# Macrobicyclic (Hexaamine)platinum(IV) Complexes: Synthesis, Characterization, and Electrochemistry

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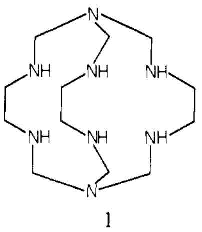
**Abstract:** Syntheses based on the reaction of $Pt(en)_3^{4+}$ with formaldehyde, and ammonia or nitromethane, yielded the macrobicyclic complexes (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)platinum(IV), $Pt(sep)^{4+}$, and (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)platinum(IV), $Pt(dinosar)^{4+}$, respectively. Reduction of the latter complex with $SnCl_2$ in acid yielded (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)platinum(IV), $Pt(diamsar)^{4+}$. These complexes are substitution-inert, diamagnetic octahedral ions and were characterized by X-ray crystallographic analysis of the $Pt(sep)^{4+}$ by absorption and NMR spectroscopy. Addition of an electron to the Pt(IV) complexes, radiolytically or electrochemically, yielded transient monomeric macrobicyclic Pt(III) ions. $\gamma$-Radiolysis of crystalline samples yielded a Pt(III) complex stabilized in the crystalline lattice, detected by ESR spectroscopy. Polarography of $Pt(diamsar)^{4+}$ in aprotic solvents showed essentially irreversible one-electron reductions at +0.17 and −1.00 V and a two-electron irreversible reduction at −2.20 V (in acetone, vs. Ag/AgCl). The Pt(III) transient of the first reduction decayed ($t_{1/2} < 10^{-3}$ s) to yield the monodeprotonated Pt(IV) complex and 0.5 mol of hydrogen/mol of complex. The lifetime of the related $Pt(sep)^{3+}$ transient was longer, though still in the millisecond range. This intramolecular redox process in aprotic solvents was not observed in water, however. In aqueous solution, the $Pt(diamsar)^{3+}$ transient decayed with a first-order rate constant of $6 \times 10^{-3}\ s^{-1}$ (pH 6.8 or 10.0) in pulse radiolysis experiments. A rate-determining C–N ring opening of the platinum(III) chelate, followed by rapid disproportionation, appears to be the major route for decay of Pt(III) in aqueous solution. This is supported by voltammetric studies and the detection of both Pt(II) and Pt(IV) macromonocyclic products.

## Introduction

The template syntheses of nitrogen analogues of the polyether cryptands about a cobalt(III) ion have been described previously.[2-6] Syntheses based on the inert complex $Co(en)_3^{3+}$ (en = 1,2-ethanediamine) have yielded the macrobicyclic complex ions (cage complexes) (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)cobalt(III) ($Co(sep)^{3+}$, ligand I) and (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)cobalt(III) ($Co(dinosar)^{3+}$, ligand II), as well as the reduced form of II, (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)cobalt(III) ($Co(diamsar)^{3+}$, ligand III).[2,7] As a consequence of encapsulation, substitution-inert cobalt(II) macrobicyclic complexes can also be prepared upon reduction of the parent cobalt(III) ions.

In this paper we report syntheses of macrobicyclic platinum(IV) analogues of the cobalt(III) complexes with ligands I–III, based on the inert $Pt(en)_3^{4+}$ precursor. The chemical and electrochemical behavior of the encapsulated Pt(IV) ions towards reduction has also been investigated with a view to seeking evidence for encapsulated platinum in lower oxidation states, particularly the octahedral d$^7$ Pt(III) state and possibly the octahedral d$^8$ Pt(II) state.



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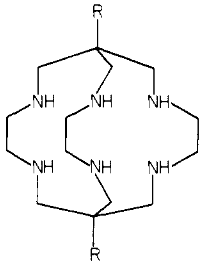

II, R = $NO_2$
III, R = $NH_2$

## Experimental Section

**1. Preparation of Complexes.** $[Pt(en)_3]Cl_4$ was prepared as previously described[8] and recrystallized thrice from aqueous HCl. Analytical reagent grade chemicals were used throughout without further purification.

**(1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]icosane)platinum(IV) Chloride Dihydrate, $[Pt(sep)]Cl_4 \cdot 2H_2O$.** $[Pt(en)_3]Cl_4$ (6.3 g) was dissolved in water (60 mL) and $Li_2CO_3$ (4 g) added. Aqueous 38% formaldehyde (70 mL) and concentrated aqueous ammonia (20 mL, diluted to 70 mL) were added slowly and separately to the stirring solution over a period of 5 h, using a peristaltic pump. After complete addition, the bright yellow solution (pH ~10) was acidified (to pH ~1) with concentrated HCl to quench the reaction. (*Note*: The reaction between HCl and HCHO solutions may lead to formation of the carcinogen $ClCH_2OCH_2Cl$.[9]) The almost colorless solution obtained was diluted (~0.5 L) and sorbed on a column of Dowex 50W-X2 ($H^+$ form) resin. After the mixture was washed with 1 M HCl (~0.5 L), the complex was eluted with 6 M HCl), the eluate being evaporated to dryness. The crude product (6.9 g) was redissolved in water (0.5 L) and sorbed on a column of SP-Sephadex C-25 ($Na^+$ form). Elution with 0.1 M sodium tartrate yielded two orange-yellow bands. The first and major band, later identified as the required product, was collected, resorbed on a column of Dowex 50W-X2 ($H^+$ form) resin, and isolated as before. The white solid obtained was finally recrystallized by dissolution in a minimum volume of 1 M HCl, followed by dropwise addition of acetone to the stirring

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solution. The small white crystals were separated, washed with acetone and ether, and dried in vacuo; yield 4.6 g, 60%. Anal. Calcd for $C_{12}H_{34}N_8Cl_4O_2Pt$: C, 21.86; H, 5.20; N, 17.00; O, 4.85; Cl, 21.51; Pt, 29.59. Found: C, 21.6; H, 5.2; N, 16.75; O, 4.95; Cl, 21.1; Pt, 29.1. The complex was also isolated as the perchlorate salt by metathesis of the chloride salt and $AgClO_4$. After removal of AgCl and evaporation to near dryness, addition of 70% $HClO_4$ and cooling yielded white crystals. Anal. Calcd for $C_{12}H_{30}N_8Cl_4O_{16}Pt$: C, 16.39; H, 3.44; N, 12.71; Cl, 16.13; Pt, 22.19. Found: C, 16.2; H, 3.6; N, 12.6; Cl, 16.3; Pt, 22.9. The anhydrous trifluoromethanesulfonate salt was prepared by dissolution of the chloride salt in concentrated aqueous $CF_3SO_3H$ (50% v/v) and crystallization upon cooling to ~5 °C. The colorless crystals were dried in vacuo over $P_2O_5$. Anal. Calcd for $C_{16}H_{30}N_8F_{12}S_4O_{12}Pt$: C, 17.83; H, 2.81; N, 10.40; F, 21.15; S, 11.90; Pt, 18.10. Found: C, 17.8; H, 3.0; N, 10.1; F, 21.4; S, 11.8; Pt, 18.0.

**(1,8-Dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosanato)platinum(IV) Chloride Trihydrate, [Pt(dinosar-H)]$Cl_3$·$3H_2O$.** [Pt(en)$_3$]$Cl_4$ (22.5 g), nitromethane (26.6 g), aqueous 38% formaldehyde (48.2 g), and $Na_2CO_3$(8.8 g) were combined in water (1.1 L), and the solution was kept at 20 °C in the dark for 14 h. The resultant orange solution was acidified (pH ~1, concentrated HCl) and evaporated to dryness. The solid was dissolved in water (~70 mL), filtered through Hyflo filter aid, and passed through a short (~3 cm) column of SP-Sephadex C-25 ($Na^+$ form) resin, yielding a golden-orange solution and retaining a dark brown byproduct on the resin. The eluate was concentrated (to ~50 mL) and refrigerated (4 h). Bright orange crystals (16 g) were collected, washed with ethanol and ether, and air-dried. Further reduction of the volume of the filtrate yielded further product (4 g). The monodeprotonated orange complex was finally recrystallized from a minimum volume of hot (~80 °C) water by cooling, collected, washed with ethanol and ether, and dried in vacuo; yield 14 g, 45%. Anal. Calcd for $C_{14}H_{35}N_8Cl_3O_7Pt$: C, 23.08; H, 4.81; N, 15.38; Cl, 14.61. Found: C, 23.5; H, 4.9; N, 15.4; Cl, 14.8.

**(1,8-Dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)platinum(IV) Chloride Trihydrate Hydrochloride, [Pt(dinosar)]$Cl_4$·$3H_2O$·HCl.** [Pt(dinosar-H)]$Cl_3$·$3H_2O$ in a minimum volume of hot (~80 °C) water treated with an equal volume of concentrated HCl gave colorless rods of the fully protonated complex on cooling to 20 °C (6 h). These were collected, washed with ethanol and ether, and dried in vacuo. Anal. Calcd $C_{14}H_{37}N_8Cl_5O_7Pt$: C, 20.96; H, 4.62; N, 13.97; Cl, 22.11; Pt, 24.33. Found: C, 21.4; H, 4.7; N, 14.0; Cl, 22.1; Pt, 24.4.

**(1,8-Diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)platinum(IV) Chloride Dihydrate, [Pt(diamsar)]$Cl_4$·$2H_2O$.** To [Pt(dinosar-H)]$Cl_3$·$3H_2O$ (25 g) in nitrogen-purged water (1 L) was added a suspension of $SnCl_2$·$2H_2O$ (85 g) in 6 M HCl (250 mL). The suspension was stirred under nitrogen at 40 °C in the dark for 30 h and then cooled to 20 °C overnight. The white solid (29 g) was collected, washed with cold water, ethanol, and ether, and air-dried. The crude product in water (3 L) was sorbed on a column of Dowex 50W-X2 ($H^+$ form) resin, washed with water (~2 L) and 1 M HCl (~1 L), and then eluted with 3 M HCl. After evaporation to ~20 mL, white crystals (22.5 g) of the product as a hydrochloride trihydrate were obtained. These were recrystallized from warm water (~180 mL) by the addition of concentrated HCl (~150 mL) and cooling to ~0 °C. The white flakes which formed were collected, washed with ethanol and ether, and dried in vacuo; yield 14 g, 60%. Anal. Calcd for $C_{14}H_{38}N_8O_2Cl_4Pt$: C, 24.45; H, 5.53; N, 16.30; Cl, 20.67; Pt, 28.38. Found: C, 24.4; H, 5.1; N, 16.2; Cl, 20.6; Pt, 28.8. The complex was also isolated as the trifluoromethanesulfonate salt by treating the chloride salt with anhydrous trifluoromethanesulfonic acid (typically 2 g in 20 mL). The suspension was warmed gently until dissolution was complete, and HCl gas evolution had ceased. After being cooled to 20 °C, the solution was stirred vigorously and ether (~150 mL/20 mL of acid) added slowly to precipitate a white solid. This was separated and could be recrystallized from a minimum volume of hot (~80 °C) water by the addition of an equal volume of anhydrous $CF_3SO_3H$ and cooling in ice. The white crystals of the dihydrate were washed with a small volume of isopropyl alcohol and then ether and dried in vacuo. Anal. Calcd for $C_{18}H_{38}N_8F_4O_{14}S_4Pt$: C, 18.95; H, 3.33; N, 9.82; F, 20.00; S, 11.23; Pt, 17.11. Found: C, 19.0; H, 3.2; N, 9.9; F, 20.1; S, 11.0; Pt, 16.8.

