

# Synthesis, characterization and electrochemical polymerization of eight transition-metal complexes of 5-amino-1,10-phenanthroline

Leonidas G. Bachas,\*† Lawrence Cullen, Richard S. Hutchins and Donna L. Scott

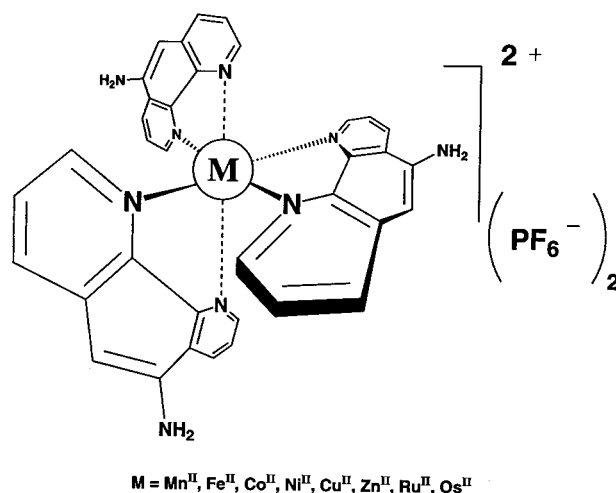
Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

The ability to prepare polymer films on the surface of glassy carbon electrodes (GCEs) by electrochemical polymerization of transition-metal complexes of 5-amino-1,10-phenanthroline (aphen) was investigated. Eight different metal ions ( $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$ ,  $Zn^{II}$ ,  $Ru^{II}$  and  $Os^{II}$ ) were studied. A simple and rapid method for the synthesis of the complexes with  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$  and  $Zn^{II}$  was also elaborated. The surface coverage obtained through electrochemical polymerization of the complexes on the GCEs can be related to the redox potential of the metal. The iron(II) and ruthenium(II) complexes generated the greatest polymer film surface coverages ( $\approx 10^{-8}$  mol  $cm^{-2}$ ), followed by the osmium(II) and cobalt(II) complexes ( $\approx 10^{-9}$  mol  $cm^{-2}$ ). Electrochemical polymerization studies with aphen, 5-nitro-1,10-phenanthroline (nphen) and the metal complex  $[Fe(nphen)_3]^{2+}$  provided further evidence that the oxidative electropolymerization mechanism for these complexes is initiated by sweeping through the oxidative potential of the aphen ligand (+1.35 V vs. Ag–AgCl).

Electrochemical polymerization of a suitable monomer onto the surface of an electrode has proven to be a most effective means to improve the selectivity and response properties of these surfaces.<sup>1–9</sup> Such chemically modified electrodes have found applications in electrocatalysis, electrochromics and electroanalysis. More recently, the use of a molecular imprinting or doping technique has resulted in the formation of electrochemically polymerized films that have a selective potentiometric response for the doped ion.<sup>10–16</sup> We and others have successfully applied this approach to the development of polypyrrole-based sensors for bromide,<sup>12</sup> chloride,<sup>12–14</sup> hexafluorophosphate,<sup>10</sup> nitrate,<sup>12,15,16</sup> nitrite,<sup>15</sup> perchlorate<sup>10,12,14</sup> and tetrafluoroborate.<sup>10,11</sup> This was accomplished by depositing the polypyrrole film on an electroactive surface in the presence of the target anion. In our search for other electropolymerizable monomer materials that could be useful in the development of potentiometric sensors, we identified 5-amino-1,10-phenanthroline (aphen) as a suitable candidate. This compound provides both a readily oxidizable amino moiety and a metal co-ordination site. Furthermore, the utility of phenanthroline complexes as ion carriers for potentiometric sensor applications is indicated by the inclusion of tris(1,10-phenanthroline)iron(II) in a number of the commercially available nitrate electrodes.<sup>17</sup> The goals of this work were to study the influence of the metal cation on polymer film formation and to explore the conditions that influence polymer growth.

The formation of films by the oxidative electropolymerization of the monomer  $[Fe(aphen)_3]^{2+}$  has been reported previously.<sup>18–20</sup> Some electrochemical characterization studies involving two other metals (Co and Ru) complexed with this ligand have also appeared in the literature.<sup>19,21</sup> However, to date no comprehensive study of the electrochemical film-forming ability of this compound with other transition metals has been reported.

This work has facilitated a more comprehensive understanding of what characteristics are needed in the phenanthroline-complexed metal to generate the most electroactive, densely coated chemically modified electrodes. Scheme 1 shows the gen-



**Scheme 1** Structure of the  $[M(aphen)_3](PF_6)_2$  complexes synthesized for electrochemical polymerization

eral structure of the complexes prepared.‡ The potential use of these electroactive polymer films as electrochromic materials, in photochemical reactions and as outer-sphere electron-transfer agents,<sup>3,18,24</sup> underlies the importance of this investigation into both the metal properties and the electropolymerization conditions that are needed to generate the best polymer films.

‡ As a consequence of the substitution at the 5 position of 1,10-phenanthroline this compound no longer has  $C_2$  symmetry. Thus, when three aphen co-ordinate to a metal an up or down orientation of the amino group of each ligand with respect to the others is possible. Scheme 1 indicates the isomer where all the amino groups are down. Two different structural isomers of  $[M(aphen)_3](PF_6)_2$  are possible, usually referred to as the meridional (*mer*) and facial (*fac*) isomers.<sup>22</sup> (It is also important to note that each of these structural isomers is in turn enantiomeric because the ligands may co-ordinate in left-helical or right-helical fashion.<sup>23</sup>) However, irrespective of the relative positions of the 5-NH<sub>2</sub> groups with regard to each other, all the complexes are electropolymerizable.

† E-Mail: bachas@pop.uky.edu

## Experimental

### Materials

Tris(5-nitro-1,10-phenanthroline)iron(II) perchlorate,  $[\text{Fe}(\text{nphen})_3][\text{ClO}_4]_2$  and 5-nitro-1,10-phenanthroline (nphen) were obtained from GFS Chemicals (Columbus, OH, USA). Tetramethylammonium nitrate and tetrabutylammonium bromide were from Eastman Chemicals (Rochester, NY, USA), tetrabutylammonium perchlorate and tetraethylammonium perchlorate from Fluka. 5-Amino-1,10-phenanthroline was supplied by Polysciences (Warrington, PA, USA). The salts  $[\text{NH}_4]_2[\text{OsCl}_6]$  and  $\text{NH}_4\text{PF}_6$  were from Alfa AESAR (Ward Hill, MA, USA) and were used as supplied. The reagents  $\text{Co}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{O}_2\text{CMe})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{O}_2\text{CMe})_2$ ,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (all Aldrich) and  $\text{Zn}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$  (Mallinckrodt, St. Louis, MO, USA) were used as supplied. Acetonitrile (Aldrich) was dried over  $\text{CaH}_2$ , distilled and stored under  $\text{N}_2$  over 4 Å molecular sieves. All other chemicals were reagent grade and were used as supplied.

