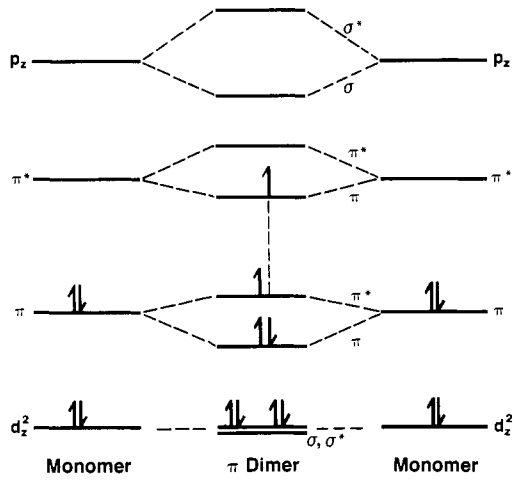

Figure 10. Schematic interaction of orbitals in Pt–ligand π dimers.

of hydration, which seems to be a dynamic variable in the solid state.

The emissions of all microcrystalline forms of $[Pt(phen)_2]Cl_2$ are significantly red-shifted from those seen in glassy solution; moreover, the solid-state emission profiles are much broader and are unstructured. These observations are reminiscent of excimer emission from planar aromatic molecules and indicate a marked effect of the crystal structure upon the electronic structure of the monomeric complex. In the case of $[Pt(phen)_2]Cl_2 \cdot 3H_2O$, the cations are known to crystallize in discrete, weakly interacting face-to-face dimers similar to those of *cis*-bis(2-phenylpyridine)platinum(II) mentioned in the introduction,[9] with a Pt–Pt distance of 3.710 Å.[17] This distance is too long to support significant metal–metal interaction, but is close enough to allow overlap of phenanthroline π^* orbitals. Thus, we suggest that the solid-state emission of this form is due to a classical excimeric interaction of the phenanthroline ligands in the two monomers. This situation is diagramed in Figure 10. Here, metal–metal interaction is negligible and the ground-state interaction between the phenanthrolines is very weak. However, the lowest energy $\pi \rightarrow \pi^*$ excitation results in a state that has net bonding character between the phenanthrolines of the two complexes.

The excitation spectrum of $[Pt(phen)_2]Cl_2 \cdot 3H_2O$ at 77 K is actually only very weakly perturbed from that of the room-temperature solution absorption spectrum, and similar behavior has been noted for solution aggregates of metal α-diimine complexes.[34] The lowest energy feature in the excitation spectrum is a band at 463 nm, compared to the absorption spectrum shoulder at ~450 nm. Thus, the crystal chromophore probably collapses, to the extent allowed by the lattice, to a shorter phen–phen distance in the excited state. This is typical excimer behavior.[35]

Conclusions

For dilute solution, we have observed two types of emission behavior for Pt(II) complexes containing α-diimine ligands. If the complex also has weak field ligands such as chloride, ligand field (d–d) excited states become the lowest energy excited states. If only strong field ligands are present, a diimine $^3(\pi-\pi^*)$ state becomes the lowest. In no case we have studied does an MLCT excited state lie lowest. The earliest assignments of MLCT emission from platinum α-diimine complexes[8,14,15] were based largely upon solid-state emission spectra, which we have shown to be strongly perturbed from solution spectra in two representative complexes.

In the solid state, absorption and emission spectra of Pt(II) complexes are seldom analogous to those of solutions. Direct Pt–Pt interactions can cause strong splitting of d_{z^2} orbitals,[11–13] which can strongly perturb the ligand field, (d–p), and/or MLCT excited states. What we wish to emphasize here is that there is another type of electronic interaction, namely ligand–ligand excimeric interaction, that may also strongly perturb emission spectra. Thus, the observation of solid-state effects in the emission spectra of d^8 complexes does not necessarily indicate metal–metal interaction. The distinctly different effects of strong metal–metal interaction for platinum(II) α-diimine complexes will be discussed by us in a future paper.