2. **Electrochemical Techniques.** Electrochemical studies were performed by using a conventional three-electrode configuration with *iR* compensation, and a PAR Model 170 electrochemical system or PAR Model 174A polarographic analyzer coupled with a Houston Instruments Omnigraphic 2000 Recorder. For rapid scan cyclic voltammograms (to 20 V/s), a Tektronix C-70 Oscilloscope Camera connected to a Tektronix 5031 dual-beam storage oscilloscope and the PAR Model 170 were used. Working electrodes employed were a dropping mercury electrode (DME) for dc, ac, and pulse techniques, a hanging mercury drop electrode (HMDE) for cyclic voltammetry, and on occasions stationary platinum or stationary gold. The reference electrode was saturated calomel for aqueous solutions or Ag/AgCl (saturated LiCl in acetone) for nonaqueous solvents and was separated from the working and auxiliary electrodes in an electrode bridge with a fine porosity frit. The electrode bridge contained the appropriate electrolyte solution used in the electrolytic cell. The auxiliary electrode was a platinum coil. Solutions were degassed with solvent-saturated argon through a standard purge tube. Double glass distilled water and dried analytical grade acetone or acetonitrile were used as solvents. Sodium perchlorate (0.1 M), perchloric acid (1.0 M), and tetramethylammonium trifluoromethanesulfonate[10] (TMAT, 0.1 M) were used in aqueous and non-aqueous solvents as electrolytes, unless otherwise stated. Complex concentrations in the millimolar range were used throughout.

Coulometric analyses were performed with a PAR Model 377A coulometry cell system using either a stirred mercury pool or platinum basket working electrode and an Amel Model 551 potentiostat and Model 731 digital integrator or alternatively the PAR Model 173 and Model 179 equivalents.

3. **Pulse Radiolysis Techniques.** Pulse radiolysis facilities at the Australian Atomic Energy Commission Research Establishment or the Argonne National Laboratory were employed. The former facility consists of a 1 MV Van der Graaf electron accelerator delivering either single electron pulses (3-μs duration) or a continuous train (50 $s^{-1}$) of fast electrons into a 1-cm "suprasil" cell. Each irradiated volume received one pulse of fast electrons, corresponding to ~$10^{-6}$ mol $L^{-1}$ of $e_{aq}^-$. The optical detection system has been described previously.[11] The Argonne facility has been described[12] and allowed determination of spectra of transients by using a "streak" camera detection system.

Buffered (pH 6.8 or 10.0) aqueous solutions ($3 \times 10^{-5}$–$1 \times 10^{-3}$ M) of Pt(diamsar)$^{4+}$ were purged with He prior to radiolysis and protected from extraneous light sources. Solutions contained 0.1 M tert-butyl alcohol, which effectively scavanged OH radicals. The reaction kinetics were determined at 390 nm for the decay of the transient. The rate of formation of the transient was measured at 600 nm by observing the rate of decay of $e_{aq}^-$ with varying [Pt(IV)], (0–3) × $10^{-4}$ M; a rate $k(e_{aq}^- + Pt^{IV})$ first-order in [Pt(IV)] was observed, independent of pH.

Circulation of a solution of Pt(diamsar)$^{4+}$ ($10^{-3}$ M, 160 mL) through the irradiation cell (10 mL/m) irradiated with a train of electron pulses, allowed determination of the products of radiolysis. The irradiated solution was collected in a flask containing HCl sufficient to bring the pH of the resultant solution to ≤1; the calculated dose yielded ~80% reaction. The solution was diluted 10-fold, sorbed onto SP-Sephadex C-25 resin (2 × 15 cm), and eluted with sodium tartrate (0.05–0.15 M) to separate possible products. The products were detected spectrophotometrically at 300 nm.

4. **Other Physical Methods.** Visible absorption spectra were recorded by using a Cary 118 spectrophotometer. Infrared spectra (KBr disks) were recorded by using a Perkin-Elmer 457 spectrometer. [$^{13}C$] NMR spectra were recorded at ambient temperature with a JEOL FX-60 spectrometer in $D_2O$ with 1,4-dioxan as internal reference. [$^1H$] NMR spectra were recorded with a JEOL HA-100 spectrometer, using DSS as internal reference. Determinations of p$K_a$ were performed in a thermostated (25 °C) microcell fitted with a Radiometer G 202B glass electrode and a salt bridge (1.6 M $NH_4NO_3$ and 0.2 M $NaNO_3$) to a saturated calomel electrode, using a Radiometer pH meter 26. The electrode system was calibrated with standard buffer solutions. Solutions were degassed with nitrogen, and titrant was added from a calibrated microsyringe.

ESR spectra were recorded by using a JEOL JES-PE spectrometer fitted with a VT-3A variable-temperature controller. An electrolysis cell designed[13] with a helical gold working electrode[14] was used for attempted generation of reduced species in solution in the ESR probe; the cell was also fitted with a Pt auxiliary electrode and a Ag/AgCl reference electrode. Reductions in situ were performed at low temperature in 0.1 M TMAT/acetone (-80 °C) or acetonitrile (-40 °C) solvents, with millimolar concentrations of Pt(IV).

γ-Radiolysis of the Pt(diamsar)$^{4+}$ complex in the solid state (chloride or trifluoromethanesulfonate salts) at liquid-nitrogen temperature using a $^{60}Co$ source was employed to generate Pt(III) species doped in the Pt(IV) crystal lattice. A calculated dose of ≥$10^5$ rad over 16 h was

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Table I. $[^{13}C]$ NMR Shifts for Pt(IV) and Co(III) Cages[a]

| | shift, ppm ($^{195}Pt$ coupling, Hz) | | | |
|---|---|---|---|---|
| assignt | $Pt(en)_3^{4+}$ | $Pt(sep)^{4+}$ | $Pt(dinosar-H)^{3+}$ | $Pt(diamsar)^{4+}$ |
| $-CH_2-$ (en) | −18.1 (. . .)[b] | −9.2 (2.5) | −7.1 (3) | −7.8 (. . .)[b] |
| $-CH_2-$ (cap) | | +2.7 (8) | −11.8 (7) | −12.4 (7) |
| $\rightarrow C-$ | | | +29.6 (52) | +6.1 (40) |

| | shift, ppm | | | |
|---|---|---|---|---|
| assignt | $Co(en)_3^{3+}$ | $Co(sep)^{3+}$ | $Co(dinosar)^{3+}$ | $Co(diamsar)^{3+}$ |
| $-CH_2-$ (en) | −21.8 | −13.2 | −11.3 | −11.6 |
| $-CH_2-$ (cap) | | +0.4 | −15.1 | −11.6 |
| $\rightarrow C-$ | | | +21.4 | −10.3 |

[a] Shifts relative to dioxane; + indicates a downfield shift; dioxane resonance is at +67 ppm relative to tetramethylsilane. [b] Coupling not resolved (⩽2 Hz).

delivered to samples sealed in evacuated tubes. One end of the tube was screened in lead to protect it from irradiation, and the tubes subsequently were inverted prior to spectroscopy; alternatively, irradiated samples were transferred to fresh tubes prior to spectroscopy, since the samples proved stable in the atmosphere for extended periods, even at room temperature. ESR spectra were recorded on the irradiated samples at liquid-helium or liquid-nitrogen temperatures. Appropriate blank experiments with empty sealed tubes or tubes containing simple salts of the anions were performed.

Visible absorption spectra of electrochemically reduced solutions in nonaqueous solvents were determined by using a short path length (2-mm) spectroelectrochemical cell with sapphire windows and a gold minigrid working electrode;[13] platinum and Ag/AgCl auxiliary and reference electrodes were employed respectively.

**5. Analysis of Reduction Products.** Attempts were made to characterize reduction products from controlled potential electrolysis or chemical reduction of the $Pt(idamsar)^{4+}$ complex below the first reduction step. In the former experiment, reduction at a stirred mercury pool was performed in acetone (at 0.0 V vs. Ag/AgCl) or 1 M aqueous $HClO_4$ (at −0.2 V vs. satd calomel). The product solutions were diluted with water, sorbed on columns of SP-Sephadex C-25 resin, washed with water, and then eluted with sodium tartrate (0.05–0.15 M). Collected bands, identified by passing the eluate through a cell in a Cary 16 spectrophotometer (at 300 nm), were sorbed on Dowex 50W-X2 ($H^+$) resin and eluted, after being washed with 0.25 M HCl, with 4 M HCl. The solutions were evaporated to dryness and characterized by $^{13}C$ and $^1H$ NMR spectroscopy. From the reduction performed in acetone ($n = 1$, coulometrically) only the starting product was obtained; reduction with zinc dust yielded the same result. However, while there was apparently one major product, in total several decomposition products were obtained from the experiment in aqueous acid, where coulometric analysis indicated a variable electron count, $1 \leq n \leq 2$, as the controlled potential was varied between −0.05 and −0.5 V. Reaction of the $Pt(diamsar)^{4+}$ with $Co(diamsar)^{2+}$ ($E_{1/2} = -0.18$ V) initiated a redox reaction again yielding several decomposition products. In each case in aqueous solution the major product was apparently a platinum(II) macromonocyclic species, with some related Pt(IV) product present.

## Results

**Syntheses and Characterizations.** Synthetic routes to the macrobicyclic Pt(IV) complexes of the ligands I–III have been developed, using similar routes to those reported previously for the cobalt analogues. The mild reductant $SnCl_2$ was employed in the high yield reduction of the dinosar complex to the diamsar complex. Reduction with Zn yielded a complex mixture of multidentate ligand species and little cage compound. The encapsulated nature of the $Pt(sep)^{4+}$ ion has been established by an X-ray crystallographic analysis.[15] Moreover, the spectra and microanalytical data for all three complexes confirmed the formation of macrobicyclic ligands; $^{13}C$ spectra, for example, are analogous to the fully characterized[3-5] cobalt(III) analogues (Table I), apart from $^{195}Pt$ coupling.

