Synthesis and Electrochemical Properties of Pt(II) 5,7,12,14-Tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene: Factors Affecting the Electropolymerization Rates

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Abstract

The Pt complex of platinum dibenzotetraaza[14]-annulene has been prepared from the reaction of the free base ligand with bis(dimethylsulfoxide)platinum-(II) chloride. This represents one of the first 14 membered tetraazaannulene macrocyclic complexes reported. The electrochemical properties of platinum 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetra-aza[14]annulene were characterized by cyclic voltammetry. The platinum tetraazaannulene as well as a Pd(II) analog, have been found to form films on electrode surfaces during cyclic voltammetry. These films form either by constant potential electrolysis at +1.4 V, by cycling from 0.0 to +1.4 V, or by cycling from +1.4 to −2.0 V (*versus* SCE). Films can be made to form on several electrode surfaces as well as in various solvents and with a variety of tetraalkyl-ammonium salts as electrolytes. The amount of film grown depends on the method of deposition, the solvent and the rate of cycling. As part of the study, a quantitative analyses of the effects of solvents, scan rate, electrode, scan range and electrolytes or the amount of film actually formed on the electrode was carried out.

Introduction

In the last five to ten years, a large amount of research has focused upon tetraazaannulene macro-cyclic ligands [1–3]. These ligands have been used as models for naturally occurring systems such as porphyrins and corrin rings which are found in biological systems. Numerous metal compounds [2] have been studied in order to more fully understand these biological systems.

Another area of research interest involving metal tetraazaannulenes is their use as catalysts. In our own laboratories, we have shown that the nickel tetramethyltetraaza[14]annulene compound [4] could be electrochemically polymerized onto an electrode and this polymerized film could be used to catalyze the reduction of carbon dioxide to formate [5, 6]. In addition, a cobalt tetraazaannulene has been used to catalyze the conversion of a *cis*-compound to a *trans*-compound [7]. Finally, the area of film formation on an electrode surface has led to a great interest since these films [8, 9] have also found use for energy storage [10], electronic devices [11], photo sensitization [12] and controlled ion release [13].

The knowledge that the nickel [4] and the palladium [14] tetramethyltetraaza[14]annulene compounds have been prepared, promoted our investigation of the platinum tetramethyltetraaza[14]annulene compound (Fig. 1). We were also impressed that, to the best of our knowledge, only one other example of a Pt(II) 14-member tetraazaannulene had been reported [15].
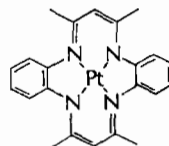

Fig. 1. Platinum 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene.

Experimental

Materials

Tetraalkylammonium salts were purchased from Southwestern Analytical Chemicals, Inc., dried overnight at 70 °C under vacuum and used without further purification. Aldrich Gold Label acetonitrile, Fisher reagent grade propylene carbonate, and EM Science methylene chloride were dried for 48 h over 4 Å molecular sieves before use. All other chemicals were purchased from Aldrich Chemical Company.

Bis(dimethylsulfoxide)palladium(II) chloride [16] and 1,8,-dihydro-5,7,12,14-tetramethyldibenzo[b,i]-

[1,4,8,11]tetraaza[14]annulene (H$_2$TMTAA) [17] were mixed in refluxing absolute ethanol for 1 h. The ethanol was removed by rotovaporization. The solid was dissolved in chloroform, applied to an alumina column where elution using chloroform removed a dark orange–brown band. The solvent was removed, the crude macrocycle compound was recrystallized and dried under vacuum for 10 h at 80 °C. Yield 53.6%, melting point (m.p.) 253–255 °C. ^{1}H (60 MHz, ppm): 2.17 (12H, 2); 4.63 (2H, s); 6.69 (8H, d of q). *Anal.* Calc. for C$_{22}$H$_{22}$N$_4$Pd: C, 58.06; H, 4.95; N, 12.48. Found: C, 58.67; H, 4.98; N, 12.42%.

