atmosphere (N_2 or Ar) were performed with a cell[33] incorporating a helical gold coil working electrode[34] with use of a JEOL JES-PE spectrometer fitted with a VT-3A variable-temperature controller. Electrolyses were performed at low temperature (~−40 °C, acetonitrile; ~−80 °C, acetone; ~−100 °C, butanenitrile) for ~5 min; the temperature was then reduced rapidly to −160 °C and the EPR spectrum recorded on the frozen solution.

The pK_a values were obtained from the variation in peak potential, E_p, with pH of the Co(III)/Co(II) couple from derivative dc polarography at the DME. The pH was monitored with a combination glass–calomel electrode immersed in the aqueous solution under study and was adjusted by addition of acid or base. The pK_a value was calculated from the best fit to the expression

$$E_p = \left\{\frac{1}{1 + K_a/[H^+]}\right\}(\Delta E_p) + E_p(B^-) \qquad (5)$$

where ΔE_p is the difference in the values for the protonated complex (E_p(BH)) and the conjugate base ($E_p(B^-)$).

Controlled-potential electrolyses were performed at potentials ~0.2 V more negative than $E_{1/2}$ for the reduction. In situ voltammetric monitoring of products following electrolysis was performed to ascertain the nature of products from functional-group electrode processes. Complexes were isolated by one of the following techniques. The solutions were reoxidized to their cobalt(III) states, diluted 20-fold with water, and sorbed on a column of SP-Sephadex C-25 resin. After they were washed with water, the complexes were eluted with 0.13 M disodium (+)$_D$-tartrate. Each band was collected separately and sorbed on a short column of Dowex 50W-X2 resin. The column was washed with 1 M HCl, the complex was eluted with 3 M HCl, and the eluant was evaporated to dryness. Alternatively, in nonaqueous solvents, the complexes were reoxidized to cobalt(III) coulometrically and were precipitated by the addition of a saturated solution of $(C_2H_5)_4NCl$ in acetonitrile. The latter procedure was employed also for isolation of cobalt(II) complexes, except solutions were deaerated with N_2 or Ar during the addition. Complexes were recrystallized by addition of excess solid $NaClO_4 \cdot H_2O$ to concentrated aqueous solutions. Isolated complexes were characterized by ^1H and ^{13}C NMR and IR spectroscopy and by comparison with well-characterized cage complexes prepared by less selective chemical means.[5-9]

Results

Nomenclature. The wide range of macrobicyclic and macropolycyclic complexes synthesized about a metal ion complex, including the range discussed here, requires the use of a practical trivial nomenclature, since IUPAC names are clearly too long for frequent use. From work in these and other laboratories,[5-10,20,35-46] greater than 30 heteropolycyclic com-

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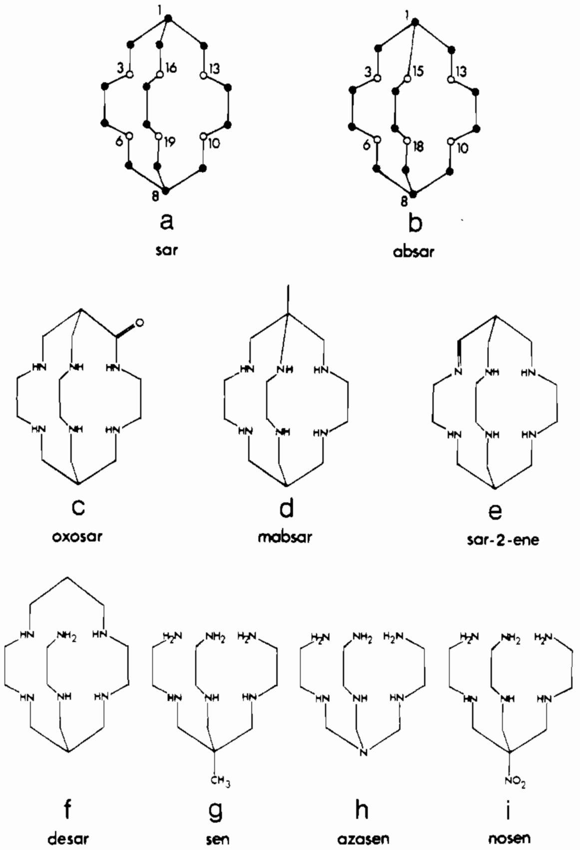
Table I. Abbreviations Used for Substituents in the Trivial Nomenclature System

pr[a]	prefix	group	pr	prefix	group
1	AZA	N⋞	27	CL	$-Cl$
2	CA[b]	$-COO^{-}$	11	CA	$-COOH$
3	AM[c]	$-N^{+}H_3$	15	AM	$-NH_2$
4	HA[c]	$-N^{+}H_2OH$	18	HA	$-NHOH$
5	MeAM[c]	$-N^{+}H_2CH_3$	19	MeAM	$-NHCH_3$
6	Me$_2$AM[c]	$-N^{+}H(CH_3)_2$	20	Me$_2$AM	$-N(CH_3)_2$
7	Me$_3$AM	$-N^{+}(CH_3)_3$	12	EF	$-COOC_2H_5$
31	NO	$-NO_2$	32	NI	$-NO$
30	ME	$-CH_3$	29	HM	$-CH_2OH$
14	HO	$-OH$	13	CN	$-CN$
16	AA	$-NHCOCH_3$	25	PI	-NPhth[e]
17	TsAM	-NHTs[d]	24	TerIM	$-NCH\text{-}4\text{-}C_6H_5CHO$
9	SalAM[c]	$-N^{+}H_2CH_2\text{-}2\text{-}C_6H_5OH$[c]	22	SalAM	$-NHCH_2\text{-}2\text{-}C_6H_5OH$
10	BzAM[c]	$-N^{+}H_2CH_2C_6H_5$[c]	23	BzAM	$-NHCH_2C_6H_5$
8	TerAM[c]	$-N^{+}H_2CH_2\text{-}4\text{-}C_6H_5CHO$	21	TerAM	$-NHCH_2\text{-}4\text{-}C_6H_5CHO$
26	BzIM	$-NCHC_6H_5$	28	HY[f]	$-H$

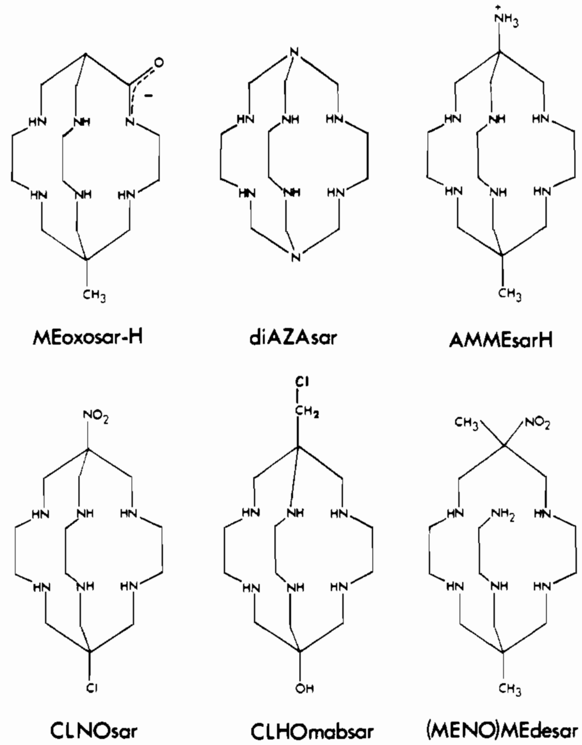
[a] Order of precedence of functional groups. [b] The suffix -H is also required to denote deprotonation. [c] The prefix H is also required to denote protonation. [d] Ts = 4-methylbenzenesulfonate. [e] -NPhth = phthalimide. [f] Rarely used and only to remove ambiguities.



a sar
b absar
c oxosar
d mabsar
e sar-2-ene
f desar
g sen
h azasen
i nosen

Figure 2. Structures and trivial nomenclature for the polydentate and macrobicyclic amine ligands.

plexes and their derivatives have been identified. They involve more than 20 basic ring systems, which may be bicyclic, tricyclic, or tetracyclic. A systematic IUPAC name can be written for each basic (unsubstituted) cage ligand, with use of IUPAC replacement nomenclature for both cyclic (IUPAC rule B4) and acyclic (IUPAC rule C.0.6) compounds.[47] We have based our nomenclature on the assignment of a trivial name to the unsubstituted parent heteropolycycle. Substituents are then ordered and numbered according to the normal IUPAC rules. For brevity, abbreviations for all substituents have been adopted (Table I).



MEoxosar-H diAZAsar AMMEsarH

CLNOsar CLHOmabsar (MENO)MEdesar

Figure 3. Examples of structures and trivial nomenclature for substituted cage ligands.