Nuclear magnetic resonance spectroscopy offered the most convenient characterization of the macrobicyclic complexes. The high symmetry of the products was apparent from the proton-decoupled $^{13}C$ spectra (Figure 1). A maximum of three signals was observed, arising from the methylene carbons of the precursor ethylenediamine ring, the methylene carbons of the capping group, and the quaternary carbon of the carbon-capped molecules. $^{195}Pt$ coupling was observed in most resonances, and increased in the order methylene (en) < methylene (cap) < quaternary C. The resonance from the methylenes of the ethylenediamine ring is relatively constant in all three cage complexes (−7.1 to −9.1 ppm, relative to dioxane). The methylenes of the cap showed similar resonance positions for the carbon-capped cage complexes, but a marked shift from ~−12 to +2.7 ppm occurred in the aza-capped complex; this is analogous to the behavior observed in the corresponding cobalt(III) cages (Table I). Similarly, the relatively weak signal from the quaternary cap carbon shifted markedly with substituent, from +29.6 ppm (nitro) to +6.1 (amino), and shows a downfield shift of ~10 ppm compared with the cobalt(III) analogues. The 100-MHz $[^1H]$ spectra of the complexes were complicated by $^{195}Pt$ coupling (Figure 2); the $^{195}Pt$-decoupled spectra, however, were consistent with the assigned structures and similar to spectra of Co(III), Rh(III), and Ir(III) analogues.[4,5,7]

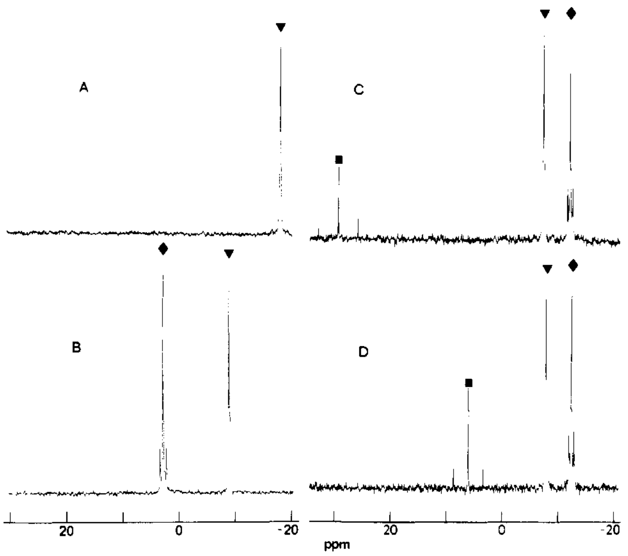

**Figure 1.** $^{13}C$ NMR spectra of (a) $Pt(en)_3^{4+}$, (b) $Pt(sep)^{4+}$, (c) $Pt(dinosar)^{4+}$, and (d) $Pt(diamsar)^{4+}$ in acidified $D_2O$ (vs. 1,4-dioxane). Assignments are as follows: ▼, ethylenediamine methylenes; ◆, cap methylenes; ■, quaternary carbons.

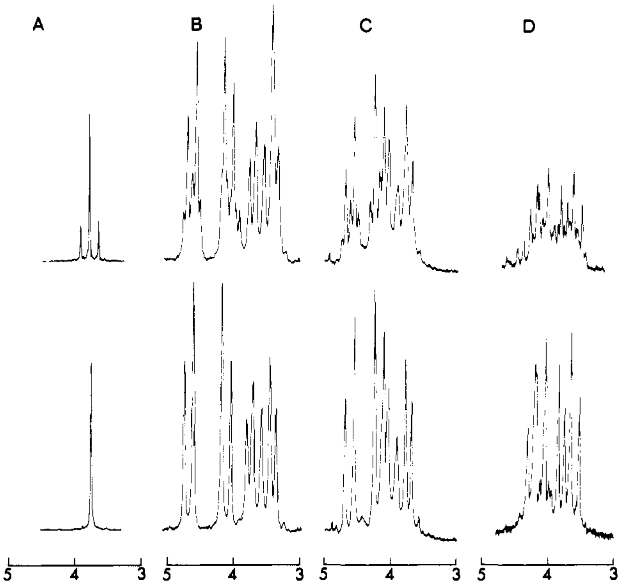

**Figure 2.** Coupled (top) and $^{195}Pt$-decoupled (bottom) $^1H$ NMR spectra of (a) $Pt(en)_3^{4+}$, (b) $Pt(sep)^{4+}$, (c) $Pt(dinosar)^{4+}$, and (d) $Pt(diamsar)^{4+}$ in acidified $D_2O$ (vs. external $Me_4Si$).

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Table II. Absorption Spectra of Macrobicyclic Pt(IV) Complexes

| | solvent | | |
|---|---|---|---|
| compd$^a$ | 1.0 M HCl | $H_2O$ | 0.1 M NaOH |
| Pt(sep)$^{4+}$ | ~250 sh (2900) | 351 (1230) | 293 (1520) |
| Pt(dinosar)$^{4+\,c}$ | 365 (95),<br>~260 sh (4600)$^b$ | 326 (2910) | 300 sh (5280),<br>253 (12 800) |
| Pt(diamsar)$^{4+}$ | ~260 sh (3900) | 346 (1540) | 295 (4380) |

$^a$ Chloride salts, [Pt] $< 5 \times 10^{-4}$ M; absorption maxima, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$); sh = shoulder. $^b$ Spectrum in 6 M HCl; the complex is monodeprotonated in 1 M HCl, with a maximum at 354 nm ($\epsilon$ 1080), while the other complexes are monodeprotonated in water and exhibit similar maxima and extinction coefficients. $^c$ Other spectra recorded: formate buffer, pH 3.8, 347 nm ($\epsilon$ 1920); phosphate buffer, pH 6.8, 339 nm ($\epsilon$ 1830).

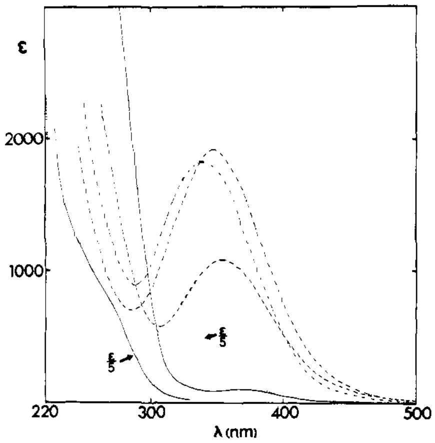

**Figure 3.** The pH dependence of the absorption spectrum of Pt(dinosar)$^{4+}$. Spectra were recorded in 6 M HCl (—), 1 M HCl (---), pH 3.8 formate buffer (-·-), pH 6.8 phosphate buffer (-···), and 0.1 M NaOH (·····).

The AB quartet of the methylene cap protons was most clearly observed in the Pt(sep)$^{4+}$ complex, centered at 4.4 ppm (Figure 2B); the methylene protons of the en ring do not appear as a simple quartet but present a more complex pattern consistent with an AA′BB′ system centered for Pt(sep)$^{4+}$ at 3.6 ppm.

The absorption spectra of the complexes in water are pH dependent (Table II), since the secondary amine protons of the complex are quite acidic. The dinosar complex is only fully protonated in strong acid (6 M HCl); i.e., the p$K_a$ of the first amine is <0. Several p$K_a$ values have been determined potentiometrically. For Pt(dinosar)$^{4+}$, p$K_a^1 < 0$, p$K_a^2 = 2.63$, p$K_a^3 = 5.05$, and p$K_a^4 = 9.23$. The Pt(diamsar)$^{4+}$ complex is less acidic, as a consequence of reduction of the nitro groups to amine groups; potentiometric titration yielded p$K_a^1 = 2.4$ and p$K_a^2 = 7.2$. For the precursor Pt(en)$_3^{4+}$ complex, the primary amines are much less acidic (p$K_a^1 = 5.5$).[16] $^1$H NMR experiments with OD$^-$/D$^+$ established that methylene groups are not deprotonated, since no C–H exchange was observed. Absorption spectra of the fully protonated complexes showed a shoulder on the charge-transfer band near 250 nm, which may be the first d–d band of the d$^6$ Pt(IV) complexes.[17] The significant variation in absorption spectra with pH is illustrated for Pt(dinosar)$^{4+}$ in Figure 3.

The acidicity of the amine protons is also evident in the infrared spectra. The N–H stretching frequency for M(dinosar)$^{n+}$ complexes, for example, are as follows: Rh(III), 3045 cm$^{-1}$;[7] Co(III), 3020 cm$^{-1}$;[5] Pt(IV), 2750 cm$^{-1}$. The acidity of amines is Rh(III) < Co(III) << Pt(IV), and the correlation is apparent. In general, the IR spectra with a particular macrobicycle and different metal ions are similar, as expected.

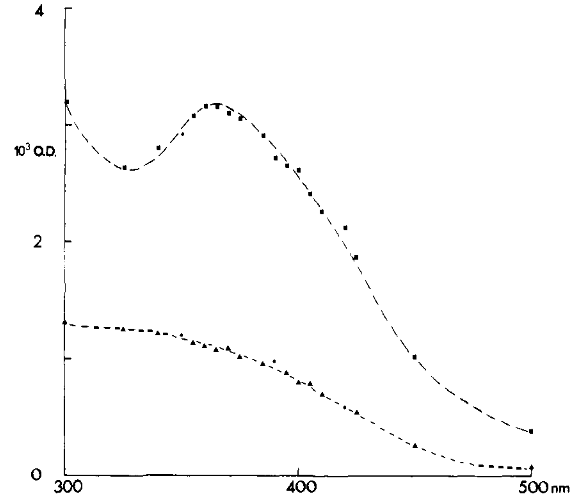

**Figure 4.** Absorption spectra of the transient (■) and product (▲) from reaction of $10^{-3}$ M Pt(diamsar)$^{4+}$ with $e_{aq}^-$ at pH 10.

**Chemistry of Pt(diamsar)$^{4+}$.** Extensive spectroscopic, chemical and electrochemical studies of this ion were performed and are now discussed collectively. Reaction with the aquated electron ($e_{aq}^-$) by pulse radiolysis was performed with a view to seeking evidence for a Pt(III) state. Reaction with $e_{aq}^-$ resulted in the formation of a transient complex ($\lambda_{max}$ ~390 nm) which decayed with a first-order rate constant of approximately $6 \times 10^3$ s$^{-1}$, independent of the $e_{aq}^-$ dose and [Pt(IV)]. Optical spectra (pH ~10) of the transient and decay products are shown in Figure 4. The rate of formation of the putative Pt(III) transient was determined as $k(\mathrm{Pt^{IV}} + e_{aq}^-) = 2.3\ (\pm 0.1) \times 10^{10}$ M$^{-1}$ s$^{-1}$ at both pH 6.8 and pH 10. No further reaction was observed following the first-order decay of the transient, apart from a very slow photochemical reaction. Product analysis from a continuous pulse experiment indicated, apart from recovered starting compound, an apparently macromonocyclic Pt(II) complex, characterized by its behavior on Dowex resin as a 2+ ion, the low acidity of the coordinated amines, and NMR spectroscopy.