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Registry No. $[Pt(bpy)(en)](ClO_4)_2$, 54806-37-0; $Pt(bpy)Cl_2$, 13965-31-6; $[Pt(bpy)_2](ClO_4)_2$, 18437-39-3; $[Pt(phen)_2]Cl_2$, 59981-72-5.

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Electrochemical Assembly of Metallopolymeric Films via Reduction of Coordinated 5-Chlorophenanthroline

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Electrochemical reduction of iron, osmium, and ruthenium complexes containing the ligand 5-chlorophenanthroline leads to the controlled growth of metallopolymers as electrode coatings. The coatings are electroactive and display a reversible electrochromic effect upon metal oxidation. Auger electron spectroscopy studies show that the polymerization mechanism involves carbon–chlorine bond cleavage and the generation of exchangeable chloride ions. The proposed linkage mechanisms involve direct carbon–carbon coupling of phenanthroline ligands. The possible utility of these new polymers in redox conductivity studies and in microstructure fabrication is noted.

Introduction

Electroactive metallopolymeric films are unique materials that have generated tremendous interest in the decade or so since their initial appearance.[1] Their development, especially as electrode coatings, has been motivated both by perceived opportunities in applications chemistry (e.g., electronic devices,[2] electrochromic technology,[3] chemical analysis,[4] electrocatalysis,[5] visible-light

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energy conversion,[6] etc.) and by a fundamental interest in their conductive and internal-transport characteristics.[7] Our own current interests are in the areas of electrochromics and redox conduction, and because of these interests we have sought to enhance the synthetic access to these materials and to broaden the overall synthetic base. In this effort our particular bias has been toward materials that can be prepared by electropolymerization techniques. These techniques offer the advantages of[1,8] (1) precise control of film thickness, (2) good reproducibility, (3) easy assembly, (4) straightforward copolymerization,[8b] and (5) multicomponent assembly with compositional modulation in one,[8n] two, or three[9] dimensions.

Among the existing electrochemically polymerizable monomers the largest and best characterized class is that based on pyridyl or polypyridyl ligation and reductive activation of olefinic sites.[8] These materials have provided the basis for much of the progress in the recent past. Nevertheless, there are a number of reasons to seek to develop materials by alternate synthetic routes. First, materials based on monodentate ligands like vinylpyridine and dipyridylethylene can suffer from extreme sensitivity to photodegradation, at least in the monomeric state.[10] Second, bidentate ligands like 4-methyl-4′-vinylpyridine or 4-vinyl-1,10-phenanthroline, which are likely to lead to more stable metallopolymers, are not commercially available. (It should be noted, however, that the synthesis of the former is now relatively straightforward.[11]) Third, synthetic routes based specifically on vinyl coupling are likely to lead predominantly to four-carbon links.[8k] From the perspective of site-to-site charge-hopping and conductivity characteristics, it may be desirable to generate materials having other linkage lengths.

In this article we describe the efficacious assembly of thin, metallopolymeric films from a collection of monomeric complexes containing 5-chlorophenanthroline as the active site. Carbon–halogen bond cleavage by electrochemical reduction is well-known for related (nonligated) compounds;[12] we reasoned that with the metal complexes such activation might lead to carbon–carbon bond formation and ultimately to polymerization and film formation. We also note that since 5-chlorophenanthroline is a chelating ligand it should impart photostability to the polymer films. Furthermore, the free ligand is reasonably stable and is sufficiently robust to be manipulated readily in most synthetic preparations.

Experimental Section

Materials. Tetraethylammonium hexafluorophosphate ($(TEA)PF_6$) was prepared by a literature method.[13] Tetraethylammonium perchlorate (TEAP; GFS Chemicals), ammonium hexafluorophosphate (95%; Aldrich), and the ligands 1,10-phenanthroline (phen; Aldrich, Gold Label) and 5-chlorophenanthroline (5-Cl-phen; GFS Chemicals) were used as received. Acetonitrile was distilled from P_2O_5.