Bis(dimethylsulfoxide)platinum(II) chloride [16] and H$_2$TMTAA [17] were refluxed in absolute ethanol for 24 h. The ethanol was removed by rotovaporization. The solid was dissolved in chloroform, applied to an alumina column and elution using chloroform removed a dark red band. The solvent was removed and the crude macrocyclic compound was recrystallized and dried under vacuum for 10 h at 80 °C. Yield 9.5%, m.p. 254–256 °C. ^{1}H (60 MHz, ppm): 2.18 (12H, s); 4.71 (2H, s); 6.72 (8H, d of q). *Anal.* Calc. for C$_{22}$H$_{22}$N$_4$Pt: C, 49.15; H, 4.13; N, 10.42. Found: C, 49.05; H, 4.22; N, 10.39%.

Physical Measurements

Electronic absorption spectra were obtained in methylene chloride solutions using matched 1 cm quartz cells and were recorded with a Cary 2300 spectrophotometer. NMR spectra were obtained in CDCl$_3$ employing a Varian EM-360 Spectrometer for 60 MHz 'H NMR. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, Ga.

Electrochemical properties were determined in acetonitrile with a 0.1 M tetraalkylammonium salt as supporting electrolyte in conventional three-compartment 'H' cells. Cyclic voltammograms were obtained using a BAS CV27 potentiostat and recorded with a YEW Model 3022 A4 X-Y recorder. The measurements were made at a Bioanalytical Systems platinum or glassy carbon disk electrode. Electrochemical potentials were recorded *versus* a saturated calomel electrode. Before use, the disk electrodes were polished sequentially with 3, 1 and 0.25 μm diamond paste (Buehler) on a Buehler nylon disk followed by ultrasonic cleaning with a Model 8150, by Universal Utrasonics, Inc., in deionized water (5 min) and in gold label acetonitrile (5 min). When necessary, solutions were degassed for approximately 20 min with solvent-saturated argon.

Apparent surface coverage was calculated as reported by Murray *et al.* [18] using the equation $\Gamma_{app} = Qc/(nFA)$, where Qc is the charge (area) under the oxidation waves as determined by cut and weigh method, n is the number of electrons per molecule oxidized, F is Faraday's constant and A is the area of the electrode in cm^2. The apparent

TABLE I. Electronic Absorption Bands for M[(Me$_4$(Bzo)$_2$-[14]tetraeneN$_4$)] Complexes[a]

M	Position (nm)	$\epsilon \times 10^{-4}$ (cm^{-1} M^{-1}) (log ϵ)
Ni	584	0.600 (3.78)
	391	1.80 (4.26)
	334	0.732 (3.86)
	266	2.98 (3.47)
Pd	482	0.852 (3.93)
	408	1.58 (4.20)
	294	0.678 (3.83)
	260	1.04 (4.02)
Pt	509	0.608 (3.78)
	394	1.19 (4.08)
	286	0.712 (3.85)
	261	0.894 (3.95)
H$_2$	340	3.30 (4.52)
	270	1.42 (4.15)
	254	1.73 (4.24)

[a]Spectra were obtained for 10^{-4} M solutions in methylene chloride; $T = 22 \pm 2$ °C; position ± 0.5 nm; $\epsilon \pm 1\%$.

number of film 'layers' was calculated by assuming that a monolayer of material corresponds to a density of 2.43×10^{-10} mol/cm [5, 19].

Results and Discussion

Electronic Spectra

Absorption spectra of the nickel, palladium and platinum macrocyles, along with the free base ligand, were examined over the 250–700 nm range, and the results are summarized in Table I. There appear to be three charge transfer absorptions in the near-UV regions for each of these compounds. These higher energy bands fall in the region characteristic of the free base ligand and apparently are intraligand electronic transitions. There also appears to be one unique charge transfer absorption for each of the metal complexes. This band in the visible region has energy 482 and 584 nm, with the absorptivities ranging from 6000–8520 cm^{-1} M^{-1}. These molar absorptivities are indicative of charge transfer absorptions, the source of which has been attributed to a ligand to metal charge transfer [20].