### General procedure for the synthesis of $[\text{M}(\text{aphen})_3][\text{PF}_6]_2$ complexes

A portion of MeCN (usually  $\approx 15 \text{ cm}^3$ ) was added to aphen (3.05–3.10 equivalents) and the yellow suspension obtained was heated (60–84 °C) until all the aphen had dissolved. A metal acetate (1.0 equivalent) was added directly to the hot mixture, and the solution was heated for 15 min. The mixture was cooled to room temperature, the MeCN removed *in vacuo* and the solid residue was then dissolved in water (10–15  $\text{cm}^3$ ). Aqueous  $\text{NH}_4\text{PF}_6$  (5–10 equivalents in 1–2  $\text{cm}^3$  water) was added dropwise to this solution and the tris(5-amino-1,10-phenanthroline)metal(II) bis(hexafluorophosphate) complex precipitated. The product was isolated by suction filtration, washed with cold water, and then dissolved in a small amount of acetone (2–5  $\text{cm}^3$ ). This solution was then added dropwise to a rapidly stirring solution of diethyl ether ( $\approx 100 \text{ cm}^3$ ). The metal complex, which precipitated immediately, was isolated by suction filtration and dried overnight in a vacuum desiccator (over  $\text{P}_2\text{O}_5$ ). The complexes prepared using this method were: *tris(5-amino-1,10-phenanthroline)manganese(II) bis(hexafluorophosphate)*  $[\text{Mn}(\text{aphen})_3][\text{PF}_6]_2$ , *tris(5-amino-1,10-phenanthroline)cobalt(II) bis(hexafluorophosphate)*  $[\text{Co}(\text{aphen})_3][\text{PF}_6]_2$ , *tris(5-amino-1,10-phenanthroline)nickel(II) bis(hexafluorophosphate)*  $[\text{Ni}(\text{aphen})_3][\text{PF}_6]_2$  and *tris(5-amino-1,10-phenanthroline)zinc(II) bis(hexafluorophosphate)*  $[\text{Zn}(\text{aphen})_3][\text{PF}_6]_2$ . The yields of these compounds and their analytical and physical data are presented in Table 1.

The copper complex *tris(5-amino-1,10-phenanthroline)copper(II) bis(hexafluorophosphate)*,  $[\text{Cu}(\text{aphen})_3][\text{PF}_6]_2$ , was also prepared using this method. However, only 0.050 g (16% yield) of material was obtained after the final precipitation step. Additional product was isolated by evaporating the aqueous mother-liquors, dissolving the resultant green residue in acetone and precipitating the product from diethyl ether as described above. The combined yield for both precipitation steps was 54%.

### Synthesis of $[\text{Fe}(\text{aphen})_3]\text{X}_2$ (X = counter ion)

The complex  $[\text{Fe}(\text{aphen})_3][\text{ClO}_4]_2$  (1.50 g, 1.61 mmol) was dissolved in concentrated HCl (15  $\text{cm}^3$ ) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (2.80 g, 12.4 mmol) was added. The mixture was heated to reflux for 1 h and then allowed to cool to room temperature. The reaction mixture was treated with concentrated  $\text{NH}_3$  until a pH of 9 was obtained. Chloroform (100  $\text{cm}^3$ ) was added and the biphasic mixture was stirred for 1 h. The organic phase remained colourless. Separation of the aqueous phase, followed by centrifugation and decanting of the aqueous supernatant, yielded a red solid. This material was dissolved in water (heating for 30 min was necessary to dissolve all material) and then filtered while hot to remove any suspended impurities. The dark red solid

obtained upon cooling was dried in a vacuum oven at 60 °C for 4 h and yielded 1.35 g.

### Isolation of $[\text{Fe}(\text{aphen})_3][\text{ClO}_4]_2$ and $[\text{Fe}(\text{aphen})_3][\text{NO}_3]_2$

A sample of crude  $[\text{Fe}(\text{aphen})_3]\text{X}_2$  product (0.10–0.11 g) was suspended in water (10  $\text{cm}^3$ ) and heated at reflux until it dissolved. After cooling to room temperature, concentrated  $\text{HClO}_4$  or concentrated  $\text{HNO}_3$  (0.5  $\text{cm}^3$ ) was added and precipitation occurred. The precipitate was isolated by filtration and then dried overnight in a vacuum desiccator (over  $\text{CaSO}_4$ ):  $[\text{Fe}(\text{aphen})_3][\text{ClO}_4]_2$ , pink-red solid, 50% yield;  $[\text{Fe}(\text{aphen})_3][\text{NO}_3]_2$ , pink solid, 26% yield.

### Isolation of $[\text{Fe}(\text{aphen})_3][\text{PF}_6]_2$

Water (50  $\text{cm}^3$ ) was added to crude  $[\text{Fe}(\text{aphen})_3]\text{X}_2$  (0.75 g) prepared by the reduction of  $[\text{Fe}(\text{nphen})_3][\text{ClO}_4]_2$  described above and the resulting suspension was heated to reflux for 30 min to dissolve all of the material. Undissolved impurities were removed by filtration of the hot solution. After cooling to room temperature, the clear aqueous solution was treated with an excess of  $\text{NH}_4\text{PF}_6$  (0.74 g, 4.5 equivalents) and a red precipitate was obtained. This was isolated by suction filtration and dried overnight in a vacuum desiccator (over  $\text{CaSO}_4$ ) to yield 0.18 g {19% yield with respect to  $[\text{Fe}(\text{nphen})_3][\text{ClO}_4]_2$  starting material} of  $[\text{Fe}(\text{aphen})_3][\text{PF}_6]_2$  as a red solid. A pure sample was obtained by precipitation once from diethyl ether.

### Synthesis of $[\text{Ru}(\text{aphen})_3][\text{PF}_6]_2$

This compound was prepared according to the method of Ellis *et al.*<sup>21</sup> However, the product did not precipitate upon addition of an excess of  $\text{NH}_4\text{PF}_6$ . Evaporation of the dimethylformamide solvent under high vacuum gave a viscous liquid, which following precipitation from diethyl ether as described above yielded 0.18 g (74% yield) of  $[\text{Ru}(\text{aphen})_3][\text{PF}_6]_2$  as a brown solid.