γ-Radiolysis of samples of Pt(diamsar)$^{4+}$ as Cl$^-$ or $CF_3SO_3^-$ salts in the solid state yielded samples which produced strong ESR signals at low temperatures, even after storage at room temperature for several days (Figure 5). The isotopic composition of platinum [$^{190}$Pt, 0.0127%; $^{192}$Pt, 0.78%; $^{194}$Pt, 32.9%; $^{195}$Pt, 33.8% ($I = {}^1/_2$); $^{196}$Pt, 25.3% ($I = 0$); $^{198}$Pt, 7.21%] should lead to a triplet for Pt(III) with a peak ratio of 1:4:1. The deconvoluted spectrum of the $CF_3SO_3^-$ salt is consistent with this and has a $g$ value of 2.01 and a coupling $A$ of ~50 G. The pattern for the chloride salt is centered at $g = 2.01$ and $A = 60$ G. It is presumed that the spectra are those of Pt(III) generated in the Pt(IV) crystal lattice and retaining an octahedral PtN$_6$ environment.

Electrochemical reduction of an aprotic solution of Pt(diamsar)$^{4+}$ in situ at −80 (acetone) or −40 °C (acetonitrile) in the probe of an ESR spectrometer was performed at a potential of −0.2 V (vs. Ag/AgCl) in an attempt to generate the short-lived Pt(III) intermediate in solution. Recording spectra during electrolysis yielded a weak signal at $g \simeq 2.1$, which decayed rapidly even at those temperatures, precluding our recording a reasonable spectrum. Further, the deprotonated Pt(IV) product of this reaction was itself reducible only at >−1 V and clearly did not yield a single product on coulometric reduction. Similar experiments with Pt(sep)$^{4+}$ also saw the generation of a better though still weak signal at $g = 2.22$. This intermediate was presumably longer lived, and the electrochemical studies also indicated the same result.

Detailed electrochemistry of the Pt(IV) complexes revealed a number of interesting features. The dc polarogram of Pt(diamsar)$^{4+}$ in acetone ($CF_3SO_3^-$ salt) exhibited three waves at $+0.16_7$, $-0.99_9$, and $-2.2_0$ V (vs. Ag/AgCl), with diffusion currents ($i_d$) in the ratio 1:1:2 (Figure 6). Further, the values of $i_d$ for the first two waves are similar to $i_d$ for the well-characterized one-electron Co(III) → Co(II) reduction of Co(dinosar)$^{3+}$ for the same concentration of complex.[18] The diffusion coefficient calculated

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[16] Palmer, J. W.; Basolo, F. *J. Inorg. Nucl. Chem.* **1960**, *15*, 279–286. Grinberg, A. A.; Gilsdengershel, K. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1948**, 479–492.

[17] Chernyaev, I. I.; Gladkaya, N. Sh.; Adrianova, O. N. *Russ. J. Inorg. Chem. (Engl. Trans.)* **1966**, *11*, 1329–1334.

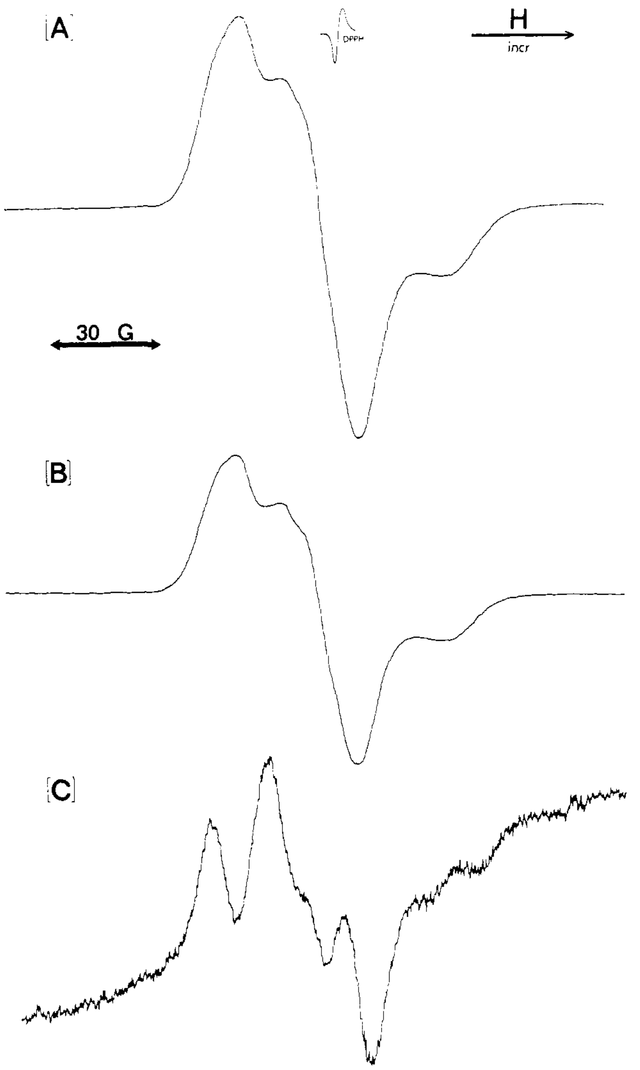

**Figure 5.** EPR spectra of the products of γ-radiolysis of a crystalline sample of [Pt(diamsar)]$Cl_4$ at (a) 4.2 K and (b) 77 K and (c) of a microcrystalline sample of [Pt(diamsar)]$(CF_3SO_3)_4$ at 77 K. Spectra were recorded with a Jeol JES-PE spectrometer at a radio frequency of 9.15 GHz and calibrated vs. dpph.

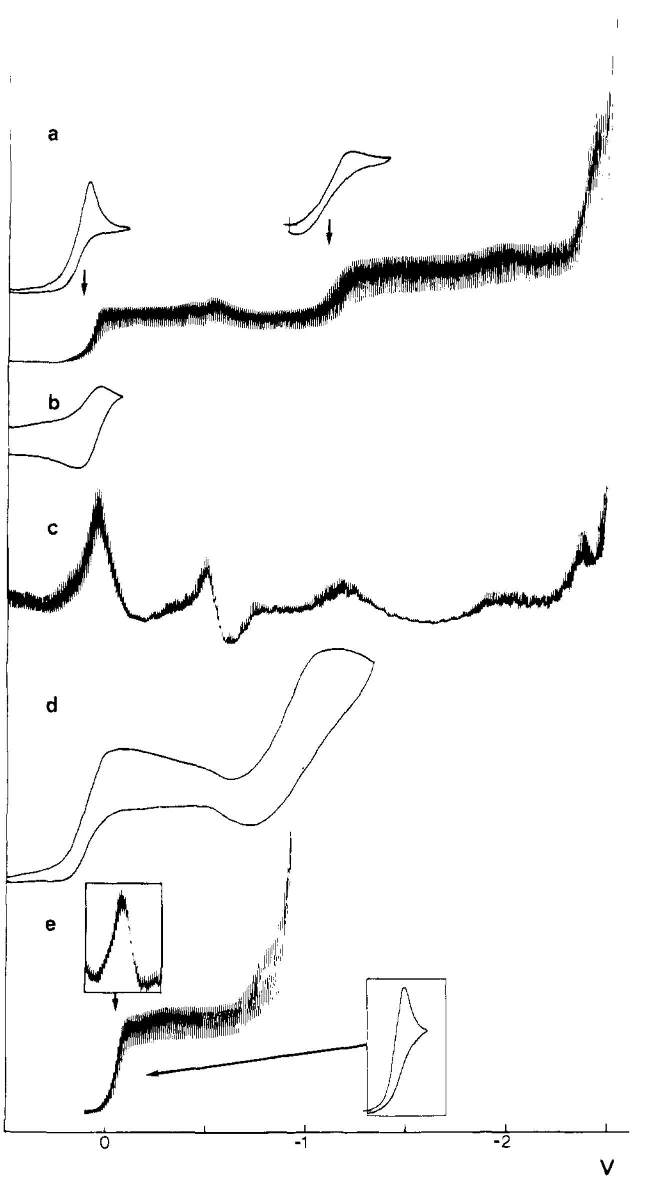

**Figure 6.** Voltammetry of Pt(diamsar)$^{4+}$: (a) dc polarogram (DME) in acetone (0.1 M $(CH_3)_4N^+(CF_3SO_3^-)$) at ambient temperature vs. a Ag/AgCl reference electrode, with cyclic dc voltammograms (HMDE, 500 mV/s scan speed) for the first two reductions superimposed; (b) cyclic voltammogram (stationary Au billet, 500 mV/s scan speed) at −80 °C in acetone; (c) in-phase ac polarogram in acetone at ambient temperature ($\omega$ = 400 Hz, $\Delta E$ = 10 mV); (d) cyclic voltammogram (stationary Au billet, 500 mV/s scan speed) in acetone at ambient temperature; (e) dc polarogram in 1 M aqueous $HClO_4$ at ambient temperature, with (top inset) the in-phase ac polarogram ($\omega$ = 400 Hz, $\Delta E$ = 10 mV) and (right inset) the cyclic voltammogram (HMDE, 500 mV/s scan speed) for the first reduction.

for the first reduction of Pt(diamsar)$^{4+}$ using the Ilkovic equation was 9.7 × $10^{-6}$ cm$^2$ s$^{-1}$, compared with 10.4 × $10^{-6}$ cm$^2$ s$^{-1}$ for Co(dinosar)$^{3+}$. Coulometry indicated that the first two reduction steps of Pt(diamsar)$^{4+}$ in acetone were one electron in nature; the third reduction was too close to the solvent front for successful coulometric analysis, but dc and pulse techniques indicated this was a two-electron process. Cyclic voltammograms showed the first reduction of Pt(diamsar)$^{4+}$ to be irreversible at scan rates of up to 1 V/s (Figure 6); further, the reduction potential was dependent on the choice of working electrode, being more negative at Pt ($E_r$ = −0.37 V) than at Hg or Au (+0.04 V). The second reduction showed a reverse (oxidation) wave in the cyclics at both Au and Hg but not at Pt; however, the large peak-to-peak separations (>280 mV) do not indicate electrochemical reversibility. Some evidence for a reverse wave for the first reduction was observed at low temperature at a Au electrode (−80 °C, acetone, $\Delta E_p$ = 180 mV, scan rate 500 mV/s), but the ratio of reduction to oxidation currents $i_r/i_o$ = 0.4 implied limited reversibility.