Electrochemistry

Typical cyclic voltammograms of the nickel, palladium, and platinum macrocycles can be seen in Fig. 2a, b, and c, respectively. Overall, each voltammogram consists of two irreversible oxidations, and a reversible reduction at more negative potentials. The voltammograms of the palladium and platinum macrocycles each have two board irreversible reductions which peak at ~ −0.50 and −0.90 V and at
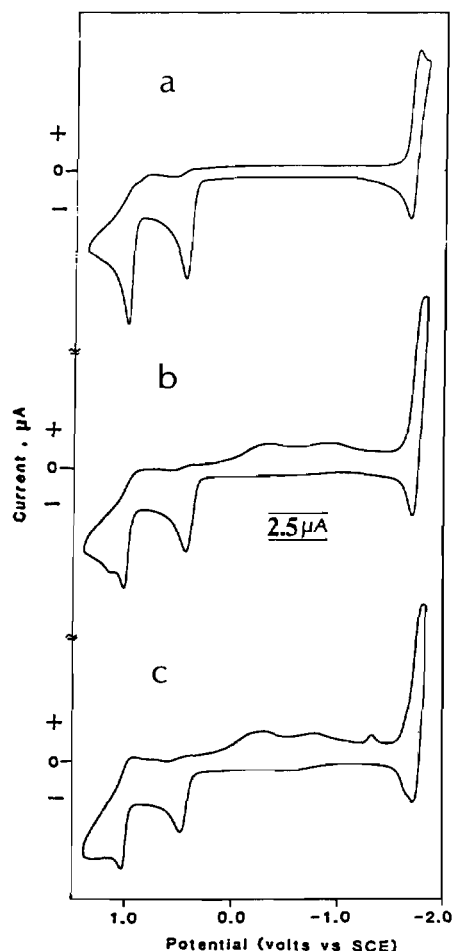
Fig. 2. Cyclic voltammograms of MTMTAA in acetonitrile solutions containing 0.1 M TEAP and 1.0×10^{-3} M complex (sweep rate 200 mV/s, +1.4 to -1.85 V *vs.* SCE): (a) Ni-TMTAA; (b) PdTMTAA; (c) PtTMTAA.

~ -0.40 and -0.80 V, respectively. They have no observable current on the scan reversal.

The voltammograms of these metal complexes were essentially the same. In a comparison of the first oxidation, $E_{p(1)}$, of the three metal complexes, the potential varied from 0.39 to 0.44 V *versus* SCE (see Table II). We have previously reported this oxidation as a ligand based oxidation [21]. In that study, a controlled oxidation of the copper macrocycle yield an ESR active product. Had the oxidation been a metal oxidation (Cu(II) → Cu(III)), the copper signal would have been lost. However, we found little change in the ESR spectrum of the copper macrocycle and attributed the oxidation wave, $E_{p(1)}$, to a ligand base oxidation. The second oxidation, $E_{p(2)}$, has an even smaller variation, 0.95 to 0.97 V *versus* SCE. This oxidation wave is a second oxidation of the ligand itself.

The reversible reduction, $E_{1/2}$, at first glance appears to be ligand based because there is little

TABLE II. Redox Properties of M[Me$_4$(Bzo)$_2$[14]tetraene-N$_4$)] Complexes[a]

M	$E_{p(1)}$ (V)[b]	$E_{p(2)}$ (V)[b]	$e_{1/2}$ (V)[b]
Ni	0.42	0.97	-1.76
Pd	0.39	0.95	-1.78
Pt	0.44	0.96	-1.79

[a]0.1 M TEAP—acetonitrile solutions; $T = 22 \pm 2$ °C. [b]Volts *vs.* SCE, ±0.01 V; sweep rates 200 mV/s.

variation in the potential at which it occurs, -1.76 to -1.79 V. Kadish and co-workers [22] were the first to carry out electrochemical studies on the free base ligand, H$_2$TMTAA. They reported that the ligand showed no reduction potential as far negative as -2.20 V *versus* SLCE (saturated lithium calomel electrode). Dabrowiak and coworkers [23] first investigated the reversible reduction. They reported a controlled reduction of the nickel macrocycle followed by an ESR study. The spectrum obtained was interpreted as that of Ni(I), therefore establishing the reversible reduction as metal based.