$[Ru(5\text{-}Cl\text{-}phen)_3](PF_6)_2$. A 1.00-g (4.68-mmol) sample of 5-Cl-phen was dissolved in a solution containing 20 mL of butanol and 20 mL of water. The mixture was deoxygenated with N_2 for 20 min, and then 0.200 g of $RuCl_3 \cdot 3H_2O$ (0.766 mmol) was added. The solution was heated at reflux under N_2 overnight and then reduced in volume by about 50%. The crude solid was precipitated with excess NH_4PF_6, collected on a glass frit, and dried. The orange solid was then reprecipitated with ether from a minimum volume of acetonitrile. The compound was purified by chromatography on an alumina column with 1:1 acetonitrile:toluene, followed by reprecipitation by drop-by-drop addition to ether with stirring; yield 75%. Anal. Calcd: C, 41.78; H, 2.05; N, 8.12; Cl, 10.28. Found: C, 42.68; H, 2.89; N, 7.79; Cl, 10.04.

$[Ru(5\text{-}Cl\text{-}phen)_2(phen)](PF_6)_2$. A 0.246-g (1.37-mmol) amount of 1,10-phenanthroline was added to a solution containing 15 mL of ethanol and 15 mL of water. After deoxygenation with N_2, 0.401 g of $[Ru(5\text{-}Cl\text{-}phen)_2]Cl_2 \cdot 2H_2O$[8k] (0.629 mmol) was added. The solution was heated at reflux under N_2 overnight. Following this, the volume was reduced by half and an excess of NH_4PF_6 was added to precipitate the crude product. The complex was then filtered, dried, and reprecipitated from ether with stirring. The complex was purified by alumina column chromatography with 1:1 acetonitrile–toluene. The final product was reprecipitated by drop-by-drop addition to stirring ether; yield 10%. Anal. Calcd: C, 43.22; H, 2.22; N, 8.40; Cl, 7.09. Found: C, 43.45; H, 2.63; N, 8.44; Cl, 7.23.

$[Ru(5\text{-}Cl\text{-}phen)(phen)_2](PF_6)_2$. To a solution containing 15 mL of ethanol and 15 mL of water was added 0.400 g of $Ru(phen)_2Cl_2 \cdot 2H_2O$[8k] (0.703 mmol) after deoxygenating briefly with N_2. A procedure analogous to that for $[Ru(5\text{-}Cl\text{-}phen)_2(phen)](PF_6)_2$ was followed to complete the synthesis; yield 63%. Anal. Calcd: C, 44.76; H, 2.48; N, 8.70; Cl, 3.67. Found: C, 44.44; H, 2.68; N, 8.38; Cl, 4.05.

$[Ru(phen)_3](PF_6)_2$. A 0.203-g sample of $RuCl_3 \cdot 3H_2O$ and 0.506 g of 1,10-phenanthroline were mixed in about 20 mL of ethylene glycol and refluxed for 3 h. After it was cooled to room temperature, the mixture was diluted with water and filtered. The product was precipitated with excess NH_4PF_6 and collected on a glass frit. The crude compound was purified by alumina column chromatography with acetone as eluent. The final product was precipitated from ether. Anal. Calcd: C, 46.41; H, 2.60; N, 9.02. Found: C, 46.65; H, 2.57; N, 8.78.

$[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2′-Bipyridine). This compound was purchased from Aldrich as the chloride salt and metathesized in water by precipitating with NH_4PF_6.

$[Os(5\text{-}Cl\text{-}phen)_3](PF_6)_2$. To 25 mL of ethylene glycol was added 0.503 g of $(NH_4)_2OsCl_6$ (1.14 mmol). The solution was bubbled briefly with N_2, and then 1.48 g of 5-Cl-phen (6.91 mmol) was added. The solution was refluxed overnight under N_2. After the solution was cooled, an excess of NH_4PF_6 was added to the reaction mixture. The precipitate was collected and purified by following the procedure for $[Ru(5\text{-}Cl\text{-}phen)_3](PF_6)_2$; yield 68%. Anal. Calcd: C, 38.47; H, 1.88; N, 7.48; Cl, 9.46. Found: C, 38.38; H, 2.08; N, 7.08; Cl, 9.16.