Controlled potential electrolysis (−0.2 V, acetonitrile) of Pt(diamsar)$^{4+}$ in a spectroelectrochemical cell proceeded with retention of isobestic points to a compound with an absorption maxima at 350 nm, analogous to that of an authentic sample of the monodeprotonated Pt(IV) complex; the spectrum did not change on exposure of the sample to oxygen. Polarography of the fully electrolyzed (−0.2 V) solution showed that only the first reduction wave, initially at +0.17 V, was absent; waves at −1.0 and −2.2 V were present, and no oxidation wave was apparent. Gas was evolved upon reduction of Pt(diamsar)$^{4+}$ in acetone with zinc dust and was measured volumetrically as 0.5 (±0.1) mol/mol of complex; further, only starting product was recovered from solution via column chromatography. A wave observed at −0.45 V for Pt(diamsar)$^{4+}$ was at essentially the same position as that observed for a hydrogen-saturated solution and was presumably related to an adsorbed hydrogen redox process. Repeat-scan cyclic voltammetry at a stationary Pt electrode also produced a wave at a position identical with that for adsorbed hydrogen, confirming the release of hydrogen in the process.

Variable-frequency ac polarography (10–1100 Hz) showed that the peak height for the first Pt(diamsar)$^{4+}$ reduction is much

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(18) Bond, A. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, in press.

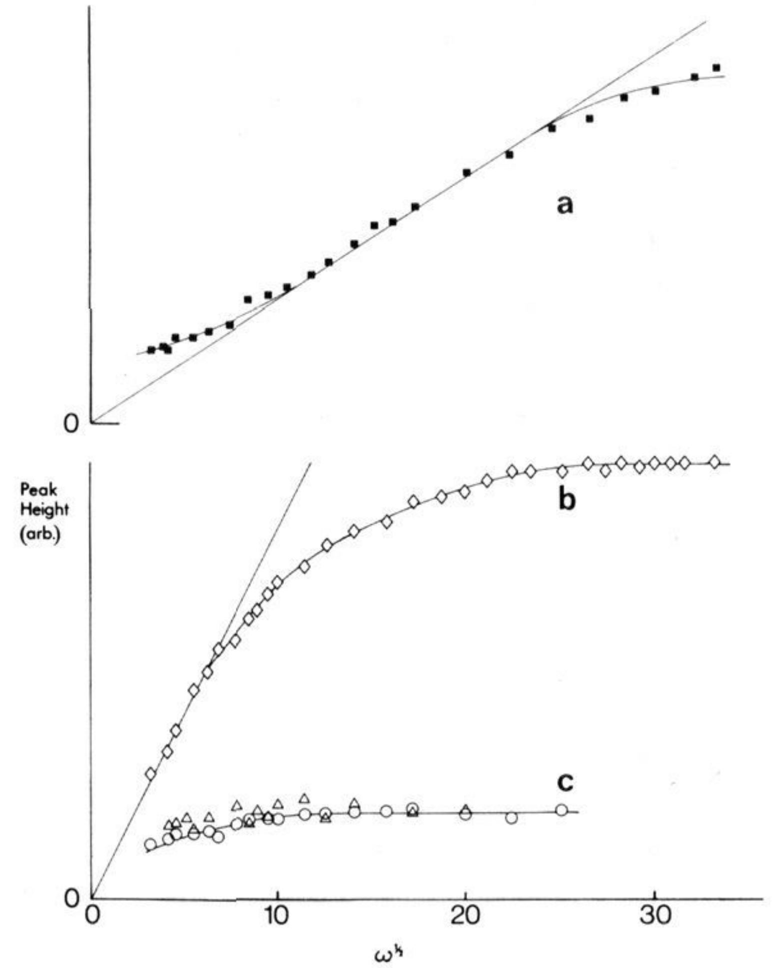

**Figure 7.** Frequency dependence of the in-phase peak current of the ac polarogram (10–1100 Hz) in acetone for the first metal-centered reduction of (a) $Pt(sep)^{4+}$, (b) $Co(dinosar)^{3+}$, and (c) $Pt(diamsar)^{4+}$. For the latter complex, peak heights, corrected for concentration, are reported for 1.9 mM (△) and 6.2 mM (○) solutions.

smaller than that observed for $Co(dinosar)^{4+}$[18] (Figure 7). The latter complex showed typical behaviour,[19] with $k_s$ controlling the peak height at high frequencies. The peak height for the first reduction of $Pt(diamsar)^{4+}$ was independent of frequency, indicative of a fast following chemical reaction ($t_{1/2} \leq 10^{-3}$ s). When the peak height was corrected for concentration, the frequency profiles for two concentrations (1.9 and 6.2 mM) were the same, consistent with first-order kinetics of the following chemical reaction.

The aqueous electrochemistry of the complex was also studied. The reduction of $Pt(diamsar)^{4+}$ was pH dependent. The first reduction wave shifted from $-0.02_8$ V (pH 0) to −0.145 V (pH 4.2) and to −0.85 V (pH 10.5). In addition, a second wave was observed at −1.10 (pH 4.2), −1.16 (pH 7.5), and −1.51 V (pH 10.5). The reduction at pH 0 corresponds to that of the fully protonated complex; irreversibility was established, since no reverse wave was observed during cyclic voltammetry at up to 20 V/s. Coulometry and controlled potential electrolysis experiments indicated that the behavior in water differs markedly from that observed in aprotic solvents. Controlled potential electrolysis of a sample in 1 M acid at −0.15 V was performed, and the products were subsequently sought. Two major products, one Pt(II) and one Pt(IV) complex, corresponding to ≥90% of total platinum, were detected chromatographically; an analogous experiment in acetone yielded only starting product. From NMR, low-symmetry ring-opened macrocyclic species with a $CH_2OH$ group form upon reduction in water. The simple $^{13}C$ NMR of the $Pt(diamsar)^{4+}$ precursor (resonances at −12.4, −7.8, and +6.1 ppm, vs. dioxane) contrasts with spectra for the Pt(II) (resonances at −28.7, −25.2, −17.1, −16.1, −11.8, and +1.3 ppm) and Pt(IV) (resonances at −31.3, −30.1, −11.9, −7.1, and +27.3 ppm) products. The major resonance near −11.8 ppm for both products is broad and asymmetric compared with all other resonances, indicative of overlapping signals. Further, the $^{195}Pt–C$ coupling of ~80 Hz observed for the lower charged product compared with <20 Hz for the higher charged product is consistent with their assignment as Pt(II) and Pt(IV) products, respectively, since this is the expected trend for coupling constants. The $^1H$ NMR ($^{195}Pt$ decoupled) spectra of the products are complex, as expected from the low symmetry. However, a separate high-field singlet at 3.2 ppm (vs. $Me_4Si$) can be assigned to a $CH_2OH$ group, by analogy with characterized analogues.

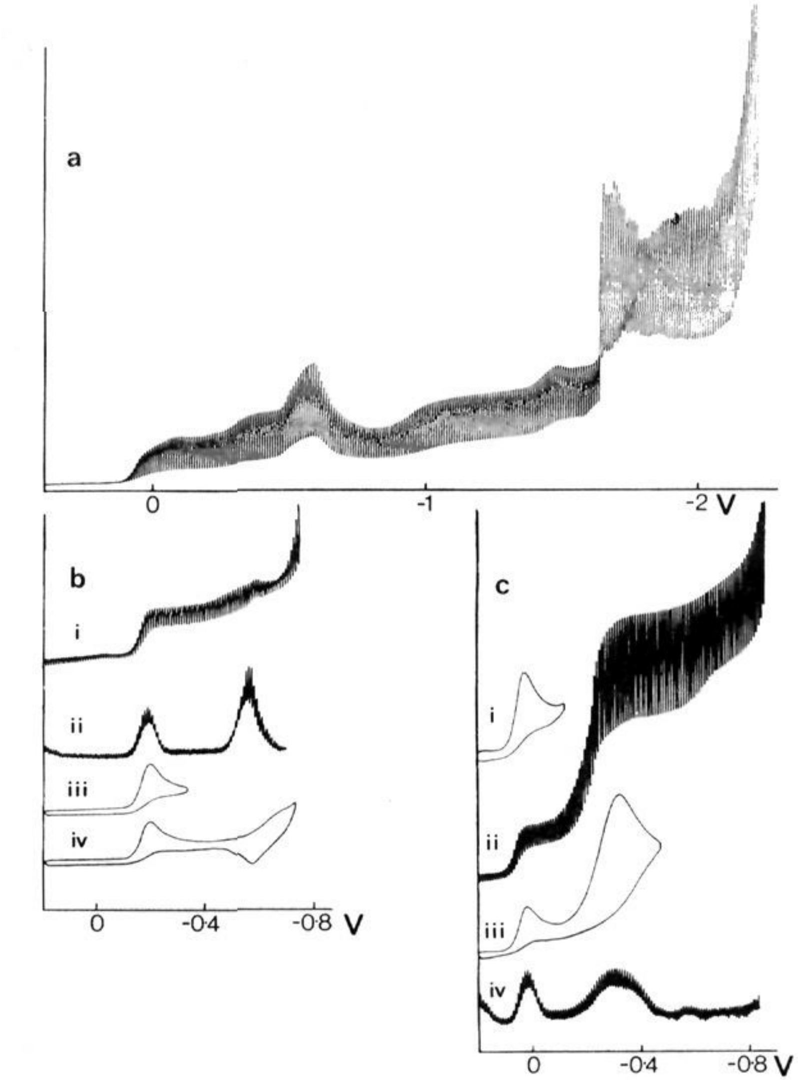

**Figure 8.** Voltammetry of macrobicyclic Pt(IV) complexes: (a) dc polarogram of $Pt(sep)^{4+}$ in acetone, vs. Ag/AgCl; (b) $Pt(sep)^{4+}$ in 1 M aqueous $HClO_4$, with (i) dc polarogram, (ii) ac polarogram ($\omega$ = 400 Hz, in-phase, $\Delta E$ = 10 mV), and (iii and iv) cyclic voltammograms (HMDE, 500 mV/s scan speed) with switching potentials of −0.35 and −0.7 V, respectively; (c) $Pt(dinosar)^{4+}$ in 1 M aqueous $HClO_4$, with (i) cyclic voltammogram (HMDE, 500 mV/s scan speed), switching potential −0.15 V, (ii) dc polarogram, (iii) cyclic voltammogram, switching potential −0.5 V, and (iv) ac polarogram ($\omega$ = 400 Hz, in-phase, $\Delta E$ = 10 mV).

Coulometric analysis of $Pt(diamsar)^{4+}$ at various controlled potentials from near the $E_{1/2}$ value to −0.5 V indicated $1.5 \leq n \leq 2$, dependent on potential. The observation of Pt(IV) and Pt(II) products suggests disproportionation is a major decay path for the Pt(III) transient in aqueous solution. However, the observation of a first-order decay rate of the Pt(III) species from pulse radiolysis experiment does not allow this disproportionation to be rate determining. Possibly, C–N bond cleavage of the Pt(III) intermediate is the slow step, followed by rapid disproportionation. The observation of other minor (≤10% of total Pt) and uncharacterized Pt(II) and Pt(IV) products suggests that several routes are available.