### Synthesis of $[\text{Os}(\text{aphen})_3][\text{PF}_6]_2$

The osmium complex of aphen was prepared by adapting the method reported for the preparation of tris(5-chloro-1,10-phenanthroline)osmium(II) bis(hexafluorophosphate)  $[\text{Os}(\text{cphen})_3][\text{PF}_6]_2$ .<sup>25</sup> In particular, anhydrous ethylene glycol (15  $\text{cm}^3$ ) was added to  $[\text{NH}_4]_2[\text{OsCl}_6]$  (0.079 g, 0.18 mmol) and argon was bubbled through the resultant dark solution for 5–10 min. The compound aphen (0.201 g, 1.03 mmol) was added and the suspension was heated at reflux for 20 h under argon. After cooling to room temperature, the mixture was treated with an excess of  $\text{NH}_4\text{PF}_6$  (0.591 g in 1  $\text{cm}^3$  water) but no precipitation was observed. The solvents were then removed under high vacuum and the resulting viscous black oil was dissolved in acetone (20  $\text{cm}^3$ ) and precipitated from diethyl ether (100  $\text{cm}^3$ ) as described above. The isolated solid was redissolved in acetone (5  $\text{cm}^3$ ) and precipitated a second time to yield 0.066 g (34% yield) of *tris(5-amino-1,10-phenanthroline)osmium(II) bis(hexafluorophosphate)*  $[\text{Os}(\text{aphen})_3][\text{PF}_6]_2$  as a black solid.

### Analytical measurements

Elemental analyses were performed by the Microanalysis Laboratory at the University of Illinois (Urbana, IL, USA) and the results are displayed in Table 1. Mass spectra were obtained using fast atom bombardment (FAB) mass spectrometry operating in the positive-ion mode by the Life Sciences Mass Spectrometry Facility at the University of Kentucky (Lexington, KY, USA). The UV/VIS spectra (data in Table 2) were recorded in acetone (spec. grade; Fisher, Pittsburgh, PA, USA) at room temperature using a Perkin-Elmer Lambda-6 UV/VIS spectrophotometer and IR spectra (KBr discs) with a Perkin-Elmer Series 1600 spectrometer.

**Table 1** Analytical and physical data for the transition-metal complexes of 5-amino-1,10-phenanthroline

Isolated complex (including solvent of crystallization)	Analysis <sup>a</sup> (%)			Colour	Yield (%)	FAB mass spectral data ( <i>m/z</i> ) <sup>b</sup>
	C	H	N			
[Mn(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·1.5H <sub>2</sub> O	45.3 (45.2)	3.1 (3.2)	12.7 (13.2)	Yellow	74	785.0 [ <i>M</i> - PF <sub>6</sub> ], 639.1 [ <i>M</i> - (2PF <sub>6</sub> + H)]
[Co(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·0.5Me <sub>2</sub> CO	46.7 (46.8)	3.1 (3.1)	13.1 (13.1)	Orange	88	789.3 [ <i>M</i> - PF <sub>6</sub> ], 644.1 [ <i>M</i> - 2PF <sub>6</sub> ], 322.1 [( <i>M</i> - 2PF <sub>6</sub> )/2]
[Ni(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	43.2 (43.0)	3.0 (3.5)	12.55 (12.5)	Green-yellow	76	788.3 [ <i>M</i> - PF <sub>6</sub> ], 448.0 [ <i>M</i> - (2PF <sub>6</sub> + aphen)], 321.6 [( <i>M</i> - 2PF <sub>6</sub> )/2]
[Cu(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	46.0 (46.0)	2.7 (2.9)	11.2 (13.4)	Green	54	793.3 [ <i>M</i> - PF <sub>6</sub> ], 453.0 [ <i>M</i> - (2PF <sub>6</sub> + aphen)]
[Zn(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	44.3 (44.3)	3.0 (3.2)	12.4 (12.9)	Yellow	90	794.4 [ <i>M</i> - PF <sub>6</sub> ], 649.1 [ <i>M</i> - 2PF <sub>6</sub> ]
[Fe(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	45.0 (44.7)	2.9 (3.2)	12.9 (13.0)	Red	19	786.5 [ <i>M</i> - PF <sub>6</sub> ], 641.1 [ <i>M</i> - 2PF <sub>6</sub> ], 446.0 [ <i>M</i> - (2PF <sub>6</sub> + aphen) + H]
[Ru(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·3H <sub>2</sub> O	41.8 (41.9)	3.0 (3.2)	11.5 (12.2)	Brown	74	832.1 [ <i>M</i> - PF <sub>6</sub> ], 686.1 [ <i>M</i> - (2PF <sub>6</sub> + H)]
[Os(aphen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·Me <sub>2</sub> CO	41.6 (41.7)	3.0 (3.0)	11.9 (11.2)	Black	34	922.2 [ <i>M</i> - PF <sub>6</sub> ], 776.1 [ <i>M</i> - (2PF <sub>6</sub> + H)], 580.1 [ <i>M</i> - (2PF <sub>6</sub> + aphen)]

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> The corresponding fragments are given; *M* denotes the molecular ion.

### Electrochemical experiments

The electropolymerization experiments were performed with a BAS 100B Electrochemical Analyzer (Bioanalytical Systems, West Lafayette, IN, USA) with data downloaded to an IBM personal computer. A glassy carbon electrode (GCE, model MF2012, Bioanalytical Systems, geometrical area = 0.0707 cm<sup>2</sup>) was used as the working electrode, a Ag-AgCl wire (diameter 0.1 mm) as the reference electrode and a platinum wire (diameter 0.5 mm) as the counter electrode. All potentials reported are *versus* the Ag-AgCl reference electrode.

Before electrodeposition onto the glassy carbon electrode, the surface was polished using Alpha A cloth (Mark V Laboratory, East Granby, CT, USA) and GAMAL alumina, particle size finer than 0.1 μm (Fisher). The electrodes were then sonicated in water for 5 min before use.<sup>16,26</sup> The electropolymerization solutions were all prepared in MeCN and contained 0.10 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> in all cases, and other components as indicated. Before electropolymerization, the solution was deoxygenated by purging it with N<sub>2</sub> for 10 min, and it was maintained oxygen-free by passing a stream of N<sub>2</sub> over the solution during the experiments. The prepared electrodes were rinsed thoroughly with acetone after electrochemical film formation and placed in an electrolyte solution where the apparent surface coverage (Γ<sub>T</sub><sup>app</sup>) was determined electrochemically. This was obtained by measuring the charge (*Q*<sub>c</sub>) under the reductive wave of the specified metal redox peak and using equation (1),<sup>2,21</sup> where *n* is the

$$\Gamma_T^{\text{app}} = Q_c/nFA \quad (1)$$

number of electrons per molecule reduced (*n* = 1 for all the complexes studied herein), *F* represents Faraday's constant, and *A* is the area of the working electrode in cm<sup>2</sup>. The apparent surface coverages reported in this article are either the average for three electrodes (± 1 standard deviation) or that for a single electrode.