The basic and most common cage ligand discussed has the 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane structure of Figure 2a; this is given the abbreviation sar (sarcophagine). The other cage ligand dealt with here has the 3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane structure of Figure 2b, abbreviated absar. Since, for the purpose of this study, substituents in other than the apical (1- and 8-) positions are rare, these cage ligands can be afforded an extended trivial nomenclature. Thus, the 2-oxo-substituted sar cage ligand of Figure 2c will be called oxosar and the substituted 1-methyl-absar cage ligand of Figure 2d will be called mabsar. The partially unsaturated sar ligand of Figure 2e will be called sar-2-ene. Various macrocyclic or multidentate ligand complexes have been studied and can be viewed as "partial" cage complexes or cage complex precursors. Subsequently, the macrocycle of Figure 2f is called desar, and the multidentate ligands of parts g, h, and i of Figure 2 are called sen, azasen, and nosen, respectively. Table I contains the abbreviations used in the trivial nomenclature for substituents on the basic cage ligands. Where both apical substituents are the same,

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(45) Biradar, N. S.; Goudar, T. R. *Inorg. Chim. Acta* **1977**, *23*, 63–66.
(46) Hammershøi, A.; Sargeson, A. M. *Inorg. Chem.*, in press.
(47) "IUPAC Nomenclature of Organic Chemistry"; Pergamon Press: London, 1979; Sections A–F, H.

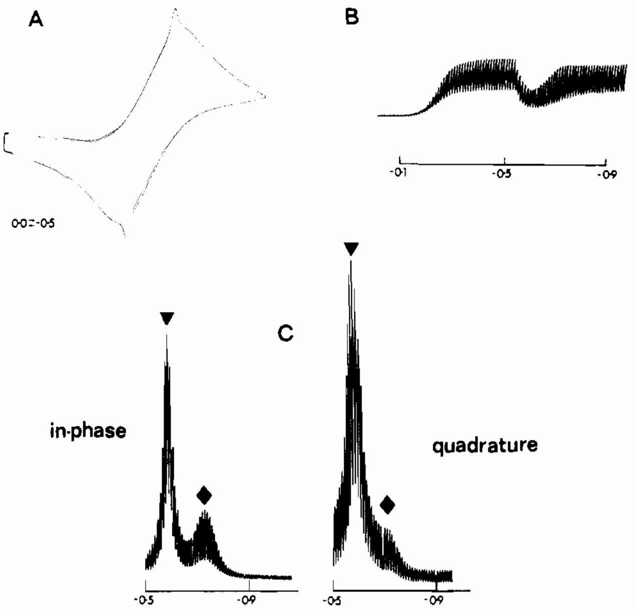

Figure 4. Adsorption/desorption processes in Co(III)/Co(II) couples: (A) tensiometric spikes in the dc cyclic voltammogram of a 2 × 10^{-3} M Co(diNOsar)$^{3+}$ solution in aqueous 0.1 M $NaClO_4$ solution at the HMDE, due to surface precipitation (scan rate 50 mV/s); (B) desorption of Co(diAZAsar)$^{3+}$ in the dc polarogram at the DME of a 2 × 10^{-3} M solution of the complex in acetonitrile with 0.1 M $Me_4NCF_3SO_3$ (drop time 0.5 s, scan rate 20 mV/s); (C) ac polarograms of a 2 × 10^{-3} M solution of Co(CLMEsar)$^{3+}$ in water with 0.1 M $NaClO_4$ at the DME showing the in-phase and quadrature components of the adsorption wave (▼) and reduction wave (◆) (drop time 0.5 s, scan rate 20 mV, ΔE = 5 mV peak to peak).

the prefix di is used immediately before the substituent's appearance in the name; otherwise, the order adopted for substituents is consistent with IUPAC precedence rules. Protonation or deprotonation is denoted by the suffix H or -H, respectively, and multiple protonations or deprotonations by a following subscript for the number of these involved. Examples of this trivial nomenclature are given in Figure 3. Substituent numbering at apical sites has been deleted in this case and will be applied only where ambiguities may otherwise occur.

Metal-Centered Oxidations and Reductions. The Co(III)/Co(II) Couple. The cobalt(III) cage complexes underwent chemically reversible reductions to their corresponding cobalt(II) complexes, with the exception of a limited number of complexes where ligand reductions interfered. In all solvents studied, similar behavior was observed. The one-electron nature of these reductions was established by the use of the Heyrovsky–Ilkovic equation and coulometry (n = 1.0 ± 0.1). Dc polarography indicated these reductions were generally electrochemically reversible ($E_{1/4} - E_{3/4} \simeq 56$ mV). However, use of the shorter time scale techniques of ac polarography and both dc and ac cyclic voltammetry resulted in the observation of quasi-reversible electron-transfer behavior.

In water, most of the reductions were accompanied by adsorption processes as shown by phase-sensitive ac polarography (Figure 4C), since cot $\phi < 1$ (i.e. the in-phase component of the ac signal was smaller than the quadrature component.[27] This adsorption wave could sometimes be distinguished from the wave predominantly due to electron transfer of the free complex, where two adjacent ac peaks were observed experimentally. Where adsorption was evident, this represented a preequilibrium, since it occurred at potentials more positive than $E_{1/2}$, the second wave showing characteristics of a quasi-reversible reduction wave. The adsorption phenomena were indicated occasionally by the presence of adsorption spikes in cyclic voltammograms and, more often, in pulsed-dc techniques. In addition, desorption waves could be detected in dc and cyclic voltammograms in some instances. These adsorption characteristics are illustrated in Figure 4. The reduction scheme in water can therefore be represented by

$$\begin{tikzcd}
\mathrm{Co^{III}} \arrow[r, shift left] \arrow[d, shift left, "e^-"'] & \mathrm{Co^{III}(ads)} \arrow[l, shift left] \arrow[d, shift left] \\
\mathrm{Co^{II}} \arrow[r, shift left] \arrow[u, shift left] & \mathrm{Co^{II}(ads)} \arrow[l, shift left] \arrow[u, shift left, "e^-"']
\end{tikzcd} \tag{6}$$

In nonaqueous solvents, such adsorption phenomena were less common. Complexes with multidentate or macrocyclic ligands also exhibited similar electrochemically reversible or quasi-reversible behavior, but the reductions in these cases were not necessarily chemically reversible.

The reversible $E_{1/2}$ values were obtained from the application of the Heyrovsky–Illkovic equation (Figure 1)[26] and/or from low-frequency ac polarography. Observed values are reported in Table II. The values of $E_{1/2}$ for the Co(III)/Co(II) couples were observed to be markedly dependent on both cavity size and substituents. The smaller preferred cavity size of the mabsar cage ligands resulted in more negative reduction potentials of the corresponding complexes (~−0.3 V) compared with those for similarly substituted sar cage complexes, and preferred cavity size effects are clearly implicated. Both sar and mabsar cage complexes have been characterized by crystal structure analyses.[5,9]

N-Methylation of [Co(diNOsar)]$^{3+}$ to produce [Co(3-MediNOsar)]$^{3+}$ caused a negative shift of −0.12 V in the reduction potential. Smaller positive shifts of +0.03 and +0.095 V occurred on N-methylation of the primary amines of the multidentate complexes [Co(sen)]$^{3+}$ and [Co(nosen)]$^{3+}$, respectively; however, the methylation generates a secondary rather than a tertiary amine center in the latter complexes.

Generally, protonation of amine and hydroxylamine substituents caused a shift in potential by an average of −0.16 V. Deprotonation of a carboxylic acid substituent caused a smaller shift of −0.07 V, while deprotonation of a coordinated amine donor caused only a small negative shift in potential of 0.02 V. Introduction of an imine, as in [Co(diNOsar-2-ene)]$^{3+}$, caused a positive shift of only 0.01 V compared with the potential of [Co(diNOsar)]$^{3+}$. Comparison of the reduction potentials of the multidentate hexaamine [Co(sen)]$^{3+}$ (−0.54 V) and the cage complex [Co(MEsar)]$^{3+}$ (−0.65 V) allowed the closest possible comparison of encapsulated and nonencapsulated species, since the latter is merely a proton-capped [Co(sen)]$^{3+}$ species. A similar comparison of [Co(azasen)]$^{3+}$ (−0.445 V) and [Co(AZAMEsar)]$^{3+}$ (−0.58 V) can be made. The potential differences (~0.1 V) observed may suggest that ring strain in the sar cages is not exceptional; the appreciably more negative potentials of absar cage complexes compared with those of sar cage complexes then implies increased strain in order to accommodate the larger Co(II) in the smaller cavity absar cage ligands.

Heterogeneous electron-transfer rate constants (k_s) were ascertained by variable-frequency ac polarography[27,29] and/or dc cyclic voltammetry[30,31] at mercury, gold, and platinum electrodes, with use of established procedures. The frequency dependence of the in-phase ac peak current for most complexes exhibited typical quasireversible behavior, as illustrated in Figure 5, and allowed an evaluation of k_s (Table II) by an established method.[29] Diffusion coefficients (D) for selected complexes were determined by using the Ilkovic equation[26] and charge-transfer coefficients (α) from variable-frequency ac or cyclic ac techniques.[29,48] The value of α was approximately 0.5 for the reversible couple in all complexes. The value of

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[48] O'Halloran, R. J. Ph.D. Thesis, University of Melbourne, 1977, Chapter 3.