$[Fe(5\text{-}Cl\text{-}phen)_3](PF_6)_2$. A 0.113-g amount of $FeSO_4 \cdot 7H_2O$ (0.407 mmol) was dissolved in water, and 0.264 g of 5-Cl-phen (1.23 mmol) was added. The solution was stirred for 1 h and heated mildly. NH_4PF_6 was added to precipitate a red solid, which was collected on a frit and dried; yield 92%. Anal. Calcd: C, 43.69; H, 2.14; N, 8.49; Cl, 10.75. Found: C, 42.53; H, 2.33; N, 8.24; Cl, 10.91.

$[Fe(phen)_3](PF_6)_2$. A 0.359-g (0.916-mmol) sample of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 0.490 g of phen (2.71 mmol) was added to 50 mL of water with stirring and then heated mildly for 1 h. The bright red product was precipitated by addition of excess NH_4PF_6, collected on a frit, and dried; yield 96%. Anal. Calcd: C, 48.78; H, 2.73; N, 9.48. Found: C, 48.47; H, 3.18; N, 8.63.

$[Fe(5\text{-}Cl\text{-}phen)_3]Cl_2 \cdot 3H_2O$. A 0.101-g (0.102-mmol) sample of $[Fe(5\text{-}Cl\text{-}phen)_3](PF_6)_2$ and 0.116 g (0.418 mmol) of tetrabutylammonium chloride were dissolved separately in small amounts of acetone. The two solutions were mixed, and a purple precipitate immediately formed. The solid was filtered, rinsed with acetone, and dried. Anal. Calcd: C, 52.42;

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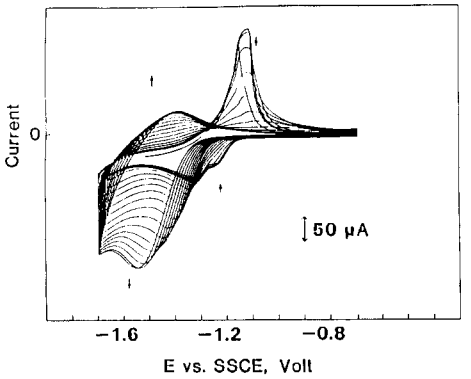


Figure 1. Cyclic voltammetric response of 2 mM $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$ in acetonitrile (0.1 M TEAP) at glassy carbon (sweep rate 50 mV/s).

H, 3.30; N, 10.19; Cl, 21.49. Found: C, 51.30; H, 3.27; N, 9.44; Cl, 22.86.

$[Fe(phen)_3]Cl_2 \cdot 6H_2O$. This compound was prepared by a method analogous to that used to prepare $[Fe(5\text{-}Cl\text{-}phen)_3]Cl_2$. Anal. Calcd: C, 55.76; H, 4.68; N, 10.84; Cl, 9.14. Found: C, 55.41; H, 4.65; N, 10.88; Cl, 9.02.

Measurements. Cyclic voltammetry was carried out by using a Princeton Applied Research polarographic analyzer (Model 264A) and a Houston Instruments X-Y recorder (Model 2000). The solvent was acetonitrile, and the supporting electrolyte was either 0.1 M TEAP or 0.1 M $(TEA)PF_6$ (for Auger specimens). Either a glassy-carbon-disk electrode (0.071 cm^2; Bioanalytical Systems) or a platinum flag (Auger specimens) was used as a working electrode. A platinum wire served as the auxiliary electrode, and a saturated sodium calomel electrode was used as a reference. Typically, a 2.0 mM solution of monomer was used. For electrochemical polymer preparation, the potential was cycled repetitively between −1.7 and −0.7 V at 50 mV/s. All experiments were run under a blanket of flowing nitrogen.

Visible-region spectroelectrochemical (absorbance) measurements were made with a Perkin-Elmer 330 spectrophotometer using metallopolymeric films on transparent indium tin oxide electrodes.