## Results and Discussion

### Synthesis and characterization of the [M(aphen)<sub>3</sub>]<sup>2+</sup> complexes

In order to determine the effect of the metal centre on the electrochemical polymerization of 5-amino-1,10-phenanthroline, a sequence of six complexes with successive metal ions from the first transition series (from manganese to zinc) was studied. The method for the synthesis of these complexes from the

corresponding metal acetates developed in our laboratory gives high yields. In addition, the synthesis is easy and can be performed rapidly. Complexes with the three metals of the iron triad (Fe<sup>II</sup>, Ru<sup>II</sup> and Os<sup>II</sup>) were also prepared. A modified literature procedure was used to prepare the ruthenium complex; this modification improved the yield significantly from the reported 30%<sup>21</sup> to 74%. The iron(II) complex was obtained by SnCl<sub>2</sub>-HCl reduction of the corresponding commercially available [Fe(aphen)<sub>3</sub>][ClO<sub>4</sub>]<sub>2</sub> complex. The synthesis and electropolymerization properties of the complexes with Mn<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup> and Os<sup>II</sup> have not been reported previously.

The counter ion used to isolate the [Fe(aphen)<sub>3</sub>]<sup>2+</sup> complexes had a significant effect on the solubility of the complex in MeCN, which was the solvent of choice for the electrochemical studies. Although the perchlorate salt gave excellent film growth as reported in the literature,<sup>18</sup> it proved much more difficult to isolate as a pure product in high yield than the hexafluorophosphate salt. Precipitation of the hexafluorophosphate salts using aqueous NH<sub>4</sub>PF<sub>6</sub> proved to be much more efficient than the addition of concentrated HClO<sub>4</sub> or HNO<sub>3</sub> to precipitate the respective salts from aqueous solutions. The hexafluorophosphate salt also had the added advantage that it could be purified by reprecipitation of a concentrated acetone solution of the salt from a stirring solution of diethyl ether. Also, because of its better solubility properties, the hexafluorophosphate salt of [Fe(aphen)<sub>3</sub>]<sup>2+</sup> proved much easier to characterize by FAB mass spectrometry than either the nitrate or perchlorate salts of this complex.

All the synthesized complexes were characterized by positive-ion FAB mass spectrometry, elemental analysis and UV/VIS and IR spectroscopy. The mass spectra of all the complexes confirmed the 3:1 ligand to metal ion stoichiometry expected for these diimine type complexes. All the complexes displayed peaks with the appropriate isotope distributions for the molecular ion less one hexafluorophosphate anion (see Table 1). Peaks were observed for the molecular ion less two hexafluorophosphates and one aphen ligand for the complexes with Ni<sup>II</sup> and Cu<sup>II</sup>, whereas the complexes formed with Mn<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup> and Ru<sup>II</sup> displayed a peak corresponding to the loss of both hexafluorophosphate anions. The complexes of Fe<sup>II</sup> and Os<sup>II</sup> displayed both of these peaks. A significant (*M* - 2PF<sub>6</sub>)/2 peak was observed for the complexes of Co<sup>II</sup> and Ni<sup>II</sup> suggesting the presence of the [M(aphen)<sub>3</sub>]<sup>2+</sup> species.

The results from the elemental analyses are presented in Table 1. All the complexes, except that with Cu<sup>II</sup>, were found to

**Table 2** The UV/VIS absorption data for aphen and [M(aphen)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> complexes recorded in acetone at 25 °C

M	$\lambda_{\text{max}}/\text{nm}$ ( $10^{-4}\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )
aphen	318 (infl) (0.45), 334 (0.64)
Co	356 (2.01), 431 (sh) (0.45)
Cu	356 (2.12), 430 (sh) (0.43)
Zn	355 (1.97), 435 (sh) (0.34)
Ni	321 (infl) (0.93), 356 (1.83), 432 (sh) (0.36)
Mn	314 (infl) (0.97), 353 (1.85), 427 (sh) (0.37)
Fe	360 (1.66), 420 (sh) (0.88), 482 (infl) (0.89), 520 (1.15)
Ru	319 (1.00), 340 (infl) (1.17), 374 (1.89), 479 (1.37)
Os	316 (sh) (1.37), 329 (1.89), 365 (1.99), 448 (1.50), 490 (1.53)

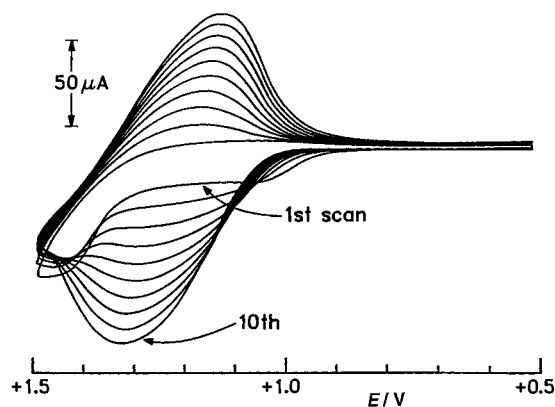
contain molecules of solvent, either water or acetone, both of which are present during the reaction work-up. The deviation in some of the observed elemental analysis data from the calculated values can be attributed to the presence of solvent in the crystals; such deviations are quite common in this type of complexes. <sup>18,25,27</sup> Two diagnostic bands at 840 and 560  $\text{cm}^{-1}$  in the fingerprint region of the IR spectra of each complex confirmed the presence of the PF<sub>6</sub><sup>-</sup> counter ion in all the complexes synthesized. <sup>21</sup>

Table 2 summarizes the UV/VIS properties of the complexes. Two trends can be distinguished. All the complexes with ions of the first transition-metal series, with the exception of that with iron(II), give a major absorbance peak with a maximum at 353–356 nm. A distinct shoulder also occurs at 427–435 nm. For the complexes of Mn<sup>II</sup> and Ni<sup>II</sup> an inflection is visible at shorter wavelengths. The absorption maximum of the ligand is shifted to longer wavelength by at least 19 nm upon complexation with Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> and increases in intensity to approximately three times that of the free aphen. The complexes of Fe<sup>II</sup>, Ru<sup>II</sup> and Os<sup>II</sup> display much more complex UV/VIS behaviour. The most intense absorption peak for these complexes is observed between 360 and 374 nm (see Table 2). Other less intense bands are also observed at longer wavelengths (>440 nm) for all three complexes, which is consistent with the occurrence of metal-to-ligand charge transfer (m.l.c.t.) transitions. <sup>27–30</sup>