Table II. Reduction Potentials for the Co(III)/Co(II) Couple of (Hexaamine)cobalt(III) Complexes and Heterogeneous Rate Constants for Electron Transfer at the Mercury Electrode

compd	$E_{1/2}$, V water[a]	$E_{1/2}$, V CH_3CN[b]	$E_{1/2}$, V $(CH_3)_2CO$[b]	10^3k_s, cm^{-1} s^{-1} [e,f]	compd	$E_{1/2}$, V water[a]	$E_{1/2}$, V CH_3CN[b]	$E_{1/2}$, V $(CH_3)_2CO$[b]	10^3k_s, cm^{-1} s^{-1} [e,f]
Multidentate Ligand Compounds									
$Co(NH_3)_6{}^{3+}$	-0.26_0				$Co(nosen)^{3+}$	-0.33_2			2.4
$Co(en)_3{}^{3+}$	-0.40_9		-0.25_3		$Co(N\text{-}Me\text{-}sen)^{3+}$	-0.51_3			1.5
$lel_3\text{-}Co(pn)_3{}^{3+}$	-0.36_9				$Co(N\text{-}Me\text{-}nosen)^{3+}$	-0.237			
$lel_3\text{-}Co(chxn)_3{}^{3+}$	-0.43_5				$Co((MENO)MEdesar)^{3+}$[c]	-0.38_0	-0.08_2		4.1
$Co(sen)^{3+}$	-0.5_4	-0.13_0			$Co((EFHM)MEdesar)^{3+}$[c]	-0.41_0			2.6
$Co(azasen)^{3+}$	-0.44_5	-0.04_0		2.0					
Encapsulated sar Compounds									
$Co(diMe_3AMsar)^{5+}$	-0.19_0			0.2	$Co(diHAsar)^{3+}$	-0.50_8			
$Co(diMe_2AMsarH_2)^{5+}$	$-0.18_6{}^d$				$Co(HAMEsar)^{3+}$	-0.57_3			
$Co(diBzAMsarH_2)^{5+}$	$-0.19_0{}^d$				$Co(diMe_2AMsar)^{3+}$	-0.53_4			
$Co(diHAsarH_2)^{5+}$	$-0.18_0{}^d$				$Co(Me_2AMMEsar)^{3+}$	-0.58_2			
$Co(diAMsarH_2)^{5+}$	$0.18_2{}^d$	$+0.14_0$	$+0.10_0$	2.6 (31)[g]	$Co(diAAsar)^{3+}$	-0.47_9			
$Co(AMHAsarH_2)^{5+}$	$-0.18_3{}^d$				$Co(AAMEsar)^{3+}$	-0.57_5			
$Co(HANOsarH)^{4+}$	$-0.19_0{}^d$			1.4	$Co(diPIsar)^{3+}$	-0.50_0			
$Co(AMNOsarH)^{4+}$	$-0.19_5{}^d$				$Co(PIMEsar)^{3+}$	-0.54_0			
$Co(diNOsar)^{3+}$	-0.20_0	$+0.25_6$	$+0.08_5$	~1.0 (14)[g]	$Co(diBzIMsar)^{3+}$	-0.55_2			
$Co(CLNOsar)^{3+}$	-0.29_8	$+0.15_9$		1.4	$Co(TsAMMEsar)^{3+}$	-0.61_8			
$Co(HONOsar)^{3+}$	-0.31_9			1.8	$Co(SalAMMEsar)^{3+}$	-0.5_9			
$Co(AMNOsar)^{3+}$	-0.36_6				$Co(diAZAsar)^{3+}$	-0.49_7	-0.22_2	-0.27_0	1.9 (14)[g]
$Co(HANOsar)^{3+}$	-0.354			1.2	$Co(AZAMEsar)^{3+}$	-0.58_0	-0.18_8		1.8
$Co(AZANOsar)^{3+}$	-0.35_8	$+0.05_7$		2.1	$Co(CAMEsar)^{3+}$	-0.55_0			
$Co(MENOsar)^{3+}$	-0.43_0	-0.00_4		1.1	$Co(CAMEsar\text{-}H)^{2+}$	-0.6_5			
$Co(AMCLsarH)^{4+}$	$-0.27_2{}^d$				$Co(MEsar)^{3+}$	-0.65_0			
$Co(AMMEsarH)^{4+}$	$-0.42_7{}^d$	-0.00_2		3.5	$Co(EFMEsar)^{3+}$	-0.55_8			0.70
$Co(HAMEsarH)^{4+}$	$-0.41_3{}^d$				$Co(sar)^{3+}$	-0.64_0	-0.20_8	-0.32_6	1.5
$Co(Me_2AMMeAMsarH_2)^{5+}$	$-0.18_7{}^d$				$Co(MENOsar\text{-}H)^{2+}$	-0.44_8			
$Co(Me_2AMMEsarH)^{4+}$	$-0.43_0{}^d$				$Co(CAMEsar\text{-}H_2)^{+}$	-0.65_0			
$Co(SalAMMEsarH)^{4+}$	-0.41^d				$Co(3\text{-}Me\text{-}diNOsar)^{3+}$	-0.32_0			2.5
$Co(diCLsar)^{3+}$	-0.37_2	$+0.06_0$	-0.05_4	1.2 (22)[g]	$Co(diNOsar\text{-}2\text{-}ene)^{3+}$	-0.18_9			0.45
$Co(HOCLsar)^{3+}$	-0.40_3	-0.00_4		1.6	$Co(EFAZAoxosar\text{-}H)^{2+}$	-0.65_3			2.1
$Co(AMCLsar)^{3+}$	-0.47_2			1.4	$Co(CANOoxosar\text{-}H_2)^{+}$	-0.57_0			
$Co(CLsar)^{3+}$	-0.50_4	-0.10_0		1.4	$Co(EFMEoxosar\text{-}H)^{2+}$	-0.74_9			2.3
$Co(CLMEsar)^{3+}$	-0.50_8			1.5	$Co(CAMEoxosar\text{-}H_2)^{2+}$	-0.72_0			
$Co(diHOsar)^{3+}$	-0.44_3	-0.05_8		2.1	$Co(MEoxosar\text{-}H)^{2+}$	-0.82_8			0.64
$Co(HOMEsar)^{3+}$	-0.54_8			2.8	$Co(CAAMoxosar\text{-}H_2)^{+}$	-0.78_6			2.4
$Co(diAMsar)^{3+}$	-0.54_0			1.6	$Co(EFAMoxosar\text{-}H)^{2+}$	-0.50_5			3.2
$Co(AMMEsar)^{3+}$	-0.58_8			2.0	$Co(CNMEoxosar\text{-}H)^{2+}$	-0.68_3			4.2
$Co(AMHAsar)^{3+}$	-0.52_1								
Encapsulated mabsar Compounds									
$Co(CLAMmabsarH)^{4+}$	-0.51_8			0.67	$Co(CLHOmabsar)^{3+}$	-0.66_0			2
$Co(CLNOmabsar)^{3+}$	-0.5_2				$Co(CLAMmabsar)^{3+}$	-0.68_0			1.8
$Co(diCLmabsar)^{3+}$	-0.60_0			2	$Co(CLMEmabsar)^{3+}$	-0.74_8			1.4

[a] $E_{1/2}$ vs. SCE, obtained from dc polarography; $\mu = 0.1$ M. [b] $E_{1/2}$ vs. Ag/AgCl/LiCl (saturated, acetone); $\mu = 0.1$ M ($R_4NCF_3SO_3$). [c] The prefixes MENO and EFME refer to disubstitution on the central methylene carbon of the macrocycle bridge at the open end of the MEdesar ligand. [d] 0.05 M $HClO_4$/0.05 M $NaClO_4$. [e] Measured by ac and cyclic dc methods at a mercury electrode; the solvent is water unless otherwise stated. [f] Rates at Pt ~100-fold slower, and at Au ~10-fold slower, relative to rates at Hg. [g] Acetonitrile solvent.

D was approximately 6.0×10^{-6} cm^2 s^{-1} in acetone and 1.0×10^{-5} cm^2 s^{-1} in water for all complexes. Thus the values of α and D did not vary significantly from complex to complex. The values of k_s determined were found to be very dependent on the choice of working electrode, the solvent, and the nature of the complex; usually k_s was found to be 100-fold slower with Pt and 10–100-fold slower with Au, when compared with the value for Hg as the working electrode.

Other Redox Processes. The cobalt(II) cage complexes invariably underwent irreversible reductions at very negative potentials (<−2 V) in nonaqueous solvents. No such reductions were observed in water before reduction of the medium. Generally, organic functional groups were reduced before the metal-centered reduction occurred; however, for the complexes $[Co(sar)]^{2+}$, $[Co(diAZAsar)]^{2+}$, $[Co(diHOsar)]^{2+}$, and $[Co(diMe_3AMsar)]^{4+}$, this second reduction was observed uncomplicated by functional-group electrochemistry. The reductions for cage complexes were invariably ~1 V more negative than for simple cobalt(II) complexes, the latter being observed even in aqueous solutions. Potentials and coulometric results for selected reductions are presented in Table III. While the reduction of $[Co(diAZAsar)]^{2+}$ was clearly an irreversible reduction to cobalt metal, the behavior was less

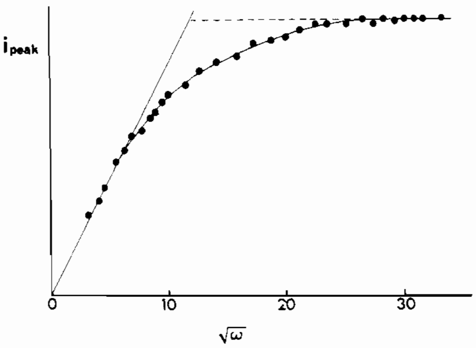

Figure 5. Plot of the ac peak current, $I_p(\omega)$, of the in-phase component for the Co(III) reduction of a 3×10^{-3} M solution of $Co(diNOsar)^{3+}$ in acetone ($\mu = 0.1$ M, $Me_4CF_3SO_3$) vs. $\omega^{1/2}$ (DME, drop time 0.5 s, scan rate 20 mV/s, $\Delta E = 5$ V peak to peak).