Auger spectra for thin polymeric films and the corresponding monomers (solvent-evaporated residues) were obtained by electron excitation, with a Model 590A scanning Auger microprobe manufactured by Physical Electronic Industries Inc. For each specimen (typically three independent specimens per sample), four or five randomly selected spots were examined with the microprobe and spectra were collected in the derivative mode. Argon ion sputtering of selected specimens revealed no evidence for compositional variations in the depth direction.

Results

Electrochemistry. Figure 1 shows consecutive cyclic voltammograms (CV) at glassy carbon in the ligand reduction region for $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$ in acetonitrile (0.1 M TEAP) as solvent. The response is unusually complex: An asymmetric pattern of both increasing and decreasing peaks exists. Inspection of the electrode following cycling reveals an adherent orange film, suggestive of polymer formation. Very similar results are found for osmium and iron analogues except that the films are, respectively, green and red. Film formation no doubt accounts in Figure 1 for the peaks that grow with repetitive cycling. Thus, current flow would be expected to increase with the progressive accumulation of electroactive material at the electrode–solution interface.

A ready explanation for the peaks that decrease is provided by an identical experiment involving the nonpolymerizable complex $Ru(phen)_3^{2+}$. In this case a steady-state CV response is obtained (Figure 2), but the response is distorted in a way that is clearly indicative of severe adsorption–desorption (or possibly precipitation) effects. The most important point, however, is that it closely resembles the first few cycles for $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$. The disappearance of sharp, distorted peaks with repetitive cycling in the latter case can likely be attributed to a progressive loss of adsorption sites due to surface polymer formation.

The identity of the remaining peaks can be assigned (at least tentatively) by examining the electrochemistry of the intact $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$-based film in a fresh solution. Figure 3 shows cyclic voltammograms for both the ligand- and metal-centered redox

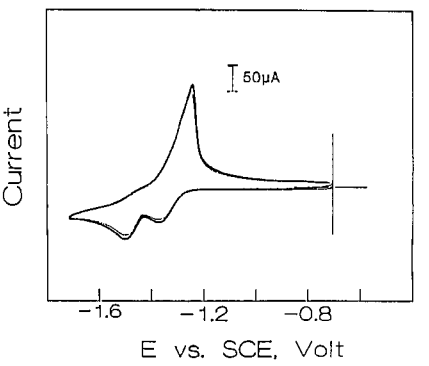


Figure 2. Cyclic voltammetric response of 2 mM $Ru(phen)_3^{2+}$ in acetonitrile (0.1 M TEAP) at glassy carbon (sweep rate 50 mV/s).

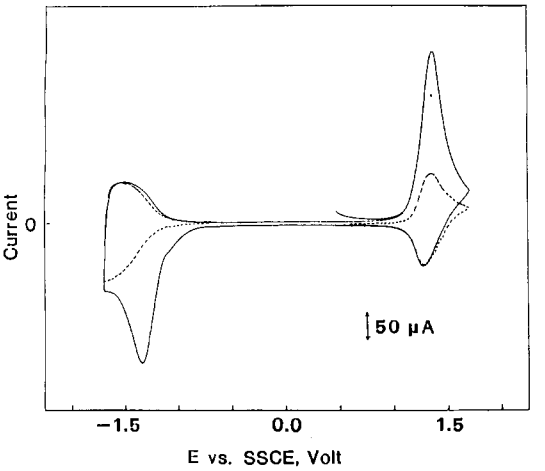


Figure 3. Electrochemical response of a $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$-based film in acetonitrile (0.1 M TEAP) at glassy carbon.