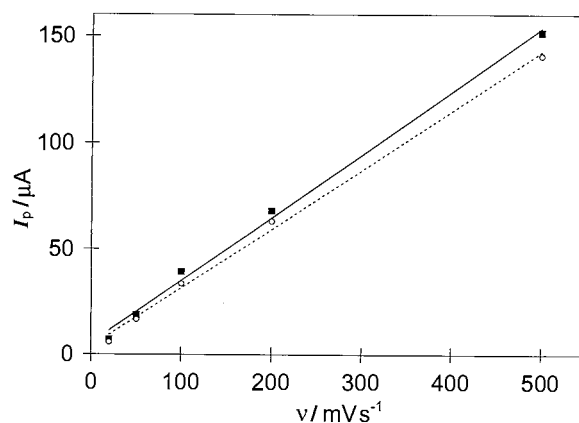
### Electropolymerization studies with the free phenanthrolines and the iron(II) complexes

The studies with electrochemically polymerized [Fe(aphen)<sub>3</sub>]<sup>2+</sup> using NBu<sub>4</sub>ClO<sub>4</sub> as the supporting electrolyte and glassy carbon electrodes will be discussed first. Although the electropolymerization of this complex was demonstrated previously, <sup>18–20</sup> it was necessary to establish its electrochemical behaviour under conditions that were identical in terms of electrode material, supporting electrolyte, scan rate, number of scans, *etc.*, to those used for the other metal complexes prepared during this work.

With the working electrode (GCE) immersed in a deaerated electropolymerization solution containing 0.0010 mol dm<sup>-3</sup> [Fe(aphen)<sub>3</sub>]<sup>2+</sup> and 0.10 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> in MeCN, the potential (*E*) was cycled 10 times between +0.500 and +1.500 V. Fig. 1 illustrates the continual increase in current observed at the Fe<sup>III</sup>–Fe<sup>II</sup> redox potential on each successive cycle, indicative of the formation of a growing polymer film on the electrode's surface. Additionally, there is a slight shift in the peak potential with each successive cycle. This shift also correlates well with previous studies and is believed to arise from the conversion of the amine groups into imine or diazo moieties. <sup>18</sup> Such functional groups are more electron withdrawing, thus enabling the iron to remain as Fe<sup>II</sup> over a wider potential range. <sup>18</sup> The appearance of a prewave (at +1.05 V) on the first scan is typical with this ligand and has been shown to be a result of an irreversible oxidation of the NH<sub>2</sub> group on the ligand. <sup>21</sup> After the GCEs had been coated with a film containing the polymer-



**Fig. 1** Electropolymerization of 1.0 mmol dm<sup>-3</sup> [Fe(aphen)<sub>3</sub>]<sup>2+</sup> in 0.10 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> in MeCN with a GCE using cyclic voltammetry between +0.500 and +1.500 V. The sweep rate was 100 mV s<sup>-1</sup>. The wave increases in size with each cycle indicating the formation of an electropolymerized film on the GCE surface



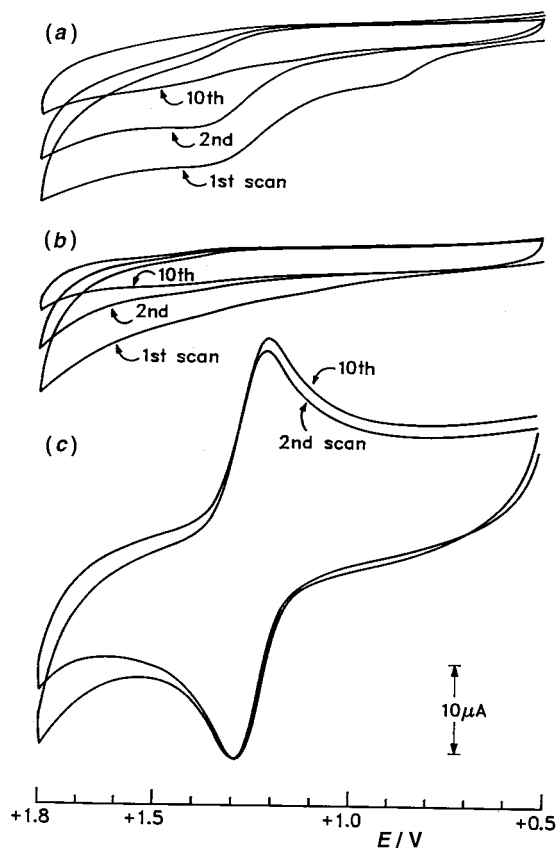
**Fig. 2** Peak current as a function of scan rate for a [Fe(aphen)<sub>3</sub>]<sup>2+</sup> electrode in 0.10 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>. Electrode was prepared as described in Fig. 1. (■), Anodic peak current; (○), cathodic peak current

ized iron complex, the electrodes were removed from solution, rinsed thoroughly in acetone and placed in a similarly prepared solution containing no monomer. The apparent surface coverage [ $\Gamma_{\text{T}}^{\text{pp}} = (2.7 \pm 0.6) \times 10^{-8} \text{ mol cm}^{-2}$ ] of the electrode was obtained by calculating the area under the reductive wave of the metal redox couple (Fe<sup>III</sup>–Fe<sup>II</sup> in this case) as outlined in the Experimental section.

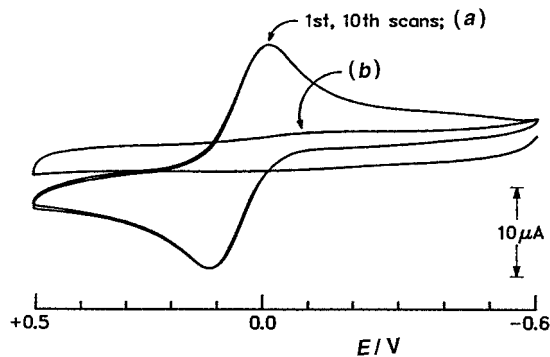
The scan rate dependence of the polymer film formed by electropolymerization of [Fe(aphen)<sub>3</sub>] was investigated by taking cyclic voltammograms at scan rates from 20 to 500 mV s<sup>-1</sup>. As expected for an immobilized species, the peak currents were proportional to scan rate (Fig. 2). The voltammograms were nearly reversible at 20 mV s<sup>-1</sup> and quasi-reversible at other scan rates, indicating some type of kinetic limitation.