Table III. Electrochemical Data for Co(II) Reduction Processes at the DME

compd	medium	n^a	$E_{1/2}$(dc), V
$Co(NH_3)_6^{2+}$	water	2.0	-1.2_0
	acetone	2.0	-0.79_6
$Co(en)_3^{2+}$	water	*b*	-1.3_0
	acetone	2.0	-1.4_6
lel_3-$Co(pn)_3^{2+}$	water	*b*	-1.5_5
lel_3-$Co(chxn)_3^{2+}$	water	2.0	-1.48_2
$Co(diMe_3AMsar)^{4+}$	acetone	1.0	-2.0_0
$Co(diAMsar)^{2+}$	acetone	1.0	-1.9_6
$Co(diHOsar)^{2+}$	CH_3CN	1.2^c	-2.2_8
$Co(diAZAsar)^{2+}$	CH_3CN	2.0^c	-2.1_5
	acetone	2.0^c	-2.0_3

[a] Obtained by comparison of the diffusion current with that of the Co(III)/Co(II) couple. [b] Complicated by adsorption. [c] Confirmed by coulometric measurement.

clear-cut for the other complexes. However, no evidence was obtained for the existence of octahedral cobalt(I) intermediates, even when cyclic voltammetry was performed in acetone at −78 °C or in butanenitrile at −100 °C with $[Co(sar)]^{2+}$ and $[Co(diAZAsar)]^{2+}$. The complete chemical irreversibilities of the Co(II) reductions were further illustrated by the absence of noticeable ac polarographic waves at room temperature.

No metal-centered oxidations were observed even at large positive potentials (≥+2 V) for any sar cage complexes studied in nonaqueous solvents.

Functional-Group Redox Processes. The dc limiting currents for the reductions of the electroactive functional groups were all linearly dependent on concentration. This strongly implies diffusion-controlled processes, which were confirmed by polarography with various drop sizes at the SMDE. A comparison, therefore, of the wave height for the one-electron Co(III)/Co(II) couples with those of functional groups allowed a determination of the number of electrons involved in the reduction. These results complemented the separate coulometric experiments. The reduction potentials and coulometric results for these processes are presented in Table IV. The functional groups $-NO_2$, −NHOH, −Cl, RC=N−, −COOR, −COOH, and $-N^+H_3$ were electroactive, although the products of the reductions were commonly pH and/or solvent dependent.

Table IV. Reduction Potentials and Coulometric Results for Functional-Group Redox Processes

compd	process	medium^a	*n*	$E_{1/2}$(dc),^{e} V	E_p(ac),^{f} V
$Co(nosen)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.68_0	-0.69_6
Co(*N*-Me-nosen)$^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.67_9	-0.69_5
$Co((MENO)MEdesar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.75_2	-0.80_6
$Co(HANOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O, pH 1	4	-0.42_3	
$Co(AMNOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O, pH 1	4	-0.42_5	
$Co(diNOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	8	-0.69_2	-0.69_7
$Co(CLNOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.71_3	-0.72_7
	$Cl \rightarrow H$	H_2O	2	-1.28_7	-1.3_6
$Co(HONOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.63_5	-0.6_6
$Co(HANOsar)^{2+}$	$NO_2 \rightarrow NO_2^{-}\cdot$	H_2O, pH 4.1	1	-0.38	
	$NO_2 \rightarrow NHOH$	H_2O, pH 7	4	-0.6_4	-0.6_8
$Co(AZANOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.71_0	-0.74_3
$Co(MENOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O, pH 6	4	-0.73	
	$NO_2 \rightarrow NHOH$	H_2O, pH 6.7	4	-0.70	
	$NO_2 \rightarrow NHOH$	H_2O, pH 7.3	4	-0.69	
	$NO_2 \rightarrow$ -N=NO-	H_2O, pH 7.8	3	-0.68	
	$NO_2 \rightarrow NO_2^{-}\cdot$	H_2O, pH 8.3	1	-0.64	
	$NO_2 \rightarrow NO_2^{-}\cdot$	H_2O, pH 9.3	1	-0.64	-0.7_0
$Co(AMCLsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.23	
$Co(diCLsar)^{2+}$	$Cl \rightarrow H$	H_2O	4	-1.22_0	-1.2_9
$Co(HOCLsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.24_2	
$Co(AMCLsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.23	
$Co(CLsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.03_5	
$Co(CLMEsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.23	
$Co(diBzIMsar)^{2+}$	C=N- → CH−NH-	H_2O	2		
$Co(EFMEsar)^{2+}$	$COOC_2H_5 \rightarrow ?^b$	H_2O	1	-1.3_0	
$Co(3$-Me-$diNOsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	8	-0.67_8	-0.68_7
$Co(diNOsar$-2-$ene)^{2+}$	C=N- → CH−NH-	H_2O	2	-0.3_8	-0.45_7
	$NO_2 \rightarrow NHOH$	H_2O	8	-0.64_8	-0.69_5
$Co(EFAZAoxosar$-$H)^+$	$COOC_2H_5 \rightarrow ?^b$	H_2O	1	-1.5_0	
$Co(CANOoxosar$-$H_2)$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.73_5	
$Co(EFMEoxosar$-$H)^+$	$COOC_2H_5 \rightarrow ?^b$	H_2O	1	-1.0_0	
	?		1	-1.2	
$Co(CAMEoxosar$-$H_2)$	$COOH \rightarrow COO^-$	H_2O	1	-1.16_0	
$Co(CLAMmabsarH)^{3+}$	$Cl \rightarrow H$	H_2O	2	-1.32	
$Co(CLNOmabsar)^{2+}$	$NO_2 \rightarrow NHOH$	H_2O	4	-0.68_6	-0.69_7
$Co(diCLmabsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.3_4	
$Co(CLHOmabsar)^{2+}$	$Cl \rightarrow H$	H_2O	2	-1.5_0	
$Co(diAMsarH_2)^{4+}$	$^+NH_3 \rightarrow NH_2$	acetone	2	-1.3_0	
$Co(diNOsar)^{2+\,c}$	$NO_2 \rightarrow NO_2H$	acetone	1	-0.49_3	
	$NO_2 \rightarrow NO_2^{-}\cdot$		1	-1.0_0	
$Co(diNOsar)^{2+\,d}$	$NO_2 \rightarrow NO_2^{-}\cdot$	acetone	2	~-1.2	
$Co(diCLsar)^{2+}$	$Cl \rightarrow H$	acetone	1	~-1.5	
			1	~-1.7	
$Co(MENOsar)^{2+}$	$NO_2 \rightarrow NO_2^{-}\cdot$	CH_3CN	1	~-0.9	
$Co(AMMEsarH)^{3+}$	$^+NH_3 \rightarrow NH_2$	CH_3CN	1	-1.2_0	
$Co(diAMsarH_2)^{4+}$	$^+NH_3 \rightarrow NH_2$	CH_3CN	1	-0.35	
			1	-1.15	

[a] $\mu = 0.1$ M $NaClO_4$ in water; $\mu = 0.1$ M $(CH_3)_4NCF_3SO_3$ in aprotic solvents. [b] Reductive cleavage of ester groups; product uncertain. [c] Complex containing 1 mol of CF_3SO_3H/mol of cobalt. [d] Complex without any acid present. [e] Vs. SCE in water or Ag/AgCl/LiCl (saturated, acetone) in aprotic solvents. [f] Conditions: 400 Hz, in-phase, $\Delta E = 5$ mV peak to peak.

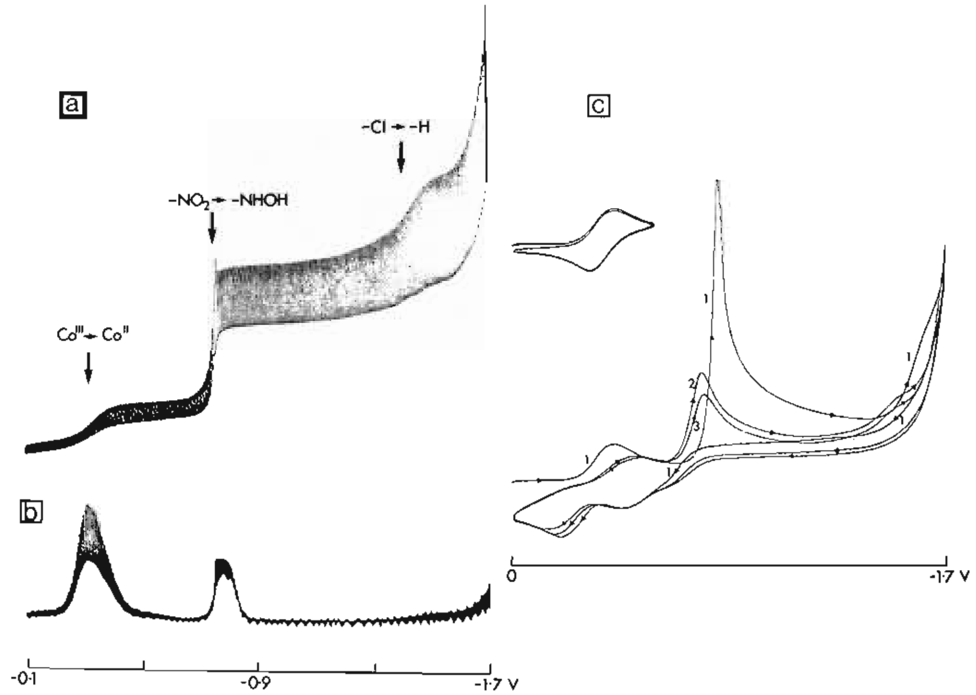

Figure 6. Redox behavior of Co(CLNOsar)$^{3+}$ in water: (a) dc polarogram (DME, drop time 0.5 s, scan rate 20 mV/s); (b) ac peak current of the in-phase component (DME, drop time 0.5 s, scan rate 20 mV/s, ΔE = 5 mV peak to peak, ω = 200 Hz); (c) repeat-scan cyclic voltammograms (HMDE, scan rate 500 mV/s), with two different switching potentials.