**Electrochemistry of $Pt(sep)^{4+}$ and $Pt(dinosar)^{4+}$.** In 1 M $HClO_4$, $Pt(sep)^{4+}$ exhibited two reductions at $-0.16_5$ and −0.5 V (Figure 8). The first reduction was irreversible, with no oxidation waves detected in the cyclic voltammograms at up to 20 V/s; some electrochemical reversibility of the second wave ($\Delta E_p$ = 85 mV at 500 mV/s, CV) was observed. The $Pt(dinosar\text{-}H)^{3+}$ complex in 1 M $HClO_4$ showed a wave at +0.06 V for the metal ion reduction and a wave at −0.22 V from nitro group reduction. Interestingly, the ratio of $i_d$ (Pt):$i_d$($NO_2$) was only 1:5, rather than the 1:8 ratio observed in the cobalt analogue.[18] This indicated the first wave is not a simple one-electron process and presumably follows the behavior of the diamsar complex. Again, the initial reduction step was completely irreversible. It is interesting to note that chemical reduction of $Pt(dinosar\text{-}H)^{3+}$ with $SnCl_2$ yielded

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(19) Bond, A. M.; Martin, R. L.; Masters, A. F. *Inorg. Chem.* **1975**, *14*, 1432–1435.

Table III. Electrochemical Data for Reduction of Platinum(IV) Complexes[a]

| | | | dc[b] | | ac[b,c] | | cyclic dc[d] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| compd | solv | electrode | $E_{1/2}$, V | ($E_{1/4} - E_{3/4}$), mV | $E_p$, V | $\Delta E_{1/2}$, mV | $E_R$, V | $E_O$, V | $\Delta E$, mV | $i_O/i_R$ |
| $Pt(diamsar)^{4+}$ | acetone | DME/HMDE | +0.167[e] | 75 | +0.187 | 110 | +0.04 | abs[g] | ... | ... |
| | | | −0.999[f] | 75 | −1.00 | 220 | $-1.11_0$ | $-0.83_4$ | 276 | ~1 |
| | | | −2.20 | ~20 | −2.08 | 40 | | | | |
| | | Au[h] | +0.111 | 43 | $-0.06_6$ | 120 | +0.04 | abs | | |
| | | | $-0.80_4$ | 120 | ... | ... | −1.02 | −0.70 | 320 | ~1 |
| | | | | | | | −0.13 | +0.05 | 180 | 0.4[i] |
| | | | | | | | −0.63 | −0.23 | 420 | ... |
| | | Pt | | | | | −0.37 | abs | ... | ... |
| | | | | | | | −1.00 | abs | ... | ... |
| | $H_2O$, 1 M $HClO_4$ | DME/HMDE | $-0.02_8$ | 50 | $-0.07_7$ | ... | $-0.11_5$ | abs | ... | ... |
| | $H_2O$, pH 4.2 | | $-0.14_5$ | 40 | −0.19 | ... | $-0.20_3$ | abs | ... | ... |
| | $H_2O$, pH 4.5 | | −0.20 | 45 | | | | | | |
| | | | −1.10 | 35 | | | | | | |
| | $H_2O$, pH 7.5 | | ~−0.7 | ~200 | | | | | | |
| | | | −1.46 | 33 | | | | | | |
| | $H_2O$, pH 10.5 | | −0.85 | ~170 | | | | | | |
| | | | −1.52 | 35 | | | | | | |
| $Pt(sep)^{4+}$ | acetone | DME/HMDE | +0.048 | 73 | $+0.04_8$ | 85 | | | | |
| | | | −0.59[j] | ... | −0.54 | ... | | | | |
| | | | $-1.77_7$ | ~5 | −1.67 | ~150 | | | | |
| | $H_2O$, 1 M $HClO_4$ | DME/HMDE | $-0.16_5$ | 35 | $-0.18_3$ | 65 | −0.18 | abs | ... | ... |
| | | | −0.45 | 95 | $-0.54_5$ | 75 | $-0.67_5$ | −0.59 | 85 | ~1 |
| $Pt(dinosar\text{-}H)^{3+}$ | $H_2O$, 1 M $HClO_4$ | DME/HMDE | +0.06 | 30 | $+0.01_5$ | 70 | $+0.01_2$ | abs | ... | ... |
| | | | −0.22[k] | 67 | −0.31 | ~200 | $-0.33_5$ | abs | ... | ... |
| $Pt(en)_3{}^{4+}$ | $H_2O$, 1 M $HClO_4$ | DME/HMDE | $-0.21_3$[l] | 30 | $-0.23_0$ | 90 | $-0.24_8$ | abs | ... | ... |

[a] Measured at ambient temperature, unless specified; aqueous solutions all 1 M in $ClO_4^-$; complexes were $CF_3SO_3^-$ salts (acetone) or chloride salts; reference electrode was SCE (aqueous solutions) or Ag/AgCl, saturated LiCl/acetone (nonaqueous solutions). [b] Scan rate = 20 mV/s; drop time = 0.5 s. [c] Frequency 200 or 400 Hz; $\Delta E_p = 5$ mV; $\Delta E_{1/2}$ = width at half-height. [d] Cyclic voltammograms recorded at 200 or 500 mV/s. [e] Coulometry, −0.1 V, yielded $n = 1.05$ (Hg pool) and $n = 1.01$ (Pt basket). [f] Coulometry, −1.25 V, yielded $n = 1.01$ (Hg pool). [g] abs indicates no reverse (oxidation) peak observed, even at high scan rates. [h] dc voltammogram recorded with a pseudo drop time of 0.5 s. [i] Recorded at −80 °C (acetone/dry ice bath). [j] Adsorption maxima. [k] Reduction of $-NO_2$ groups; $i_d(Pt):i_d(NO_2) \simeq 1:5$. [l] Wave broadens and moves to lower potentials as the pH is increased, due to chemical equilibria effects.

an appreciable amount of the diamsar cage, in addition to ring-opened products.

The reduction of $Pt(sep)^{4+}$ in acetone was complicated (Figure 8a), with the initial reduction ($+0.04_8$ V) being followed by various adsorption phenomena (maximum at ~−0.6 V). While an apparently two-electron reduction was also distinguished at −1.78 V, no others were detected, but they may have been present under the complex adsorption waves. Variable-frequency ac polarography (Figure 7) indicated that the chemical reaction dominated peak heights at low frequencies (<40 Hz) while diffusion and electrode kinetics dominated above 100 Hz. The behavior observed is analogous to that previously seen in the reduction of chromium complexes, where similar peak height vs. $\omega^{1/2}$ profiles are reported.[19]

Details of the electrochemical parameters determined are presented in Table III. In addition, no oxidation waves were observed in acetone or acetonitrile for the complexes up to the solvent limit (≥2 V), precluding nominally Pt(V) species, and such a result is not surprising.

## Discussion

**Synthesis and Characterization.** Despite the extensive coordination chemistry of platinum(IV), including the reported preparations of a range of platinum(IV) amine complexes,[20] the chemistry of platinum with macrocyclic amine ligands is very limited.[21] The macrobicyclic amine complexes reported in this study are the first of this type of complex of platinum(IV) to appear. The preparative philosophy employed parallels that developed for the cobalt(III) analogues,[2-5] and the mechanism of formation of encapsulated complexes of this type has been described elsewhere.[2]

The encapsulation reactions effectively trap the metal ion in a tight ligand cage with octahedral donor atoms. The close-knit nature of the macrobicyclic cages formed about the platinum(IV) ion can be ascertained from the published crystal structure of $[Pt(sep)](S_2O_6)_2 \cdot 2.5H_2O$.[15] The complex is structurally similar to the cobalt(III) analogue,[4] except the flattening of the aza caps at each end of the molecule is more marked, indicative of more strain in the Pt(IV) complex. Nevertheless, Pt–N bond lengths (207 pm) are close to those in $Pt(en)_2Cl_2{}^{2+}$ (208 pm).[22]

The high symmetry of the encapsulated (or "cage") complexes is clear from the nmr data (Table I). Both $^{13}C$ and $^1H$ spectra, together with microanalytical data, also characterize the prepared complexes as macrobicyclic in nature, and analogies with the structurally characterized cobalt(III) macrobicyclic complexes are apparent.

The acidities of the amine protons are consistent with those of secondary amines coordinated to platinum(IV). The primary amines of $Pt(en)_3{}^{4+}$ ($pK_a{}^1 = 5.5$) are appreciably less acidic, e.g., $pK_a{}^1 = 2.4$ for $Pt(diamsar)^{4+}$. The exceptional acidity of the amine protons in $Pt(dinosar)^{4+}$ is a consequence of the electronic influence of the nitro groups, since reduction of these groups to amines causes a change in $pK_a{}^1$ from <0 to 2.4. Monodeprotonation of the cages leads to an absorption maximum in the visible region which is absent in the fully protonated complex (Table II); the moderately intense maximum ($\epsilon > 10^3$ $M^{-1}$ $cm^{-1}$) observed near 350 nm is presumably a ligand-to-metal charge-transfer band. This maximum is unlikely to arise from a d–d transition, since the assigned first d–d band in $Ir(en)_3{}^{3+}$[23] and the assigned band in $Pt(en)_3{}^{4+}$[17] occur at or below 250 nm. Rather, a shoulder detected around 260 nm in strong acid solution is most likely the first d–d band for the fully protonated complexes. In strong base,

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(20) "Inorganic Chemistry of the Transition Elements"; The Chemical Society: London; Vols. 1-6.

(21) Macromonocyclic amine complexes of platinum have been prepared but not reported: Curtis, N. F., personal communication.

(22) Larsen, K. P.; Hazell, R. G.; Toftlund, H.; Andersen, P. R.; Bisgard, P.; Edlund, K.; Eliasen, M.; Herskind, C.; Laursen, T.; Pedersen, P. M. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 499-504.

(23) Jørgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 500-517.

where multiple deprotonations occur, a shoulder is observed near 300 nm, probably charge-transfer in nature. An intense band with a maximum at 253 nm observed in basic solution for the dinosar complex (Figure 2) is absent in the other cage complexes. We suggest this arises from a $\pi \rightarrow \pi^*$ transition localized on the nitro group. Particularly in basic solution, we have observed that the cage complexes appear to undergo photochemical reactions slowly in the spectrophotometer beam. However this photochemistry has not been pursued.