Film Growth

Oxidation of M[Me$_4$(Bzo)$_2$[14]tetraeneN$_4$] (M = Ni [5], Pd, Pt) yields stable electrochemically active films on electrode surfaces. These films can be formed on Au, Pt, glassy carbon and SnO$_2$ surface, and they form film solutions of acetonitrile, methylene chloride, or propylene carbonate with tetraethylammonium perchlorate (TEAP), tetrabutylammonium hexafluorophosphate (TBAH), or tetraethylammonium hexafluorophosphate (TEAH) as the electrolyte (0.1 M). The films deposit on the surface by repeatedly scanning the potential region from 0.0 to 1.4 V or from +1.4 to -2.0 V or alternatively, by holding the potential at 1.4 V *versus* SCE.

Cyclic voltammograms of the Ni, Pd, and Pt macrocyclic compound can be seen in Fig. 3a, b and c, respectively. As can be noted in these figures, with each scan there is an increase in current. The increase in current is due to the growth of film on the electrode. Before the reversible reduction wave and before the first oxidation waves, there are new waves that increase with the amount of film on the electrode. This phenomenon was first noted by Murray and co-workers [24] and the new features were called prewaves. It has been determined that these prewaves are due to imperfections in the film formation or film growth. The reversible waves remain reversible until they are engulfed by the prewaves.

As mentioned above, films deposit on the electrode also by repeatedly scanning the potential region from 0.0 to 1.4 V. The cyclic voltammograms
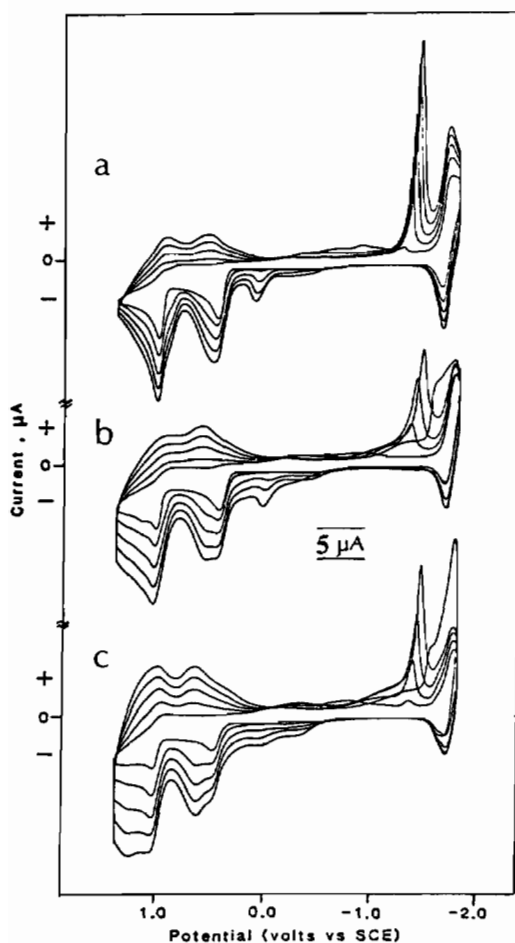
Fig. 3. Cyclic voltammograms of film growth on Pt electrodes in acetonitrile solutions containing 0.1 M TEAP and 1.0 X 10^{-3} M complex: (a) [Ni(Me₄Bzo₂[14]tetraeneN₄)]; (b) [Pd(Me₄Bzo₂[14]tetraeneN₄)]; (c) [Pt(Me₄Bzo₂[14]tetraeneN₄)]. The scan range was +1.4 to −2.0 V *vs.* SCE. The scan rate was 200 mV/s.
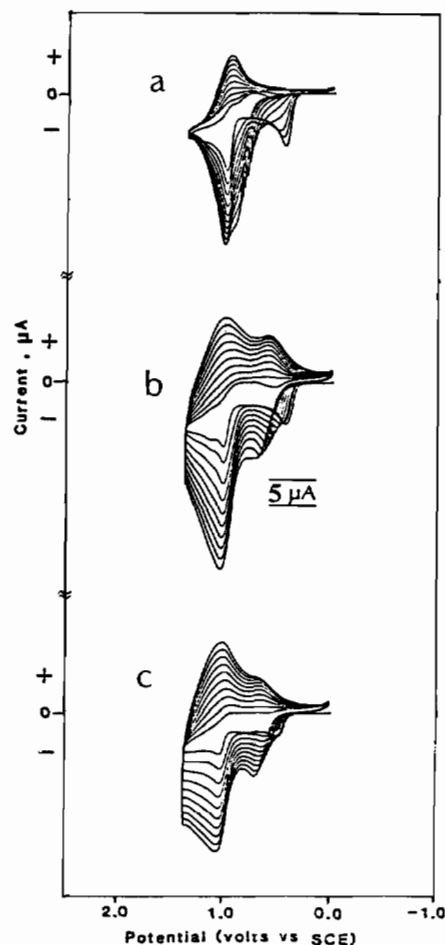
Fig. 4. Cyclic voltammograms of film growth on Pt electrodes in acetonitrile solutions containing 0.1 M TEAP and 1.0 X 10^{-3} M complex: (a) [Ni(Me₄Bzo₂[14]tetraeneN₄)]; (b) [Pd(Me₄Bzo₂[14]tetraeneN₄)]; (c) [Pt(Me₄Bzo₂[14]tetraeneN₄)]. The scan range was +1.4 to 0.0 V *vs.* SCE. The scan rate was 200 mV/s.