Table I. Coverage and Redox (vs SSCE) Data for Electrochemically Prepared Metallopolymers

monomer complex[a]	$E°$-(monomer), V	$E°$-(polymer), V	Γ, mol/cm^2 [b]	no. of monolayers[c]
$Ru(5\text{-}Cl\text{-}phen)_3^{2+}$	1.36	1.32	1.4×10^{-7}	1900
$Ru(5\text{-}Cl\text{-}phen)_2(phen)^{2+}$	1.33	1.31	2.7×10^{-8}	350
$Ru(5\text{-}Cl\text{-}phen)(phen)_2^{2+}$	1.30	1.30	1.1×10^{-9}	15
$Os(5\text{-}Cl\text{-}phen)_3^{2+}$	0.91	0.89	1.5×10^{-7}	1900
$Fe(5\text{-}Cl\text{-}phen)_3^{2+}$	1.17	1.12	7×10^{-8}	900

[a] Solution concentrations 2 mM. [b] Based on 60 cycles at 50 mV/s between the limits of −0.7 and −1.7 V vs SCE. [c] Assuming a monomer radius of ca. 15 Å.

regions together (solid line) and for each of these in isolation (dashed lines). The salient features are (1) the appearance of a reversible, surface-confined Ru(III/II) couple at $E_{1/2} = 1.32$ V (cf. 1.36 V for the monomer couple in solution), (2) the existence of a broad, reversible wave at ca. −1.46 V and beyond, presumably due to overlapping phen reductions, and (3) the appearance of so-called "trapping" peaks[8n] at the onset potential for either Ru(II) oxidation or phen reduction. The dashed lines show that the trapping peaks are dissipated when cycling is confined to either the metal-centered or ligand-centered redox region. They can be regenerated repeatedly, however, by simply scanning sequentially through both regions.

We find that a complex with only two chlorophenanthroline ligands ($Ru(5\text{-}Cl\text{-}phen)_2(phen)^{2+}$) will also reductively polymerize, but less efficiently. Electrochemically detectable film formation also occurs to a very small extent with prolonged cycling of $Ru(5\text{-}Cl\text{-}phen)(phen)_2^{2+}$.

Table I summarizes the electrochemical potential and surface coverage data for five redox films. The coverage data were calculated from areas for M(III/II) CV peaks, without taking into account the charge due to "trapping". Thus, the actual coverages may well be higher. In any case, an important point

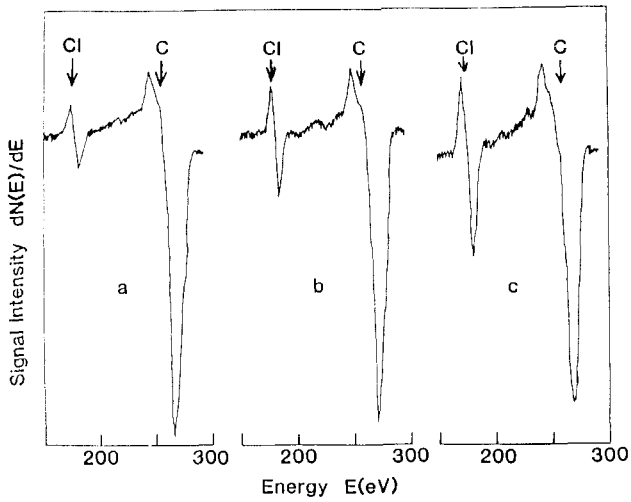


Figure 4. Representative Auger spectra in the chlorine and carbon region for (a) $[Ru(5\text{-}Cl\text{-}phen)(phen)_2](PF_6)_2$, (b) $[Ru(5\text{-}Cl\text{-}phen)_2(phen)](PF_6)_2$, and (c) $[Ru(5\text{-}Cl\text{-}phen)_3](PF_6)_2$.