**Pt(III) Chemistry**: Evidence for the relatively rare octahedral monomeric rhodium(II) state with a macrobicyclic hexaamine ligand has recently been obtained,[24] which encouraged our search for the equally rare monomeric octahedral platinum(III) oxidation state. The only well-documented monomeric Pt(III) coordination complex is the bis(diphenylglyoximato)platinum(III) perchlorate.[25] All other Pt(III) complexes are either dimeric,[26] contain ligands with the ability to delocalize unpaired electrons,[27] or are short-lived transients observed in various processes.[28-31] In the solid state, Pt(III) can be stabilized in crystal lattices either by $\gamma$-irradiation,[32] thermal decomposition of Pt(IV),[33] growth in yttrium aluminium garnet,[34] or electrolytic growth into a rutile host lattice.[35]

The fast-reaction technique of pulse radiolysis offers a means whereby an electron can frequently be added directly at the metal in a complex in solution, via reaction with the aquated electron ($k \approx 10^{10}$ M$^{-1}$ s$^{-1}$). Appropriate instrumentation allows both the rates of formation and decay of transients, as well as their spectra, to be recorded. A recent application of this technique to the formation of Pt(III) species involved reaction of $Pt(en)_2^{2+}$ with the oxidant OH or reaction of $Pt(en)_2(OH)_2^{2+}$ with the reductant $e_{aq}^-$.[31] The mechanism in these reactions is complicated by acid–base, anion substitution, and water elimination processes; nevertheless, lifetimes in the microsecond range were observed for the putative Pt(III) transients. Earlier pulse radiolysis and flash photolysis studies of $PtCl_6^{2-}$ suggested formation of a Pt(III) transient which decayed rapidly in a second-order process via disproportionation to Pt(II) and Pt(IV).[28]

The nature of the macrobicyclic ligand used in this study severely limits the possibility of substitution reactions; further, the geometrical constraints presumably act to retain octahedral-type geometry, whereas square-planar or pentacoordinate geometries have been suggested for Pt(III) transients generated from substitution-labile systems.[31] Pulse radiolysis of Pt(diamsar)$^{4+}$ in aqueous solution (pH 6.8 or 10.0) yielded a transient which decayed by first-order kinetics with $k_{obsd} = 6 \times 10^3$ s$^{-1}$. Apparently a rate-determining disproportionating reaction is not involved, since this would require second-order kinetics. The spectrum of the transient is consistent with addition of an electron initially at the metal center, since it differs appreciably from the spectrum of the precursor and decay products (Figure 4); addition of an electron at a site on the ligand should not lead to such a marked spectral change, extending well into the visible region.

The formation of a short-lived Pt(III) intermediate is implied by the pulse radiolysis experiment. However, paramagnetic d$^7$ platinum(III) should be detectable by ESR spectroscopy, both in solution and in the solid state. Stabilization of Pt(III) in crystal lattices by $\gamma$-irradiation of platinum compounds has been well documented,[32] and ESR spectra of the metal ion in these environments have been reported. We have applied this approach to crystalline and microcrystalline samples of Pt(diamsar)$^{4+}$ as the chloride and trifluoromethanesulfonato salts, respectively. In each case a strong ESR signal consistent with trapping of Pt(III) in the crystalline lattice in the solid state was obtained. The Pt(III) ion is presumably retained in the octahedral environment of the macrobicyclic ligand, and the absence of anisotropy in the simple ESR signal observed near $g = 2.0$ is consistent with this assertion. In the solid state the species is quite stable, although the observed spectrum differs somewhat upon changing the anion, presumably because the space group of the crystal lattice varies. Only at 4 K is a further very weak signal centered near $g = 4$ observed for the chloride salt; this most likely arises from some long-range coupling phenomenon between Pt(III) centers in the lattice, and such effects are not unusual.[36]

The isotopic composition of platinum, with 33.8% of $^{195}$Pt ($I = {}^1/_2$), leads to the expectation of an ESR with a central peak with side bands in the approximate ratio 1:4:1. Radiolysis of $Pt(en)_3Cl_4$ in a frozen aqueous solution yielded such a spectrum with $g = 2.3$ and a hyperfine splitting of $\sim$200 G.[29] Retention of the $PtN_6^{3+}$ coordination sphere is uncertain in that case, although no evidence for the axially or rhombically distorted spectra obtained from oxidation of square-planar Pt(II) species was reported. The spectra obtained for Pt(diamsar)$^{3+}$ show a hyperfine coupling of $\sim$50 G, somewhat smaller than that reported for the putative $Pt(en)_3^{3+}$ ion,[29] but appreciably smaller than the coupling reported for axially and rhombically distorted Pt$^{3+}$ species of $\sim$800 G.[32] The low hyperfine coupling for Pt(diamsar)$^{3+}$ possibly indicates some delocalization over the nitrogen donor atoms of the macrobicyclic ligand.

Attempts to characterize Pt(III) in frozen solution following electrochemical reduction were less successful, since the following decay reactions are fast even at $\sim -80$ °C. However, a weak transient was observed near $g = 2.1$ for reduced Pt(diamsar)$^{4+}$ and a stronger signal at $g = 2.22$ for reduced Pt(sep)$^{4+}$. This order of stability follows that observed from our electrochemical investigations and indicates that Pt(III) is an intermediate in reductions of the Pt(IV) cage complexes in solution.

**Electrochemistry**. The prospect of trapping the Pt(III) oxidation state in the cage complexes and of generating octahedral Pt(II) was of particular interest, since these are clearly unstable conditions for platinum.[25] Platinum(IV) complexes usually undergo a two-electron reduction to platinum(II). Such a reduction has been reported[37] for $Pt(en)_3^{4+}$ and was confirmed by this study. Although a Pt(III) intermediate was inferred from the shape of the two-electron dc reduction wave,[37] our reexamination of the system found no evidence for this.[38] However, the pattern of events for the reduction of the caged Pt(IV) ions was substantially different from those of the simple amines and the behavior in protic and aprotic solvents also differed.

The first reduction wave of Pt(diamsar)$^{4+}$ is one-electron in nature in aprotic solvents, established from coulometry experiments in acetone. Spectroelectrochemistry showed the fully reduced compound exhibited a maximum at 350 nm, typical of a deprotonated Pt(IV) cage; this formulation was also supported by the absence of any reoxidation process (by oxygen or electrochemically) and the absence of an ESR signal in the reduced solution. Further, ion-exchange chromatography of the solution from controlled potential electrolysis (at −0.2 V, vs. Ag/AgCl) yielded only Pt(diamsar)$^{4+}$ quantitatively. A quantitative experiment

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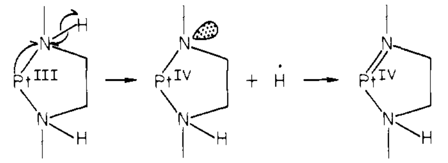
[38] We have confirmed the two-electron nature of the first reduction of $[Pt(en)_3]^{4+}$ from coulometry at a Hg pool. Further, all other electrochemical analyses indicated a simple two-electron irreversible reduction.

detected 0.5 mol of gas/mol of platinum when the diamsar complex was reduced with zinc in acetone. Waves detected at both mercury and platinum electrodes in acetone at positions identical to waves observed for hydrogen saturated acetone confirmed the generation and adsorption of hydrogen on the electrode surface in aprotic solvents. The reduction was irreversible at room temperature, although some limited reversibility was detected at low temperature (−80 °C) in a slush bath. This series of observations is consistent with the initial formation of Pt(diamsar)$^{3+}$, followed by a rapid intramolecular process involving the evolution of hydrogen and the formation of monodeprotonated Pt(diamsar-H)$^{+}$ (eq 1).



(1)

$$2\dot{H} \xrightarrow{\text{fast}} H_2$$

This mechanism is also consistent with the observed electrode dependence of the reduction potential, since the hydrogen atom is liable to be adsorbed on the electrode surface initially.[39] If the reaction involves abstraction of a hydrogen atom directly by the electrode surface, the affinity of the electrode for H atoms may be important in determining the reduction potential. The rapidity of the following chemical reaction ($t_{1/2} < 10^{-3}$ s) suggests that the electron-transfer process may be rate determining. Since the value of the heterogeneous rate constant ($k_s$) is usually lower at Pt than Hg electrodes,[18,19] this may account for the lower reduction potentials observed at the former electrode. Since first-order kinetics have been characterized for this first one-electron reduction by variable-frequency ac polarography, alternative decomposition modes such as disproportionation or dimerization can be eliminated, and the proposal of eq 1 is consistent with the variety of physical evidence, at least in aprotic solvents.

Several factors act to militate against reduction of the Pt(IV) cage directly to Pt(II) in a two-electron step: (i) d$^8$ Pt(II) prefers a square-planar environment,[25] and while Pt(III) (d$^7$) may prefer a coordination number of less than six,[28,31] it should tolerate a distorted octahedral geometry like the cobalt(II) ion does. (ii) Energy minimization calculations indicate that the preferred hole size for 20-membered macrobicyclic sar type ligands is intermediate between that which would accommodate Co$^{3+}$ and Co$^{2+}$ perfectly, but closer to Co$^{3+}$.[40] Since Pt$^{4+}$ has a similar radius to Co$^{3+}$,[41] and ion size increases with decreasing oxidation state, it is not unreasonable to expect strain to increase in the order Pt$^{4+}$ < Pt$^{3+}$ ≪ Pt$^{2+}$. The importance of hole size is also exemplified by the difficulty in reducing hexaazacobalt cages beyond Co(II) without breaking the cage, a phenomenon not observed in macromonocyclic Co(II) complexes.[18] The constraints imposed by encapsulation do not apply in simple amine complexes such as Pt(en)$_3$$^{4+}$. (iii) The amine protons of the encapsulated complexes are more acidic than those of simple amine complexes. This weakening of the NH bonds should facilitate abstraction of a hydrogen atom.

The second one-electron reduction observed for Pt(diamsar)$^{4+}$ is quasi-reversible. The ac polarogram indicated a very broad peak which changed in shape and height with frequency; however, its behavior was too complex to rationalize. This step represents reduction of the monodeprotonated cage, and it is apparent that the deprotonated Pt(III) complex initially produced is more stable than the protonated analogue formed in the first reduction. The observation of a half-life of the deprotonated Pt(III) complex in the millisecond range in the pulse radiolysis experiments (where pH of solutions used required this to be the dominant species) is consistent with this assertion. A subsequent two-electron reduction is observed in aprotic media near −2.2 V; this process is irreversible. While controlled potential electrolysis and spectroelectrochemistry have established the formation of Pt(diamsar-H)$^{3+}$ as the only reduction product from the first step, the second step is more complex on a coulometric time scale (≥10 min). Spectroelectrochemistry at −1.25 V indicated that isosbestic points are not maintained in the second reduction, where two maxima appear. The production of more than one species by consecutive reactions is likely. While coulometry at −1.25 V indicates a one-electron process, several products are indicated by chromatography, including Pt(II) species. Electrochemistry is consistent with the reaction sequence

$$\mathrm{Pt^{IV}(diamsar)^{4+}} \xrightarrow[(+0.17\ \mathrm{V})]{1e^-} \mathrm{Pt^{III}(diamsar)^{3+}} \xrightarrow[\text{fast}]{k_1} \mathrm{Pt^{IV}(diamsar\text{-}H)^{3+}} + \mathrm{H}\cdot \quad (2)$$

$$\mathrm{Pt^{IV}(diamsar\text{-}H)^{3+}} \xrightarrow[(-1.00\ \mathrm{V})]{1e^-} \mathrm{Pt^{III}(diamsar\text{-}H)^{2+}} \xrightarrow[\text{fast}]{k_2} \text{products} \xrightarrow[(-2.2\ \mathrm{V})]{\sim 2e^-} \text{products} \quad (3)$$

where the products of reduction at lower potentials have not been fully characterized but are clearly not Pt(IV)- or Pt(II)-encapsulated species.