The experiments with [Fe(aphen)<sub>3</sub>]<sup>2+</sup> also established that the presence of perchlorate in the electrolyte facilitated much better film growth than did nitrate (present either as tetramethylammonium nitrate or HNO<sub>3</sub>). When [Fe(aphen)<sub>3</sub>][ClO<sub>4</sub>]<sub>2</sub> was cycled between 0.000 and +1.700 V at 100 mV s<sup>-1</sup> in the presence of 0.20 mol dm<sup>-3</sup> tetramethylammonium nitrate in MeCN negligible film growth was observed after 10 scans. However, when NEt<sub>4</sub>ClO<sub>4</sub> was used as electrolyte under similar conditions (+0.150 to +1.700 V, 100 mV s<sup>-1</sup>) film growth was still observed after 50 scans. In both experiments some difficulty was encountered in dissolving all of the iron complex in MeCN and suspensions of the monomer were used. Subsequent use of the PF<sub>6</sub> salt of the complex avoided this difficulty.

Recently, the effect of the electrolyte on the overall charge transport rate in electropolymerized [Fe(aphen)<sub>3</sub>]<sup>2+</sup> has been



**Fig. 3** Cyclic voltammetry between +0.500 and +1.800 V ( $100 \text{ mV s}^{-1}$ ) of aphen (a), nphen (b), and the complex  $[\text{Fe}(\text{nphen})_3]^{2+}$  (c), all present at  $1.0 \text{ mol dm}^{-3}$  in MeCN with  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  as electrolyte



**Fig. 4** (a) Electropolymerization of  $1.0 \text{ mol dm}^{-3}$   $[\text{Co}(\text{apen})_3]^{2+}$  on a GCE in MeCN containing  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$ , cycled 10 times between  $-0.600$  and  $+0.500$  V at a scan rate of  $100 \text{ mV s}^{-1}$ . (b) The electrode from (a) was transferred to a solution containing  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  in MeCN and was cycled once over the same potential range using the same scan rate

examined.<sup>31</sup> Two electrolytes,  $\text{NEt}_4\text{ClO}_4$  and tetraethylammonium toluene-*p*-sulfonate, were studied and it was found that the change in electrolyte from perchlorate to toluene-*p*-sulfonate had a much more significant effect on the electron-hopping rate between the redox active centres than it had on the counter ion diffusion-migration rate through the polymer. This effect was thought to be most likely the consequence of stronger charge pairing between the sulfonate anions and the  $\text{Fe}^{\text{III/II}}$  than between perchlorate and the metal centres, causing increased resistance to counter ion movement and, as a result, a decrease in the rate of electron exchange between metal centres. An alternative explanation is that the increase in counter ion size from perchlorate to toluene-*p*-sulfonate results in an

**Table 3** Apparent surface film coverages of electropolymerized 5-amino-1,10-phenanthroline transition-metal complexes on glassy carbon electrodes

Potential range (V)	Monomer complex electropolymerized	Apparent film coverage <sup>a</sup> ( $\text{mol cm}^{-2}$ )	Relative coverage <sup>b</sup>
+0.500 $\leftrightarrow$ +1.500	$[\text{Fe}(\text{apen})_3][\text{PF}_6]_2$	$(2.7 \pm 0.6) \times 10^{-8}$	1.00
+0.500 $\leftrightarrow$ +1.175		$3.3 \times 10^{-10}$	0.012
+0.500 $\leftrightarrow$ +1.125		n.f.	—
-0.600 $\leftrightarrow$ +0.500	$[\text{Co}(\text{apen})_3][\text{PF}_6]_2$	n.f.	—
-0.600 $\leftrightarrow$ +1.000		$(4 \pm 2) \times 10^{-9}$	0.15
-0.600 $\leftrightarrow$ +1.500		$(6.8 \pm 0.6) \times 10^{-9}$	0.25
-0.600 $\leftrightarrow$ +0.500	$[\text{Ni}(\text{apen})_3][\text{PF}_6]_2$	n.f.	—
-0.600 $\leftrightarrow$ +1.000		$(8 \pm 2) \times 10^{-11}$	0.0030
-0.600 $\leftrightarrow$ +1.500		$(1.0 \pm 0.2) \times 10^{-10}$	0.0037
-0.600 $\leftrightarrow$ +0.500	$[\text{Cu}(\text{apen})_3][\text{PF}_6]_2$	n.f.	—
-0.600 $\leftrightarrow$ +1.000		$1.2 \times 10^{-11}$	0.0004
-0.600 $\leftrightarrow$ +1.200		$1.1 \times 10^{-11}$	0.0004
-0.600 $\leftrightarrow$ +1.500		$1.3 \times 10^{-11}$	0.0005
-0.600 $\leftrightarrow$ +1.800		$8.5 \times 10^{-12}$	0.0003
+0.500 $\leftrightarrow$ +1.500	$[\text{Ru}(\text{apen})_3][\text{PF}_6]_2$	$(3.3 \pm 0.1) \times 10^{-8}$	1.22
+0.500 $\leftrightarrow$ +1.800	$[\text{Os}(\text{apen})_3][\text{PF}_6]_2$	$(2.5 \pm 0.2) \times 10^{-9}$	0.092

<sup>a</sup> Standard deviations given are for  $n = 3$ ; n.f. denotes conditions under which no film formation was detected. <sup>b</sup> Compared to that of the  $[\text{Fe}(\text{apen})_3][\text{PF}_6]_2$  monomer. All films were prepared using 10 cycles at  $100 \text{ mV s}^{-1}$  in solutions with  $1.0 \text{ mol dm}^{-3}$  monomer and  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  in MeCN.

increase in the polymer's ionic resistance and hence a decrease in the electron-hopping rate. In our case, the nitrate counter ion is smaller than the perchlorate and this suggests that the poorer film growth observed with this counter ion arises because of stronger ion pairing between the nitrate and  $\text{Fe}^{\text{III/II}}$ . This is not surprising given the higher charge density of nitrate in comparison to perchlorate.

The oxidation potential of the  $\text{NH}_2$  group in the ligand overlaps that of the  $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$  oxidation peak. In an attempt better to understand the mechanism by which the films are formed, an electropolymerization solution was prepared containing  $0.0010 \text{ mol dm}^{-3}$  aphen and  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  in MeCN. Fig. 3(a) shows successive scans in this solution between +0.500 and +1.800 V. On the first scan two peaks are observed, a pre-peak at +0.9 V (see also Fig. 1 and earlier discussion) and the amine oxidation peak at +1.35 V. This oxidative wave is irreversible and decreases over successive scans. When the  $\text{NH}_2$  group is absent no such oxidation peak is observed. For example, when nphen instead of aphen was studied under similar conditions [Fig. 3(b)] the electrodes were once again rapidly passivated and by the tenth cycle the voltammogram was identical to that of the background electrolyte (*i.e.* electropolymerization solution with no ligand present). This result indicates that the irreversible peak seen in Fig. 3(a) at +1.35 V arises from the 5-amino group of the phenanthroline ligand. When electrodes were cycled over the same potential range in a solution containing  $[\text{Fe}(\text{nphen})_3][\text{ClO}_4]_2$  a reversible, non-growing,  $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$  redox couple appeared [Fig. 3(c); note the smaller current scale compared to Fig. 1]. These studies emphasize the importance of having both the metal centre and the amine group of the ligand present in order to promote electroactive film growth.