Table V. Controlled-Potential Electrosynthesis of Cage Complexes[a]

complex	process	solvent	n	product[b]
Co(diNOsar)$^{3+}$	Co(III) → Co(II)	all[c]	1.0 → 1.2	Co(diNOsar)$^{2+}$
Co(diAZAsar)$^{3+}$	Co(III) → Co(II)	all[c]	1.0	Co(diAZAsar)$^{2+}$
Co(diAAsar)$^{3+}$	Co(III) → Co(II)	water	1.0	Co(diAAsar)$^{2+}$
Co(diMe$_2$AMsarH$_2$)$^{5+}$	Co(III) → Co(II)	water	1.0	Co(diMe$_2$AMsarH$_2$)$^{4+}$
Co(CLMEsar)$^{3+}$	Co(III) → Co(II)	water	1.1	Co(CLMEsar)$^{2+}$
Co(diNOsar)$^{2+}$	NO_2 → NHOH	water	8.3	Co(diHAsarH$_2$)$^{4+}$
Co(MENOsar)$^{2+}$	NO_2 → NHOH	water	4.1	Co(MEHAsarH)$^{3+}$
Co(CLMEsar)$^{2+}$	Cl → H	water	2.1	Co(MEsar)$^{2+}$
Co(diNOsar)$^{2+}$	$NO_2 \rightarrow NO_2^{-}\cdot$	acetone	2.3	*d*
Co(MENOsar)$^{2+}$	$NO_2 \rightarrow NO_2^{-}\cdot$	acetone	2.3	*d*
Co(MENOsar)$^{2+}$	NO_2 → –N=NO–	water, pH 7.8	3.0	{[Co(MEsar)]$_2$–N=NO–}$^{4+}$
Co(HAMEsarH)$^{4+}$	NHOH → NO	acetone	2.0	Co(MENIsar)$^{3+}$

[a] Electrolysis at −0.15 V more negative than $E_{1/2}$, at ambient temperature. [b] Isolated as the solid cobalt(II) compound or, for functional-group reductions, oxidized and isolated as the corresponding cobalt(III) compound; characterized by spectroscopy and/or by comparison with authentic samples of the presumed product. [c] Water, acetone, and acetonitrile. [d] Dimeric and polymeric products apparently formed, which were not completely characterized.

The reduction potential of the nitro group in water was pH dependent. At pH ~0 the reduction occurred at −0.4 V, shifting to −0.7 V (vs. SCE) at neutral pH, although coulometry and dc polarography indicated this to be a four-electron step to hydroxylamine at either pH. At higher pH, eventually more than one step was observed, with two-electron and one-electron reductions observed for [Co(MENOsar)]$^{3+}$ at different basic pH values (Table IV). In nonaqueous aprotic solvents, the nitro group was reduced with greater difficulty, and large negative potentials (~−1 → −1.5 V) were required. Even under these conditions, coulometry indicated only one electron per nitro group was involved in the reduction. The reduction potential was dependent on the availability of a proton donor. For example, the complex [Co(diNOsar)]-$(CF_3SO_3)_3\cdot CF_3SO_3H\cdot H_2O$, containing 1 mol of acid/mol of complex, exhibited two well-defined one-electron waves in acetone at −0.49 and −1.0 V vs. Ag/AgCl, corresponding to the reductions of the two nitro groups. This contrasted with the result obtained for [Co(diNOsar)]$(CF_3SO_3)_3$, where only a single unresolved broad two-electron reduction at ~−1.2 V was observed. The mixture of products obtained from these processes is discussed later.

The hydroxylamine complexes were able to be oxidized in either a one- or a two-electron step, depending on solvent and pH. In acetonitrile, the nitroso group was generated following a two-electron oxidation. The redox behavior of cages with electroactive substituents is illustrated for [Co(CLNOsar)]$^{3+}$ in Figure 6. In certain cases, the products of the reductions or oxidations were identified by isolation after controlled-potential electrolyses.

Controlled-Potential Electrolyses. Metal-Centered Reductions. The use of controlled-potential electrolyses allowed the ready preparation of several cobalt(II) cage complexes such as [Co(diNOsar)]$^{2+}$, which were difficult to obtain by other means due to their readily reducible functional groups (Table V). When chiral forms of the complexes [Co(diNOsar)]$^{3+}$, [Co(diAZAsar)]$^{3+}$, and [Co(diAMsarH$_2$)]$^{5+}$ were exhaustively reduced to cobalt(II) and then reoxidized to the cobalt(III) state, no observable changes in visible absorption spectra or optical activity of the final products were evident, consistent with the chemical reversibility of this couple. Furthermore, the electronic spectra of the air-sensitive cobalt(II) complexes were recorded conveniently for several compounds by in situ reduction in a spectroelectrochemical cell and reoxidation

Table VI. pK_a values of Functional Groups Determined Electrochemically

acid complex	process	pK_a[a]	E_p(acid),[b] V	E_p(base),[b] V	ΔE_p, mV
$Co(MENOsar)^{3+}$	NH/N^-	7.2	-0.45_3	-0.48_6	33
$Co(CAMEsar)^{3+}$	$COOH/COO^-$	1.6[c] (1.7)[d]	-0.58_0	-0.65_1	71
	NH/N^-	12.3 (~12)[d]	-0.65_0	-0.68_1	31
$Co(diAMsarH_2)^{5+}$	$^+NH_3/NH_2$	3.2 (3.4)[e]	-0.19_5	-0.55_3	358
$Co(diHAsarH_2)^{5+}$	$^+NH_2OH/NHOH$	~2	-0.20_1	-0.52_9	328
$Co(diBzAMsarH_2)^{5+}$	$^+NH_2Bz/NHBz$	~2	-0.20_9	-0.56_0	351
$Co(diMe_2AMsarH_2)^{5+}$	$^+NH(CH_3)_2/N(CH_3)_2$	~2	-0.20_6	-0.55_4	348
$Co(CAMEoxosar)^{3+}$	$CoNHCO/CoNCO^-$	−0.4[f] (−1)[e]	-0.70_1	-0.75_0	49

[a] $\mu = 0.1$ M ($NaClO_4$), at 20 ± 2 °C. [b] Vs. SCE, obtained from the peak potentials of the Co(III)/Co(II) couples observed in derivative pulse polarograms. [c] $\mu = 1.0$ M. [d] Reference 10, pH titration. [e] Reference 9, pH titration. [f] $\mu = 6.0$ M.

regenerated the original spectra. Representative cobalt(II) spectra are those of $[Co(diAZAsar)]^{2+}$, with maxima (λ, nm (ε, M^{-1} cm^{-1})) at 650 (0.5), 610 (0.4), 548 (3), 554 (3), and 473 (10), and $[Co(diAAsar)]^{2+}$, with maxima at 638 (2.8), 600 (3.0), 472 (13) sh, and 456 (14.5).

Exhaustive electrolysis of $[Co(diAZAsar)]^{2+}$ at the potential of the Co(II) → Co(0) reduction resulted in the isolation of ligand fractions, when the solution was treated subsequently with gaseous HCl to precipitate amine hydrochlorides. This was ascertained by ^1H NMR spectroscopy of the precipitate, which indicated a spectrum more complex than that for the free cage ligand. Such ligands exhibit 2 well-defined singlets due to the 12 equivalent methylene and 12 equivalent ethylene protons.[49]

The exhaustive reduction of the carbon-capped Co(II) cage complexes has been hampered by the proximity of their reduction potentials to those of the nonaqueous solvent media. A two-electron reduction of Co(II) → Co(0) is expected. However, the results suggest that in certain case Co(I) species are formed (dc polarography and coulometry). The absence of reversibility, even at low temperature, indicates rapid rearrangement reactions with considerable change in ligand structure, possibly to form a square-planar macromonocyclic Co(I) complex. We are currently trying to define these reductions more extensively, but isolation and characterization of such powerful reductants ($\lesssim -2$ V) is proving difficult.