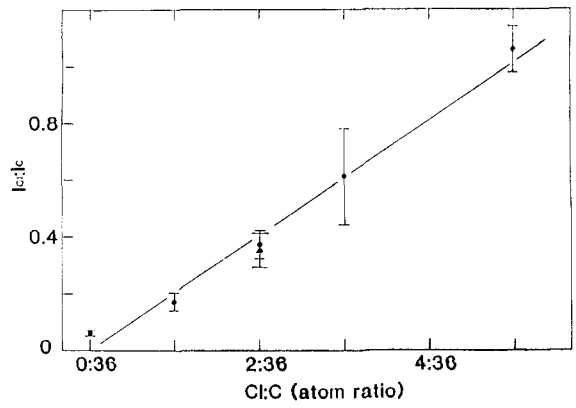


Figure 5. Auger (derivative) peak intensity ratios (chlorine vs carbon) plotted against elemental composition (chlorine vs carbon) for the following monomeric species: $[Fe(phen)_3](PF_6)_2$, $[Ru(5\text{-}Cl\text{-}phen)(phen)_2](PF_6)_2$, $[Ru(5\text{-}Cl\text{-}phen)_2(phen)](PF_6)_2$, $[Fe(phen)_3]Cl_2 \cdot 6H_2O$ (▲), $[Ru(5\text{-}Cl\text{-}phen)_3](PF_6)_2$, and $[Fe(5\text{-}Cl\text{-}phen)_3]Cl_2 \cdot 3H_2O$. Error bars represent 1 standard deviation.

from the tabulation is that in all cases the coverages are much too high to be attributed to monolayer adsorption phenomena.

Finally, we note that spectroelectrochemical experiments (indium tin oxide) reveal an electrochromic transition (red to transparent) for the polymer-based Fe(III/II) couple.

Auger Electron Spectroscopy. The energy of an emitted electron in the Auger process is element specific and so should provide a means for determining the fate of the chloro substituent in the electropolymerization process. Figure 4 shows portions of Auger spectra for evaporated residues of $[Ru(5\text{-}Cl\text{-}phen)(phen)_2](PF_6)_2$, $[Ru(5\text{-}Cl\text{-}phen)_2(phen)](PF_6)_2$, and $[Ru(5\text{-}Cl\text{-}phen)_3]_2(PF_6)_2$ on platinum foil. The important point in the figure is that the signal due to chlorine increases (relative to carbon) as the number of chlorophenanthroline ligands increases. Figure 5 illustrates the same point in a more quantitative way for a larger collection of compounds, including $[Fe(phen)_3](PF_6)_2$, $[Fe(phen)_3]Cl_2$ and $[Fe(5\text{-}Cl\text{-}phen)_3]Cl_2$. In the figure, ratios of Auger (derivative) peak intensity (I_{Cl}:I_C) are plotted against ratios of elemental composition. From the plot, a semiquantitative intensity/structure relationship clearly exists. Also, it is important to note that in the Auger experiment Cl and Cl^- are indistinguishable, as one would expect from the underlying theory for secondary electron ejection.[14]

With this background, the Auger technique was extended to studies of film composition. Figure 6 shows a chlorine:carbon ratio

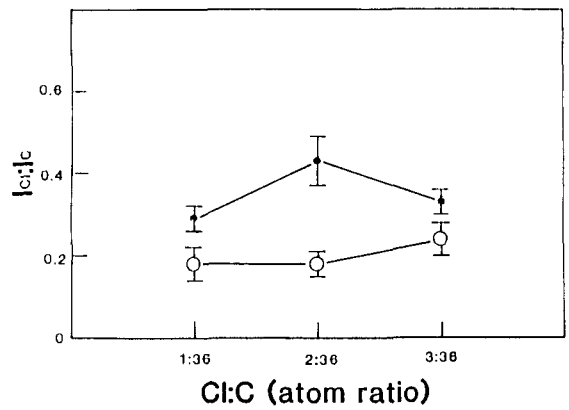


Figure 6. Auger (derivative) peak intensity ratios (chlorine vs carbon) plotted against elemental composition (chlorine vs carbon) for electropolymerized films based on $Ru(5\text{-}Cl\text{-}phen)(phen)_2^{2+}$, $Ru(5\text{-}Cl\text{-}phen)_2(phen)^{2+}$, and $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$: (closed circles) films as initially grown; (open circles) films soaked in aqueous NH_4PF_6 (see text). Error bars represent 1 standard deviation.