#### Other first-row transition-metal complexes

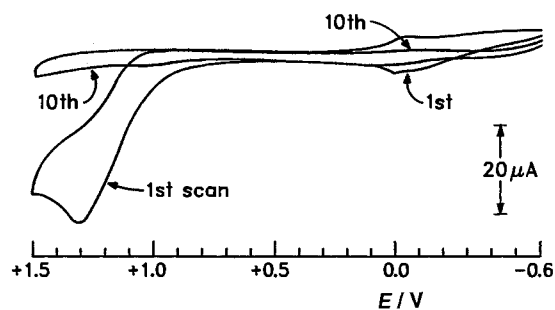
Five additional complexes were prepared and tested using different first transition-series metals. Of these, only studies performed with the cobalt complex had appeared previously in the literature with the general conclusion that the surface coverage was considerably poorer than that of the iron complex.<sup>19</sup> In an electropolymerization solution containing  $0.0010 \text{ mol dm}^{-3}$   $[\text{Co}(\text{apen})_3]^{2+}$  and  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  in MeCN, the redox couple  $\text{Co}^{\text{III}}-\text{Co}^{\text{II}}$  was found to occur at a much lower

potential than that of  $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ , with an anodic peak potential,  $E_{\text{pa}}$ , of +0.11 V. After cycling 10 times between -0.600 and +0.500 V, a stable, quasi-reversible  $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$  couple was evident [Fig. 4(a)]. When electrodes prepared in this fashion were subsequently rinsed and placed in an electrolyte solution containing no monomer, a voltammogram closely resembling the background electrolyte scan was obtained [Fig. 4(b)]. This further emphasizes the findings with the iron complex that, without initiation of the electropolymerization reaction by the amine group of the ligand, no film growth can take place. With the iron complex, the oxidation potentials of the iron and the amine are so close that the only way to determine what effect each oxidation potential has on polymer film formation was to test the iron complexed to the nphen ligand [Fig. 3(c)]. With the cobalt complex the  $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$  redox potential is far removed from the oxidation potential of the amine and therefore the importance of both the metal redox potential and the oxidation potential of the aromatic amine can be observed more easily. This can be demonstrated by cycling the potential in a range that includes the oxidation potential of the amine as discussed below.

When electrodes are placed in the same electropolymerization solution as that used in Fig. 4(a) and now cycled between -0.600 and +1.500 V polymer film growth does occur. Although the growth was not as efficient as that with the iron complex, the apparent film coverage under these conditions was equal to  $(6.8 \pm 0.6) \times 10^{-9}$  mol  $\text{cm}^{-2}$ . The film coverage obtained with  $[\text{Co}(\text{aphen})_3]^{2+}$ , however, was not as high as that observed with the iron complex. Many potential ranges and conditions for electropolymerization were tried with these complexes and the conditions found to generate the best film coverage are those presented herein. Table 3 summarizes some of the results obtained using a variety of conditions for many of these metal complexes. The results are displayed as the apparent film coverage in mol  $\text{cm}^{-2}$ , as well as the apparent surface coverage relative to that obtained for the  $[\text{Fe}(\text{aphen})_3]^{2+}$  complex cycled 10 times between +0.500 and +1.500 V.

The nickel complex was tested using  $0.0010$  mol  $\text{dm}^{-3}$   $[\text{Ni}(\text{aphen})_3]^{2+}$  in the same electrolyte solution. When electrodes were cycled in the same potential range used for successful cobalt film formation, -0.600 to +1.500 V, the redox peak for the metal was observed to increase over the 10 cycles as was the case with the iron(II) complex. The apparent film coverage for the nickel complex under these conditions was calculated as  $(1.0 \pm 0.2) \times 10^{-10}$  mol  $\text{cm}^{-2}$ . No film coverage at all was observed with the  $[\text{Zn}(\text{aphen})_3]^{2+}$  and  $[\text{Mn}(\text{aphen})_3]^{2+}$  complexes, regardless of the potential range employed.

When the copper complex,  $[\text{Cu}(\text{aphen})_3]^{2+}$ , was prepared and tested (10 cycles between -0.600 and +1.500 V), the redox peak for the metal was observed (see Fig. 5) to decrease over the 10 cycles rather than increase. The apparent film coverage was  $1.3 \times 10^{-11}$  mol  $\text{cm}^{-2}$ , about an order of magnitude less than that obtained with the nickel complex. This surface coverage of the copper complex corresponds to less than a monolayer (which is *ca.*  $8 \times 10^{-11}$  mol  $\text{cm}^{-2}$ ),<sup>20,21</sup> and the redox potential seen in the fresh solution might be attributed to simple adsorption of the copper complex onto the surface of the GCE. However, as was observed with the  $[\text{Fe}(\text{aphen})_3]^{2+}$  complex when cycled below the oxidation peak of the amino group (+0.500 to +1.125 V, see Table 3) and with the  $[\text{Co}(\text{aphen})_3]^{2+}$  complex when cycled between -0.600 and +0.500 V, the  $[\text{Cu}(\text{aphen})_3]^{2+}$  complex also did not generate any apparent surface film coverage when cycled in a potential range (-0.600 to +0.500 V, Table 3) that does not include the amino group oxidation potential. Fig. 5 illustrates the presence of an oxidation peak at  $\approx +1.35$  V, which is ascribed to the (irreversible) oxidation of the amine. This indicates that the submonolayer coverage when a solution of the copper complex is cycled between -0.600 and +1.500 V arises not because of simple adsorption, but is the consequence of the amine-initiated electropolymerization of



**Fig. 5** Electropolymerization of  $1.0$  mol  $\text{dm}^{-3}$   $[\text{Cu}(\text{aphen})_3]^{2+}$  on a GCE in MeCN containing  $0.10$  mol  $\text{dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  cycled 10 times between -0.600 and +1.500 V at a scan rate of  $100$  mV  $\text{s}^{-1}$

the monomer to give polymer film formation on localized areas of the electrodes.