Electroorganic Derivatizations. Four-electron reductions of the nitro groups of the cage complexes $[Co(diNOsar)]^{2+}$ and $[Co(MENOsar)]^{2+}$ at acidic or neutral pH in water resulted in high-yield (>95%) synthesis of the corresponding hydroxylamine-derivatized cage complexes with trace amounts of amine complexes (Table V). At high pH, a three-electron reduction of $[Co(MENOsar)]^{2+}$ to an azoxy-bridged dimeric complex $\{[Co(MEsar)]_2{-}N{=}NO{-}\}^{4+}$ was observed. The cobalt(III) form of this dimer was characterized by its ion-exchange properties, IR spectroscopy (ν(N=N) 1650 cm^{-1}, strong), ^1H NMR spectroscopy (36% DCl: δ(NH) 6.9, 7.2; $\delta(CH_2)$ 2.3–4.0), and ^{13}C NMR spectroscopy (D_2O (vs. dioxane): $\delta(-CH_2-$, en) −11.7; $\delta(-CH_2-$, cap) −15.2, −11.7; δ(tert-C) −5.4, −6.7; $\delta(CH_3)$ −47.4). This product was then selectively reduced to the azo species in a two-electron per dimer step. In dry aprotic media, the nitro groups of $[Co(diNOsar)]^{2+}$ and $[Co(MENOsar)]^{2+}$ underwent one-electron reductions to apparently nitro radical anions. In situ generation at low temperature in the probe of an ESR spectrometer allowed the observation of narrow signals at $g \approx 2$ due to these radical anions. At liquid-nitrogen temperature these signals were readily distinguished from the very broad (>1000 G), and weak, cobalt(II) signal. At room temperature, the radical anions underwent chemical reactions to yield mixtures of dimeric and polymeric complexes that have not been characterized, as yet.

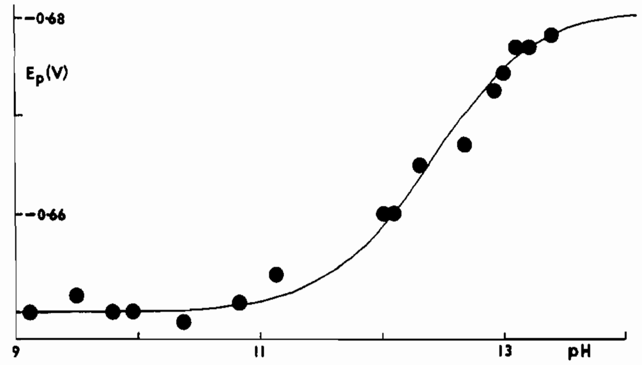

Figure 7. Variation of E_p(derivative pulse) with pH for $Co(CAMEsar)^{3+}$, applied in the determination of pK_a with eq 5.

Electrolysis of $[Co(CLMEsar)]^{2+}$ in *N,N*-dimethylformamide resulted in reductive cleavage of the chloro group. A radical intermediate was implicated by the observation of a very weak ESR signal at $g \approx 2$, and the final product was the hydro-capped species $[Co(MEsar)]^{2+}$. After oxidation, the prduct was characterized by its ^1H NMR spectrum (36% DCl: δ(NH) 6.89; $\delta(CH_2)$ 2.3–4.4) and ^{13}C NMR spectrum (D_2O (vs. dioxane): $\delta(-CH_2-$, en) −11.8 $\delta(-CH_2-$, cap) −11.8, −17.4; δ(tert-C) −24.6, −31; $\delta(CH_3)$ −47.3). In aqueous solution, a two-electron reduction to yield $[Co(MEsar)]^{2+}$ also occurred. Two-electron oxidation of $[Co(HAMEsarH)]^{4+}$ in acetonitrile was observed, due to oxidation of the hydroxylamine to the nitroso derivative. Coulometric experiments performed are summarized in Table V.

pK_a Determinations. During aqueous voltammetric experiments, it was noticed that protonation or deprotonation of functional groups altered the potential of the Co(III)/Co(II) couple, often appreciably (Table II). Consequently, the pH dependence of the potential of this couple offered a convenient method of monitoring these equilibria (Figure 7). The pK_a values of several compounds were determined as described in the Experimental Section and are reported in Table VI. Where values have been determined previously by conventional methods, comparisons were possible, and close agreements were observed. The pK_a values of functional groups in the apical position were relatively independent of the nature of the group at the other apical site. The increased acidity of the functional groups in comparison to typical organic groups was due to inductive field effects of the Co metal center. This is discussed in a following paper.[50]

Discussion

Metal-Centered Redox Chemistry. The redox properties of the macrobicyclic hexaamine cage complexes parallel those

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of the simple hexaamine complexes such as $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$,[11-14] since reduction proceeds by a one-electron step to cobalt(II), followed by an irreversible reduction of Co(II). Macromonocyclic and multidentate hexaamine ligands investigated in this study behaved in the same manner. Furthermore, studies of macrotricyclic hexaamine cage complexes indicate similar behavior.[51] These observations contrast with results obtained from electrochemical experiments on $[Co(bpy)_3]^{3+}$,[21] the cobalt complex of ligand II,[20] complexes with the ability to stabilize square-planar cobalt(I),[16-19] and mixed triamine–trithioether donor macrobicyclic icosane (capten) complexes,[52] which all indicate the existence of putative cobalt(I) species.

The observation that cobalt(I) is stabilized by ligands such as macrocycles, which prefer square-planar geometries, is not surprising, since this geometry is common in other diamagnetic d^8 systems.[53] However, the differences between the electrochemical properties of the macrobicyclic hexaamine cages and those of hexacoordinate $[Co(bpy)_3]^{3+}$,[21] cobalt complexes of ligand II,[20] and capten cage complexes[52] are not immediately obvious, since no stereochemical change is implicated during reduction of the latter compounds. Variations in $E_{1/2}$ for the Co(II)/Co(I) couple with substitution on the bpy ligands led to the conclusion that the reduction is metal rather than ligand centered.[54] Conversely, an earlier IR spectroscopic study on the Co–N stretching frequency of $[Co(aa)_3]^+$ (aa = bpy, phen) indicated considerable delocalization of electron density over the ligands.[55] Further, diimine ligands, which are more easily reduced, stabilize the cobalt(I) state to a much greater extent.[56] Therefore, it is reasonable to relate the stability of the octahedral "Co(I)" complexes of diimine ligands to π back-donation of electron density from filled d orbitals of cobalt(I) to empty π^* orbitals of the ligands. The similarity in electronic spectra of the cobalt(I) complexes of bpy and ligand II[20] suggest that similar factors apply to the stabilization of the latter compound.

The differences between the electrochemistry of the saturated hexaamine cage complexes and that of the saturated triamine–trithioether complexes do not appear to arise from such considerations. Coupled electrochemical and ESR studies of capten complexes implied that the 1+ species are better described as cobalt(I) rather than cobalt(II)–radical anion species.[52] Consequently, the difference between the sar and capten type cage ligands may be related to preferred cavity size variations, due to the longer C–S bonds, when compared with the C–N bonds in the ligands.[57] Preferred cavity size has been shown previously to be important in the stabilization trends for various oxidation states of macromonocyclic ligand complexes.[58] For the cage ligands, the metal ion cannot easily escape the cavity of the ligand, whereas the ion can coordinate out of the plane of macromonocyclic ligands in order to relieve strain. Therefore, it is anticipated that preferred cavity size may be more critical in stabilizing oxidation states for the cage ligands. Molecular mechanics calculations indicate that the preferred cavity of the sar ligands can best accommodate an ion intermediate in size between the cobalt(III) and cobalt(II) ions.[59] The larger Co(I) ion may not be easily accommodated in the sar cavity but may be stabilized in cage ligands with larger cavity sizes such as the capten ligands. This prospect is being pursued further by the design of cage ligands with appreciably larger preferred cavities.[35] The mechanism for reduction of the Co(II) species may involve initial reduction of the Co(II) sar cage complexes to Co(I). The resultant strain could lead to ligand rupture and subsequently very rapid reduction of the Co(I) transient to Co(0) for $[Co(diAZAsar)]^{2+}$, giving the net two-electron irreversible process observed. For the more robust carbon-capped cage complexes, rearrangement to form macromonocyclic square-planar Co(I) species may be the preferred mode of decomposition of the octahedral Co(I) transients. The role of the metal ion in the chemistry of sar cages is not yet well understood. For example, in aqueous solution, the Pt(III) diamsar intermediate undergoes cage rupture and subsequent disproportionation,[60] while the Cu(II) diamsar intermediate is reduced irreversibly to Cu(0) with full recovery of the free diamsar cage.[49] We are currently trying to define the nature of the products of the cobalt(II) cage reduction.

Another indication of the importance of constraints brought about by the preferred cavity size is the ~1-V stabilization of the Co(II) cage complexes toward reduction compared with the case for simple amine compounds such as $[Co(en)_3]^{2+}$. Similarly, the reduction potential of the smaller Co(III) mabsar cage complexes, where there is one methylene link less than in sar cages, is ~0.3 V more negative than for sar cages with comparable substituents. Energy minimization calculations combined with redox behavior suggest that both the preferred Co–N bond length and the conformational isomerism in macrobicyclic complexes are factors in determining the potential of the redox couple.[59]

The stabilization of Co(IV) species might be achieved with cage ligands of smaller cavity size, but this has not been realized to date. No evidence for oxidation waves up to +2 V was obtained in any case involving sar ligands. However, apparently authentic Co(IV) species can be generated from dimethylglyoximato complexes such as $[Co(dmg)_2X_2]^{n+}$ species, where ESR measurements indicated the complexes were substantially Co(IV) in nature[61] and not Co(III) ligand radical cation species. The Co(IV) ion would presumably be stabilized by a smaller preferred ligand cavity to accommodate the smaller Co(IV)–N bond length, since strain in the sar cage ligands would be considerable.