One remarkable feature of the electrochemistry of Pt(diamsar)$^{4+}$ is the stabilization of the Pt(IV) oxidation state by ~1.2 V upon deprotonation. Similar stabilization of Os(IV) complexes on deprotonation have also been observed recently[42] and was attributed to considerable back-donation of electron density from the filled p$_z$ orbital of the aminate ion to a t$_{2g}$ orbital of the metal.

The electronic configuration of the octahedral Pt(IV) (low-spin, 5d$^6$) has the three t$_{2g}$ orbitals filled, so that such a $\pi$-bonding process is not possible unless higher energy levels are used. In this respect the Pt(IV) chemistry differs from the Os(IV) where there is an empty t$_{2g}$ orbital available to accept the lone pairs of electrons. Although the effect of deprotonation on the reduction potential is similar in the two instances (~−1 V), it remains to be seen whether the donation of charge which is reflected in a very short Os–N bond is also evident in the structures of deprotonated Pt(IV) amine complexes. Such effects are at present being investigated.

The Pt(sep)$^{4+}$ complex in aprotic solvents also underwent an initial one-electron reduction. The lifetime of the Pt(III) intermediate appears somewhat longer in this case, however, as illustrated by variable frequency ac polarography and ESR experiments. The crystal structure of the Pt(sep)$^{4+}$ ion[15] showed a marked flattening of the aza caps. This distortion, which is more difficult to achieve in sar cages, helps to generate a larger cavity in the macrobicycle and subsequently stabilizes the Pt(III) state to a greater extent. Energy minimization calculations indicate that the most favorable cavity size in the aza-capped sep ligand is slightly larger than that in the carbon-capped sar ligands.[40] Subsequent to the initial reduction, a complex reduction pattern is observed (Figure 6), probably involving ring-opening reactions. Adsorption–desorption phenomena are involved in the observed electrode process at negative potentials, which complicate the observed polarograms.

The electrochemistry of the cage complexes in water does not follow the pattern established in aprotic solvents. The reduction of Pt(diamsar)$^{4+}$ in aqueous solution is dependent on pH. However, the apparent separation of E$_{1/2}$ for Pt(diamsar)$^{4+}$ at pH 0 and the monodeprotonated forms at higher pH (Table III) was appreciably smaller than the 1 V observed in aprotic solvents. The apparent discrepancy arises as a result of the rapid equilibrium

$$\mathrm{H^+ + Pt(diamsar\text{-}H)^{3+}} \underset{(\mathrm{p}K_a = 2.4)}{\rightleftharpoons} \mathrm{Pt(diamsar)^{4+}} \quad (4)$$

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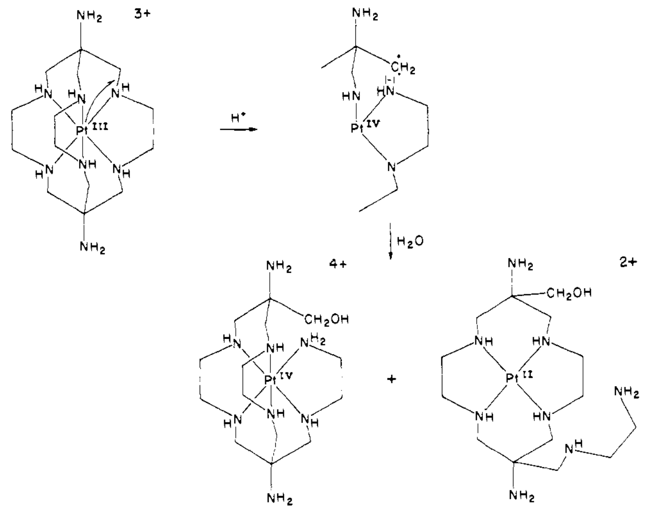
Scheme I



Although the deprotonated complex is the dominant species in solution above pH 3, the ease of reduction of the fully protonated form requires this to be the electroactive species; its observed reduction potential is moved to more negative potentials because of the necessary preequilibrium condition.[43] Subsequent deprotonations at higher pH ($pK_a^2 = 7.2$) complicate the electrochemistry further, and the initial reduction is then very broad and is shifted to considerably lower potentials. A wave observed below $-1$ V at high pH is presumably the reduction wave of the monodeprotonated complex. The separation of the reduction potentials of Pt(diamsar)$^{4+}$ and Pt(diamsar-H)$^{3+}$ in aqueous solution were estimated from data for solutions which contain the appropriate species as the major component. Potentials of $-0.02_8$ (1 M $HClO_4$) and $-1.16$ V (pH 4.5, second wave) show a separation similar to the 1.17 V separation observed in acetone.

The most important distinction between the behavior in aqueous and nonaqueous solution arose from the nature of the product of the first reduction. Chromatographic separation yielded two major products: a colorless Pt(II) species (eluted rapidly) and a pale yellow Pt(IV) compound which eluted more slowly. In both species the cage is clearly broken. These two species accounted for about 90% of total platinum, and at least two other minor bands were seen. Coulometry at various potentials from near the reduction potential in 1 M $HClO_4$ ($-0.02_8$ V) to as low as $-0.5$ V did not give a constant value. Near the reduction potential, $n \approx 1.5$ was observed, while at more negative potentials $n$ became progressively larger and approached $\sim 2$. These observations are consistent with a scheme of the type shown in Scheme I.

Following electron transfer, the cage-breaking process appears to be the rate-determining step, since the Pt(III) species has been shown to decay by a first-order process in pulse radiolysis experiments. A rapid disproportionation can subsequently occur, yielding Pt(II) and Pt(IV) products. The Pt(IV) product will have a different $E_{1/2}$ from the precursor complex and hence will be reduced to Pt(II) at a different potential; the variation in the coulometric $n$ with applied potential is consistent with this analysis. Further, since several minor products are observed in the reduction, more than one decay path for the Pt(III) intermediate may be implied. The simple one-electron reduction observed in aprotic solvents does not occur in the presence of added water, when $n \approx 2$ is observed; this indicates that water (as $OH^-$ or $H^+$) has a role to play in the ring-opening process, which presumably proceed via a radical mechanism to yield the opened cage illustrated in Scheme I as the major product.

Ring-opened species of the type illustrated are known in the Co(III) cage chemistry, and they can be synthesized directly. The nmr spectroscopy of the major products of reduction of the Pt(diamsar)$^{4+}$ in water is consistent with a formulation where one cap is preserved and the other is broken with the formation of a $-CH_2OH$ group in both the Pt(II) and Pt(IV) products. Presumably the d$^7$ Pt(III) ion feeds an electron back into the N–H or C–H bond and the three-electron bond ruptures heterolytically, yielding the N anion and a H atom or the N anion and the C radical cation at the electrode surface. The latter presumably captures $OH^-$ and regenerates a Pt(III) methylene hydroxy species which disproportionates rapidly to square-planar Pt(II) with one chelate arm pendant and octahedral broken cage Pt(IV) complexes. The reason why C–N rupture occurs in the aqueous and acidic media, whereas N–H rupture is quantitative in the aprotic media eludes us. In some respects at least it would be more reasonable in reverse since the proton is more acidic in the aqueous than in the nonaqueous conditions. Clearly, the Pt(III) cage chemistry is complex and merits further investigation. The impact of the metal ion is subtle because d$^7$ Co(II) which is considerably more reducing than d$^7$ Pt(III) is unable to effect the cage rupture. The extension of the d orbitals may be the significant factor here. Experiments on these problems are proceeding especially with the Pt(IV), Ir(III), and Rh(III) cage systems.

The possibility of a catalytic path for hydrogen generation in aprotic solvents, by addition of excess anhydrous acid ($CH_3COOH$ or $CF_3SO_3H$) during controlled potential electrolysis, was not realized. Rather, the reaction tended to halt when $n \approx 2$, suggesting that the mechanism is sensitive to acid, anion, or traces of water. The sensitivity of the behavior in aprotic solvent to added water alone implies that the application of this complex in a catalytic role is unlikely, but once the N–H and C–N rupture is controlled complexes of this type should be viable catalysts for $H_2$ production by electrolysis at a low overvoltage.

The reduction of Pt(dinosar-H)$^{3+}$ in 1 M $HClO_4$ should involve an equilibrium similar to that of eq 4, with Pt(dinosar)$^{4+}$ as the electroactive species; reduction of the nitro group at $-0.22$ V clearly complicates the electrochemistry. The reduction of Pt(sep)$^{4+}$ in water is similar to that of the diamsar, with the observed reduction potentials again mediate by the preequilibrium condition discussed earlier. The similar behavior of the sep and diamsar complexes in aqueous solution suggest that the complex pattern observed for the former compound in acetone may involve a similar one to one to two electron reduction process also but complicated in this case by severe adsorption–desorption phenomena.

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**Registry No.** [Pt(sep)]$Cl_4$, 71935-75-6; [Pt(sep)]$(ClO_4)_4$, 85781-17-5; [Pt(sep)]$(CF_3SO_3)_4$, 85781-18-6; [Pt(dinosar-H)]$Cl_3$, 72528-92-8; [Pt(dinosar)]$Cl_4{\cdot}HCl$, 85800-02-8; [Pt(diamsar)]$Cl_4$, 85781-19-7; [Pt(diamsar)]$(CF_3SO_3)_4$, 85781-21-1; Pt(diamsar)$^{2+}$, 85781-22-2; Pt(diamsar)$^{3+}$, 85781-23-3; Pt(diamsar-H)$^{+}$, 85781-24-4; Pt(diamsar-H)$^{2+}$, 85781-25-5; Pt(diamsar)$^{3+}$ (disproportionation product 1), 85781-26-6; Pt(diamsar)$^{3+}$ (disproportionation product 2), 85781-27-7; [Pt(en)$_3$]$Cl_4$, 12079-33-3; HCHO, 50-00-0; ammonia, 7664-41-7; nitromethane, 75-52-5.

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