of the Ni, Pd and Pt macrocyclic compound can be seen in Fig. 4a, b and c, respectively. As the number of scans increase, less and less current is seen in the first oxidation wave. The second oxidation wave, however, continues to grow with scan as docs the film that is formed on the electrode surface.

A comparison of these two methods of film growth as a function of the number of polymerization scans is in Figs. 5 and 6 for the palladium and platinum complexes, respectively. It can be seen that a fairly linear growth of film on the electrode occurs up 5 or 6 scans after which time there is a drop off in the amount of film being formed on the electrode and a loss in uniformity in the rate of film formation. This is believed to be due to the loss of uniform electron transfer through the film, imperfections of the film itself, and the depletion of monomer at the film surface.

By investigating the film growth under a variety of conditions, a better understanding of how the film growth occurs can be obtained as well as how to more carefully control the growth. Five polymerization scans were carried out and the number of mono-layers were determined as explained in 'Experimental.' Those data are listed in Table III for Pd[Me₄-(Bzo)₂[14]tetraeneN₄] and in Table IV for Pt[Me₄-(Bzo)₂[14]tetraeneN₄]. Decreasing the scan rate increases the film growth at almost inverse proportionality. Changing the growth range (cycle range) appears to slow the amount of film formed at the electrode (in going from a range of +1.4 to −2.0 V to 0.0 to 1.4 V *versus* SCE). The smaller range likely allows less time for the electrolyte to diffuse away from the electrode and thus allows less monomer to diffuse in to polymerize at the surface of the already formed film. Changing the electrode
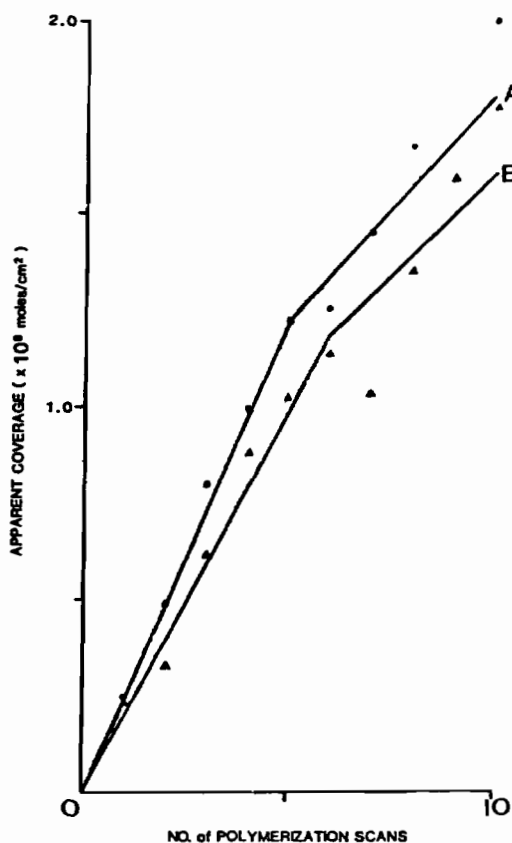
Fig. 5. Electrode surface coverage dependence of $[Pd(Me_4-Bzo_2[14]tetraeneN_4)]_n$ on the number of cyclic voltammetric scans: method A, scan range from +1.4 to −2.0 V *vs.* SCE; method B, scan range from 0.0 to +1.4 V *vs.* SCE. The solvent was acetonitrile, the electrolyte was 0.1 M TEAP, the complex concentration was 1.0×10^{-3} M, and the scan rate was 200 mV/s.

Fig. 6. Electrode surface coverage dependence of $[Pt(Me_4-Bzo_2[14]tetraeneN_4)]_n$ on the number of cyclic voltammetric scans: method A, scan range from +1.4 to −2.0 V *vs.* SCE; method B, scan range from 0.0 to +1.4 V *vs.* SCE. The solvent was acetonitrile, the electrolyte was 0.1 M TEAP, the complex concentration was 1.0×10^{-3} M, and the scan rate was 200 mV/s.
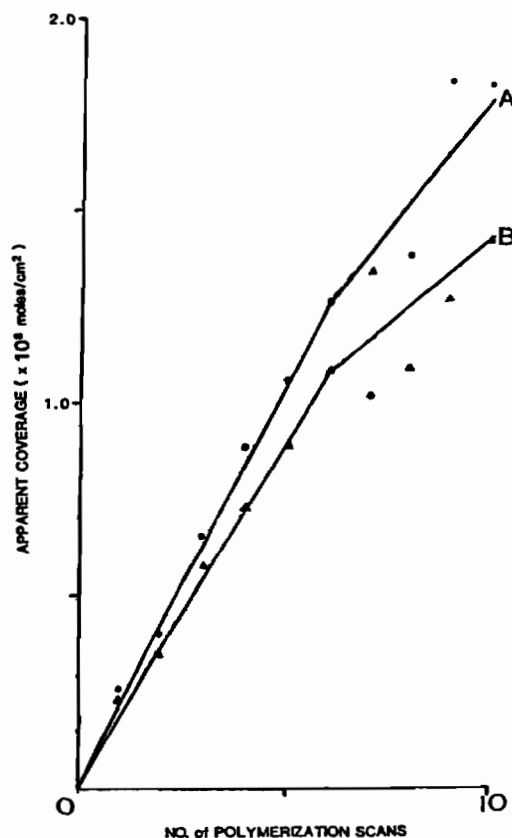
from platinum to glassy carbon has no effect on film growth. Solvents seem to have a large effect. On changing from acetonitrile to methylene chloride, approximately half the amount of film is formed. Propylene carbonate decreases the amount of film by a factor of nearly 10. Varying electrolytes changes the amount of film formed to a lesser extent.