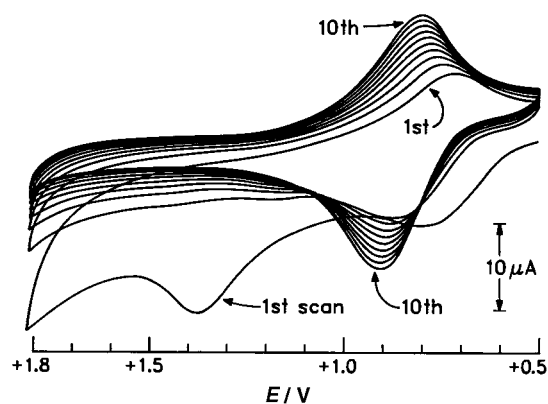
It has been reported previously using a pyrrole monomer that redox mediators may enhance electropolymerization.<sup>32</sup> Therefore, we investigated the electrochemical polymerization of the  $[\text{Cu}(\text{aphen})_3]^{2+}$  complex using bromide (solution of tetrabutylammonium bromide in electrolyte) as a redox mediator. It was found that a passive film was being formed (lower currents and greater peak separations) even in the presence of this mediator. However, the mediator did have some effect and gave films with a slightly larger coverage.

#### Other transition-metal complexes

Besides  $\text{Fe}^{\text{II}}$  and  $\text{Co}^{\text{II}}$ , the only other previously reported transition-metal complex with aphen was that of  $\text{Ru}^{\text{II}}$ .<sup>21</sup> Under conditions similar to those reported herein for optimum film formation using  $[\text{Fe}(\text{aphen})_3]^{2+}$  (+0.500 to +1.500 V), we obtained similar surface coverages for  $[\text{Ru}(\text{aphen})_3]^{2+}$ , *i.e.*  $(3.3 \pm 0.1) \times 10^{-8}$  mol  $\text{cm}^{-2}$ , which are consistent with the previously reported surface coverage for this ruthenium(II) complex.<sup>21</sup> The complexes of  $\text{Ru}^{\text{II}}$  and  $\text{Fe}^{\text{II}}$ , which generated the most electroactive and best surface coverages, had one unique feature in common that the other metal complexes lacked. Both  $\text{Ru}^{\text{II}}$  and  $\text{Fe}^{\text{II}}$  have redox potentials that are close to that of the amine oxidation potential of the ligand. The peak potential (+1.5 V) of  $\text{Ru}^{\text{II}}$  is slightly higher than that observed with the iron complex, which itself overlaps the redox peak of the ligand. Thus, it is possible that the electropolymerization of these complexes is more effective because the metal centre serves as a means to transport electrons between the polymer film and the surface of the electrode. As the oxidation of the metal centre moves to more negative potentials and hence electron transfer becomes more difficult to achieve, the role of the metal in polymer film growth declines and a poorer surface coverage results.

An electroactive polymer film was also obtained from the complex of aphen with osmium. Fig. 6 shows the results obtained with electrodes cycled 10 times between +0.500 and +1.800 V in  $0.0010$  mol  $\text{dm}^{-3}$   $[\text{Os}(\text{aphen})_3]^{2+}$  and  $0.10$  mol  $\text{dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  in MeCN. It can be seen that the redox peak  $\text{Os}^{\text{III}}\text{-Os}^{\text{II}}$  occurs at a more negative potential relative to that of the amine oxidation peak, with  $E_{\text{pa}} = +0.85$  V (first scan). The electrodes were tested for surface coverage and  $\Gamma_{\text{app}}^{\text{app}}$  was determined to be  $(2.5 \pm 0.2) \times 10^{-9}$  mol  $\text{cm}^{-2}$ .

In general, it may be concluded that superior film formation is observed if one cycles through the oxidation potential of the ligand. Further, by comparison with the uncomplexed phenanthroline, the presence of the metal centre is necessary to ensure formation of a conductive polymer film *via* electropolymerization. The metal not only provides the necessary redox conductivity for electropolymerization, but can also be regarded as a three-dimensional scaffold onto which the ligands are attached (see Scheme 1). The resultant arrangement of ligand amino groups effectively ensures that film growth can occur in all directions rather than the unidirectional mode of growth



**Fig. 6** Electropolymerization of  $1.0 \text{ mmol dm}^{-3}$   $[\text{Os}(\text{aphen})_3]^{2+}$  on a GCE in MeCN containing  $0.10 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$  cycled 10 times between  $+0.500$  and  $+1.800 \text{ V}$  at a scan rate of  $100 \text{ mV s}^{-1}$

available to the uncomplexed free phenanthroline. Hence, a more highly cross-linked polymer containing dispersed metal redox centres can be obtained.

The exact mechanism of the aphen polymerization reaction is not known but all evidence to date suggests that a  $\text{NH}^\cdot$  radical is involved.<sup>18–21,25</sup> The initial step is a ligand-based one-electron oxidation to form an  $\text{aphen}^{\cdot+}$  radical cation. This is supported by the fact that, to achieve film formation with the  $[\text{M}(\text{aphen})_3]^{2+}$  complexes, one has to cycle through the oxidation peak of the ligand (see above). The radical cation thus formed is then thought to lose a proton to form an active  $\text{NH}^\cdot$  radical species which propagates polymer growth. This radical has a number of possible resonance structures that can react with other aphen ligands to form N–N, N=N (reaction of  $\text{NH}^\cdot$ ) and N=C type [reaction of 5-imino (iphen $^\cdot$ )] linkages.<sup>21</sup> Although our studies indicate the formation of polymeric structures, the length of the formed polymer chains and the level of cross-linking cannot be inferred from the data. However, assuming a hard-sphere model,<sup>21</sup> the apparent number of 'layers' of the polymeric material for the ruthenium(II) complex is ca. 400.

Given the electropolymerization properties of the complexes of  $\text{Fe}^{\text{II}}$ ,  $\text{Ru}^{\text{II}}$ ,  $\text{Os}^{\text{II}}$  and  $\text{Co}^{\text{II}}$  of aphen, these complexes have potential for application in the development of electrochemically based sensors using the 'wired enzyme' approach.<sup>33,34</sup> In this class of sensors the electrode surface is directly wired to the sensing element, in this case an enzyme, by a long chain polymer that contains periodic complexation sites onto which osmium-bipyridine type complexes are attached. Thus, the polymer contains a number of redox active centres that can conduct electrons directly between the enzyme and the electrode. To increase the stability of the 'wired electrode', a cross-linking agent is normally added in the final stages of the sensor preparation. Complexes of aphen, such as  $[\text{Os}(\text{aphen})_3]^{2+}$ , have the potential to provide the redox active centres, the cross-linking agent and sites for direct attachment to the enzyme all in the same chemical entity.

In conclusion, it was demonstrated that a number of transition-metal complexes of aphen can form electroactive polymer films. The influence of the metal centre and the oxidation of the ligand on conductive film formation has been discussed. The most dense electroactive polymer films were obtained with the ruthenium(II) and the iron(II) complexes. In the case of the osmium and cobalt complexes smaller surface coverages were obtained. Cobalt may represent the limit of effective involvement of the metal centre in polymer film formation.

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