Substituent effects are also important in influencing the redox potential of the Co(III)/Co(II) couple. A span of ~0.6 V of redox potentials for sar cage complexes was observed where the cavity size of the ligand is essentially constant. Clearly, substituent effects of this nature can be subjected to a Hammett type treatment,[62] and this approach is covered in a following paper.[50]

Adsorption waves for all voltammetric techniques and particularly on mercury electrodes were evident during the Co(III) → Co(II) reductions, especially in aqueous solution. For the simple amine complexes, one possibility was that such processes involved ligand dissociation in the Co(II) state, followed by adsorption of the ligand on the electrode surface. The observation that adsorption was more evident in the cage complexes, where ligand dissociation does not occur, negates such a possibility as the sole factor causing adsorption. However, the adsorption does involve the Co(II) complex since

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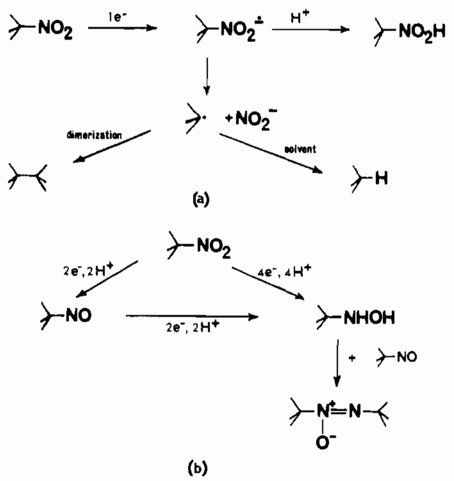
it occurs only at the onset of reduction, regardless of the $E_{1/2}$ of the couple. Where two waves were observed in ac polarography, the first was the adsorption wave and the second that of the free complex. This observation is fully consistent with the Co(II) species being more strongly adsorbed, and indeed adsorption of the reduced species is more generally observed in polarography of metal complexes.[63] Hence, the majority of adsorption occurs when the Co(III) species is reduced to the Co(II) species. The latter species is then adsorbed and the adsorbed species reoxidized, thus forming a prewave.[63] If the Co(III) species were more strongly adsorbed, then the energy required to reduce it to Co(II) would involve the energy required to both desorb and reduce the complex, yielding a wave more negative than that observed for the free anion. Recent chronocoulometric and rapid-scan cyclic voltammetric studies[64] have established that both the Co(III) and the Co(II) complexes are adsorbed but that adsorption is much stronger for Co(II). Two possibilities that may explain these processes are specific adsorption of the aliphatic or functional groups of the ligands on the electrode surface or deposition of the Co(II) complex in the electrode double layer and subsequent adsorption of the complex ion on the electrode. Experiments to differentiate between these possibilities are proceeding and will be reported elsewhere.

Adsorption processes observed in the irreversible Co(II) reduction step appear to be different in nature. Such interactions have been studied in detail for the $[Co(dien)_2]^{2+}$ complex,[13] where adsorption of dissociated ligands on the mercury and subsequent oxidation of surface mercury to form $[Hg(dien)_2]^{2+}$ occurred. Presumably, like processes occurred in the present study, since a similar pattern of electrochemical behavior was observed.

Although an equilibrium between adsorbed and free complexes exists in aqueous perchlorate media, apparent values of the heterogeneous rate constant could be evaluated. It is notable that, for cage complexes of the same type of ligand and same charge, the rate constants are the same, within experimental error. Such observations are in accord with the theories of Hush[65] and Marcus,[66] which predict such behavior, since work terms and reorganizational energy terms are all essentially constant. Of course, to make better comparisons between theory and experiment, work corrections are essential,[67] and this and other complications due to double-layer corrections with adsorption will be discussed fully in a following paper.

Functional-Group Electrochemistry. The reduction of aliphatic nitro groups in organic chemistry is a complex function of pH, electrode, solvent, and nature of the molecule.[68–71] By variance of the solvent and pH of the reacting media, marked differences in the distribution and structures of the products of nitro reductions can be obtained due to a control of proton availability. Different electrodes influence the nature of products via differing overpotentials for reduction of the various intermediates. Finally, the type of compound influences the course of reductions, since primary or secondary nitro groups can tautomerize to oximes on reduction to nitroso intermediates, unlike tertiary nitro groups.

Scheme I



The reduction chemistry of nitro substituents on the ligands of the cage complexes parallels that observed in the chemistry of the purely organic aliphatic tertiary nitro compounds, as shown in Scheme I. In aprotic nonaqueous solvents, the tertiary radical anion species initially formed may undergo a variety of reactions, all of which involve an initial cleavage of the radical anion, which was observed as a transient signal in low-temperature ESR experiments. However, we were not able to get a well-resolved signal in order to make a detailed analysis. The radical anion species is stabilized by protonation;[68–71] therefore, the presence of a proton source facilitates the reduction of the nitro group. This effect has been illustrated by the reduction of $[Co(diNOsar)](CF_3SO_3)_3 \cdot CF_3SO_3H$ in nonaqueous media, where the acidity of the solution brought about by the acid of crystallization causes a positive shift of ~0.5 V in the reduction potential of one of the nitro groups in comparison to that for the simple salt, $[Co(diNOsar)](CF_5O_3)_3$. In aqueous media, at a mercury electrode, the four-electron reduction of the nitro group to hydroxylamine occurs over the pH range 0–7. This reduction compliments the Zn-dust reduction of the nitro group,[7,9] which proceeds completely to the amine group if sufficient Zn is added. If the pH of the solution is increased beyond ~7, the number of electrons involved and the position of the reduction potential of the nitro groups alter, with potentials moving more negative. Normally, the reduction potentials of nitroso compounds are more positive than those of the corresponding nitro compounds.[68–71] However, when the concentration of protons is reduced, the nitroso compounds should be stabilized thermodynamically toward reduction in comparison to the nitro group, since four protons are required to reduce a nitro group to an hydroxylamine group, while only two are required to reduce nitro groups to nitroso groups (Scheme I, part b). The enhanced stability of the nitroso groups allows condensation reactions with hydroxylamine groups to form azoxy-bridged species. At even higher pH values (>9) only one-electron reductions of the nitro groups are observed to presumably form radical anion species whose subsequent reactivity is still being explored.

The reduction of alkyl halides at the Hg electrode has been studied in aqueous and nonaqueous systems, and the overall two-electron process has been shown to proceed in two one-electron steps (Scheme II).[72–74] It has been shown that, during reduction, the mercury electrode reacts with the radicals to

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form organomercury intermediates. A similar mechanism probably accounts for the chloro reductions of chloro-capped cage complexes, and we are currently pursuing this reaction as a way of preparing the parent [Co(sar)]$^{3+}$ complex from [Co(diCLsar)]$^{3+}$. It is notable that, under some conditions, these cage complexes exhibited two one-electron steps, consistent with the stepwise reduction mechanism of Scheme II. The observation of a weak radical signal in the low-temperature ESR experiments may have been due to R· and/or RX^{-}·; however, we were unable to obtain sufficient resolution to distinguish coupling. For reductions in which two consecutive one-electron reductions were observed, the possibility exists that controlled-potential electrolysis may prove useful in the synthesis of dimeric cage complexes via radical coupling mechanisms (Scheme II), and this is being pursued.

Scheme II

$$\mathrm{R{-}X} + e^- \rightarrow \mathrm{R{-}X^{-}\cdot} \rightarrow \mathrm{R\cdot} + \mathrm{X^-} \rightarrow \mathrm{R{-}R}$$

$$\mathrm{R\cdot} + e^- \rightarrow \mathrm{R^-}$$

$$\mathrm{R^-} + \mathrm{H^+} \rightarrow \mathrm{RH}$$

Reductions of protons of acidic groups ($^+NH_3$, CO_2H), of imines to amines, and of ester functions attached to the cage ligands were observed, and the chemistry was not significantly modified in comparison to regular electroorganic chemistry.[68–70]

Conclusions

The Co(III)/Co(II) redox couples exhibited chemically reversible and basically metal-centered behavior at all electrodes, whereas the Co(II) reduction steps were chemically irreversible and led to rupture of the cage structure. In perchlorate media, the electrode process was characterized by preferential adsorption of Co(II) over Co(III). The heterogeneous rate constants for the reduction of Co(III) were extracted from the cyclic voltammetry scan rates, where they were relatively uncomplicated by adsorption effects. These were sufficiently slow to impair the electrochemical reversibility of the Co(III)/Co(II) couples so that the redox processes at the electrodes are best described as quasi-reversible. From these and previous studies of the electrochemistry of cobalt amine donor complexes, it appears that the stabilities of the various oxidation states are influenced by factors such as (i) the nature of the substituents on the ligands, (ii) the preferred cavity size of the ligand, (iii) the ability to delocalize electron density from the cobalt to the ligand, (iv) the ability or inability to undergo stereochemical change in order to attain a preferred geometry, (v) outer-sphere effects such as solvation and ion pairing.