Properties of the Film

The film forms through the diiminate backbone of the macrocycle [5]. It was first demonstrated by McElroy and Dabrowiak [25] that $Ni[Me_4(Bzo)_2-[14]tetraeneN_4]$ could be joined at the diiminate backbone to form a dimer (see Fig. 7). The Pd and Pt complexes of tetraannulene also form dimers by controlled potential oxidations. They are purplish pink and bright pink, respectively. The dimers can be formed by controlled potential oxidation between the first and second oxidation waves, or at 1.4 V *versus* SCE. However, there is one difference in these

two methods. In the first method there is no film formed at the electrode, whereas in the second method there is a film formed at the electrode surface. The phenomenon supports the theory of how the film is formed.

The palladium and platinum films are insoluble in DMSO, acetone, methylene chloride, propylene carbonate, and acetonitrile. They are slightly soluble in concentrated nitric acid and sodium hydroxide. They are very soluble in sulfuric acid. Cyclic voltammograms of the nickel, palladium and platinum films in neat electrolyte solutions are presented in Fig. 8. Repeated scans of the films in neat electrolyte result in a 10 to 20% loss of electroactivity. If, however, instead of using the full scan range of +1.4 to −2.0 V, the restricted range of 0.0 to −2.0 V is used, then there is only a 2 to 3% loss in electroactivity [5]. In Table V the oxidation and reduction potentials of the surface waves of the various metal films are noted. The redox waves of the reversible reduction

TABLE III. Electrode Surface Coverage by $Pd[Me_4(Bzo)_2$-$[14]tetraeneN_4]$ Complexes[a]

Variation	Γ_{app}[b] (mol/cm^2)	'Monolayers'
	1.22×10^{-8}	502
Scan rate 100 mV/s	2.74×10^{-8}	1130
Scan rate 50 mV/s	6.75×10^{-8}	2780
Growth range 0.0 to +1.4 V	1.02×10^{-8}	420
Electrode Glassy carbon	1.21×10^{-8}	498
Solvent CCl_2H_2	5.85×10^{-9}	241
Solvent Propylene carbonate	1.36×10^{-9}	56
Electrolyte 0.1 M TBAH	7.60×10^{-9}	313
Electrolyte 0.1 M TEAH	7.52×10^{-9}	309

[a]Unless otherwise noted, cyclic voltammograms were obtained by using 1×10^{-3} M solutions in 0.1 M TEAP–acetonitrile on a Pt electrode *vs.* SCE, scan rate = 200 mV/s. Film growth scan range was from +1.4 to −2.0 V. [b]Area used for apparent surface coverage calculations was from 0.2 to 1.4 V.

TABLE IV. Electrode Surface Coverage by $Pt[Me_4(Bzo)_2$-$[14]tetraeneN_4]$ Complexes[a]

| Variation	Γ_{app}[b] (mol/cm^2)	'Monolayers'
	1.06×10^{-8}	436
Scan rate 100 mV/s	1.76×10^{-8}	724
Scan rate 50 mV/s	3.37×10^{-8}	1390
Growth range 0.0 to +1.4 V	8.91×10^{-9}	367
Electrode Glassy carbon	9.87×10^{-9}	406
Solvent CCl_2H_2	5.13×10^{-9}	211
Solvent Propylene carbonate	1.49×10^{-9}	61
Electrolyte 0.1 M TBAH	6.19×10^{-9}	255
Electrolyte 0.1 M TEAH	7.46×10^{-9}	307

[a]Unless otherwise noted, cyclic voltammograms were obtained by using 1×10^{-3} M solutions in 0.1 M TEAP–acetonitrile on a Pt electrode *vs.* SCE, scan rate = 200 mV/s. Film growth scan range was from +1.4 to 2.0 V. [b]Area used for apparent surface coverage calculations was from 0.2 to 1.4 V.