The instability of the Co(0) and Co(I) cage ions can be ascribed to factors ii, iii, and iv. The absence of a Co(IV) ion is probably due to the high ionization potential for Co(IV), although a cage ligand with a reduced cavity size may allow the observation of this oxidation state.

The effect of substituents on the cages for the Co(III)/Co(II) couple was substantial ($\Delta E \approx 0.5$ V from diNOsar → sar) and allows a Hammett type treatment connecting $E_{1/2}$ with a variety of physical properties.[50] The electrochemistry of the substituents does not differ significantly from that observed in organic chemistry.

The variety, stability, and redox range of the complexes makes them potentially useful as one-electrode redox reagents. Dimeric cages may be useful two-electron reagents. These features, along with self-exchange rates and the synthesis of related metal cages of both expanded and reduced cavity sizes, are currently under investigation.

Acknowledgment. The authors thank the School of Chemistry, The University of Melbourne, for use of electrochemical facilities in the initial stages of this work. We wish to acknowledge Drs. J. M. Harrowfield, I. I. Creaser, R. J. Geue, and W. Petri for supplying certain compounds used in this study.

Registry No. Co(NH$_3$)$_6^{3+}$, 14695-95-5; Co(en)$_3^{3+}$, 14878-41-2; lel$_3$-Co(pn)$_3^{3+}$, 16786-53-1; lel$_3$-Co(chxn)$_3^{3+}$, 41970-05-2; Co(sen)$^{3+}$, 85663-63-4; Co(azasen)$^{3+}$, 85663-64-5; Co(nosen)$^{3+}$, 85663-65-6; Co(*N*-Me-sen)$^{3+}$, 85663-66-7; Co(*N*-Me-nosen)$^{3+}$, 85680-83-7; Co((MENO)MEdesar)$^{3+}$, 85663-67-8; Co((EFHM)MEdesar)$^{3+}$, 85663-68-9; Co(diMe$_3$AMsar)$^{5+}$, 85663-69-0; Co(diMe$_2$AMsarH$_2$)$^{5+}$, 85663-70-3; Co(diBzAMsarH$_2$)$^{5+}$, 85663-71-4; Co(diHAsarH$_2$)$^{5+}$, 85663-72-5; Co(diAMsarH$_2$)$^{5+}$, 85663-73-6; Co(AMHAsarH$_2$)$^{5+}$, 85663-74-7; Co(HANOsarH)$^{4+}$, 85663-75-8; Co(AMNOsarH)$^{4+}$, 85663-76-9; Co(diNOsar)$^{3+}$, 85663-77-0; Co(CLNOsar)$^{3+}$, 85663-78-1; Co(HONOsar)$^{3+}$, 85663-79-2; Co(AMNOsar)$^{3+}$, 85663-80-5; Co(HANOsar)$^{3+}$, 85663-81-6; Co(AZANOsar)$^{3+}$, 85663-82-7; Co(MENOsar)$^{3+}$, 85663-83-8; Co(AMCLsarH)$^{4+}$, 85663-84-9; Co(AMMEsarH)$^{4+}$, 85663-85-0; Co(HAMEsarH)$^{4+}$, 85663-86-1; Co(Me$_2$AMMeAMsarH$_2$)$^{5+}$, 85663-87-2; Co(Me$_2$AMMEsarH)$^{4+}$, 85663-88-3; Co(SalAMMEsarH)$^{4+}$, 85663-89-4; Co(diCLsar)$^{3+}$, 85663-90-7; Co(AMClsar)$^{3+}$, 85663-91-8; Co(CLsar)$^{3+}$, 85663-92-9; Co(CLMEsar)$^{3+}$, 85663-93-0; Co(diHOsar)$^{3+}$, 85663-94-1; Co(HOMEsar)$^{3+}$, 85663-95-2; Co(diAMsar)$^{3+}$, 85663-96-3; Co(AMMEsar)$^{3+}$, 85663-97-4; Co(AMHAsar)$^{3+}$, 85663-98-5; Co(diHAsar)$^{3+}$, 85663-99-6; Co(HAMEsar)$^{3+}$, 85664-00-2; Co(diMe$_2$AMsar)$^{3+}$, 85664-01-3; Co(Me$_2$AMMEsar)$^{3+}$, 85664-02-4; Co(diAAsar)$^{3+}$, 85664-03-5; Co(diPIsar)$^{3+}$, 85680-84-8; Co(PIMEsar)$^{3+}$, 85664-04-6; Co(diBzIMsar)$^{3+}$, 85664-05-7; Co(TsAMMEsar)$^{3+}$, 85664-06-8; Co(SalAMMEsar)$^{3+}$, 85664-07-9; Co(diAZAsar)$^{3+}$, 72496-77-6; Co(AZAMEsar)$^{3+}$, 85664-08-0; Co(CAMEsar)$^{3+}$, 85664-09-1; Co(CAMEsar-H)$^{2+}$, 85664-10-4; Co(MEsar)$^{3+}$, 85664-11-5; Co(EFMEsar)$^{3+}$, 85664-12-6; Co(sar)$^{3+}$, 85664-13-7; Co(3-Me-diNOsar)$^{3+}$, 85664-14-8; Co(diNOsar-2-ene)$^{3+}$, 85664-15-9; Co(EFAZAoxosar-H)$^{2+}$, 85664-16-0; Co(CANOoxosar-H$_2$)$^{+}$, 85664-17-1; Co(EFMEoxosar-H)$^{2+}$, 85664-18-2; Co(CAMEoxosar-H$_2$)$^{+}$, 85664-19-3; Co(MEoxosar-H)$^{2+}$, 85664-20-6; Co(CAAMoxosar-H$_2$)$^{+}$, 85664-21-7; Co(EFAMoxosar-H)$^{2+}$, 85664-22-8; Co(CNMEoxosar-H)$^{2+}$, 85664-23-9; Co(CLAMmabsarH)$^{4+}$, 85680-85-9; Co(CLNOmabsar)$^{3+}$, 85680-86-0; Co(diClmabsar)$^{3+}$, 85680-87-1; Co(CLHOmabsar)$^{3+}$, 85680-88-2; Co(CLAMmabsar)$^{3+}$, 85680-89-3; Co(CLMEmabsar)$^{3+}$, 85680-90-6; Co(NH$_3$)$_6^{2+}$, 15365-75-0; Co(en)$_3^{2+}$, 23523-25-3; lel$_3$-Co(pn)$_3^{2+}$, 46469-74-3; lel$_3$-Co(chxn)$_3^{2+}$, 27910-76-5; Co(diMe$_3$AMsar)$^{4+}$, 85664-24-0; Co(diAMsar)$^{2+}$, 72560-63-5; Co(diHOsar)$^{2+}$, 85664-25-1; Co(diAZAsar)$^{2+}$, 63218-22-4; Co(nosen)$^{2+}$, 85664-26-2; Co(*N*-Me-nosen)$^{2+}$, 85664-27-3; Co((MENO)MEdesar)$^{2+}$, 85664-28-4; Co(HANOsar)$^{2+}$, 85664-29-5; Co(AMNOsar)$^{2+}$, 85664-30-8; Co(diNOsar)$^{2+}$, 71935-80-3; Co(CLNOsar)$^{2+}$, 85664-31-9; Co(HONOsar)$^{2+}$, 85680-91-7; Co(AZANOsar)$^{2+}$, 85664-32-0; Co(MENOsar)$^{2+}$, 85664-33-1; Co(AMCLsar)$^{2+}$, 85664-34-2; Co(diCLsar)$^{2+}$, 85664-35-3; Co(HOCLsar)$^{2+}$, 85680-92-8; Co(CLsar)$^{2+}$, 85664-36-4; Co(diBzIMsar)$^{2+}$, 85664-37-5; Co(EFMEsar)$^{2+}$, 85664-38-6; Co(3-Me-diNOsar)$^{2+}$, 85664-39-7; Co(diNOsar-2-ene)$^{2+}$, 85664-40-0; Co(EFAZAoxosar-H)$^{+}$, 85664-41-1; Co(CANOoxosar-H$_2$), 85664-42-2; Co(EFMEoxosar-H)$^{+}$, 85664-43-3; Co(CAMEoxosar-H$_2$), 85680-93-9; Co(CLAMmabsarH)$^{3+}$, 85680-94-0; Co(CLNOmabsar)$^{2+}$, 85680-95-1; Co(diCLmabsar)$^{2+}$, 85680-96-2; Co(CLHOmabsar)$^{2+}$, 85680-97-3; Co(diAMsarH$_2$)$^{4+}$, 85664-44-4; Co(AMMEsarH)$^{3+}$, 85664-45-5; Co(diAAsar)$^{2+}$, 85664-46-6; Co(diMe$_2$AMsarH$_2$)$^{4+}$, 85664-47-7; Co(MENIsar)$^{3+}$, 85664-48-8; Co(diHAsarH$_2$)$^{4+}$, 85664-49-9; Co(MEHAsarH)$^{3+}$, 85664-50-2; Co(MEsar)$^{2+}$, 85664-51-3; [Co(MEsar)]$_2$-N=NO-$^{4+}$, 85664-52-4; Co(CAMEoxosar)$^{3+}$, 85664-53-5; Co(CLMEsar)$^{2+}$, 85664-54-6; Hg, 7439-97-6; NaClO$_4$, 7601-89-0; Me$_4$NCF$_3$SO$_3$, 25628-09-5.