TABLE V. Redox Properties of $[M(Me_4Bzo_2[14]tetraeneN_4)]_n$ Complexes[a]

M	First oxidation (V)[b]		Second oxidation (V)[b]		Reduction (V)[b]	
	oxid.	red.	oxid.	red.	oxid.	red.
Ni	0.52	0.50	0.95	0.90	−1.76	−1.84
Pd	0.52	0.50	1.02	0.92	−1.79	−1.84
Pt	0.58	0.56	1.09	0.96	−1.78	−1.84

[a]0.1 M TEAP–acetonitrile solutions; $T = 22 \pm 2$ °C. [b]Volts *vs.* SCE, ±0.01 V; sweep rates 200 mV/s.
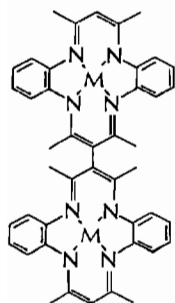
Fig. 7. Dimer of $M[Me_4(Bzo)_2[14]tetraeneN_4]$.

and the first oxidation wave have little variance in comparing the films of the different metals. The second oxidation redox waves have the greatest variation with 0.14 V being the difference in the nickel and platinum films oxidation of the second oxidation.

Conclusions

The synthesis of platinum tetraazaannulene has been reported. An electrochemical study of it and
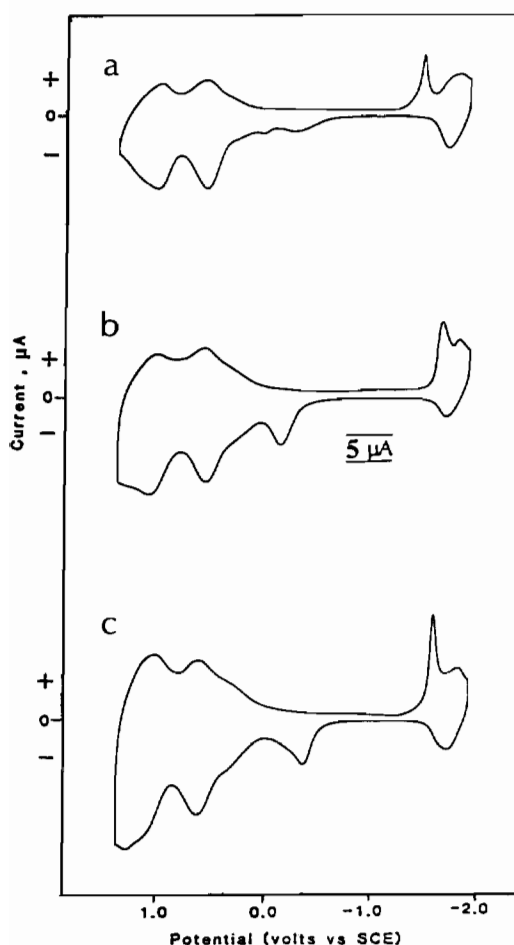
Fig. 8. Cyclic voltammograms of film on Pt electrodes in acetonitrile solutions containing 0.1 M TEAP: (a) [Ni(Me$_4$-Bzo$_2$[14]tetraeneN$_4$)]$_n$; (b) [Pd(Me$_4$Bzo$_2$[14]tetraeneN$_4$)]$_n$; (c) [Pt(Me$_4$Bzo$_2$[14]tetraeneN$_4$)]$_n$. The scan range was +1.4 to −2.0 V *vs.* SCE. The scan rate was 200 mV/s.

palladium tetraazaannulene has provided interesting results. The electropolymerization of these compounds on electrode surfaces presents a new range of possible uses. These films have electrochemical properties and can find uses as possible catalysts by controlling the electron transfer for a desired redox reaction. Since the amount of film formed on electrode surfaces can be controlled by varying conditions under which the films are formed, it should be plausible to predetermine the amount of film to be formed in the implementation of these films as possible electronic devices. Also by varying the tetraazaannulene used the conductive properties of the film formed should vary. If these different compounds were allowed to copolymerize, it would be possible to control the conductive properties of the films by controlling the amount of each monomer used in the make-up of the film. Another area of interest would be to sequentially polymerize the appropriate

tetraazaannulenes to form rectifiers and diodes. We look forward to reporting more on studies in these areas in the future.

Acknowlegements

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