plot of Auger peak intensities for various polymeric films versus the corresponding *monomer* compositions. The key findings are as follows: first, a surprisingly large amount of chlorine is retained in the films; second, I_{Cl}:I_C is relatively constant for the three films based on $Ru(5\text{-}Cl\text{-}phen)(phen)_2^{2+}$, $Ru(5\text{-}Cl\text{-}phen)_2(phen)^{2+}$, and $Ru(5\text{-}Cl\text{-}phen)_3^{2+}$; third, the number of chlorine atoms per metal site is ca. 1.5:2, based on Figure 4 as a calibration. These results imply that either the chloro substituent is somehow retained during electropolymerization or it indeed is lost but that the resulting chloride is retained as the film counterion. To distinguish these possibilities, we performed the following experiment: Films prepared in a fashion identical with that above were soaked in a saturated aqueous NH_4PF_6 solution for 1 h and dried for 2 days under vacuum. The chlorine:carbon ratios were measured (open circles, Figure 6) and found to be about 2-fold smaller than for unsoaked films. This diminution and the observation of phosphorus and fluorine within the film[15] indicate that Cl can be exchanged with solution ions and therefore must exist as a free ion.[16]

Discussion

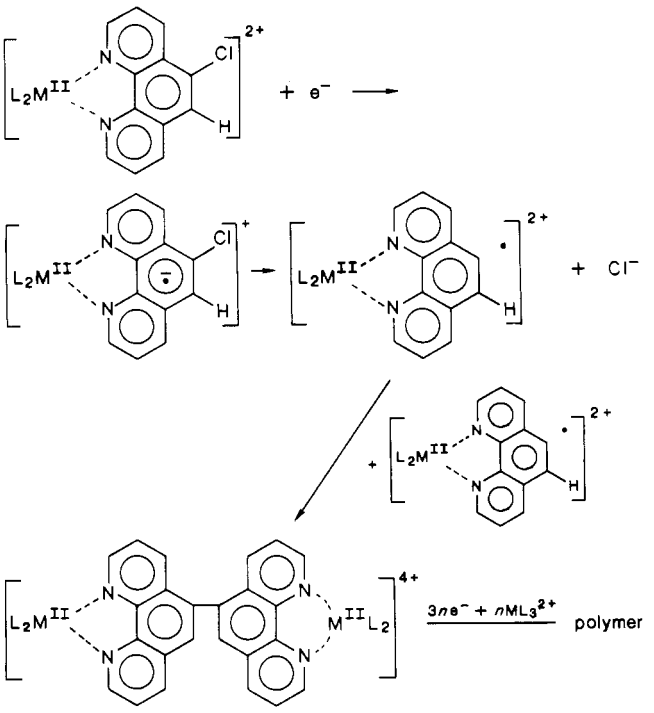
The available electrochemical and spectroelectrochemical data show that a series of related electroactive and electrochromic, polymeric films can be prepared from monomeric complexes of 5-chlorophenanthroline. The key remaining question is the mechanism of polymerization. From the available experiments the following pertinent observations exist: (1) By comparison with the electronic absorption spectrum for $Fe(5\text{-}Cl\text{-}phen)_3^{2+}$, film-based spectroelectrochemical results show that the central chromophoric unit remains largely intact upon polymerization. (2) The Auger experiments clearly show, however, that the peripheral chloro substituent is converted to a free chloride anion. (3) The $E_{1/2}$ data in Table I hint at the same conclusion as in point 2. Thus, in the ruthenium monomer series as each 5-Cl-phen is replaced by an unsubstituted ligand, the Ru(III) reduction potential decreases, as one would expect from substituent electronegativity considerations. With film formation, similar decreases in $E_{1/2}$ occur. The ligand-based reductions, although more com-

(14) Ewing, G. W. *Instrumental Methods of Chemical Analysis*, 4th ed.; McGraw-Hill: New York, 1975; Chapter 11.

(15) The Auger-detected phosphorus and fluoride could be from excess NH_4PF_6, in addition to PF_6^- counterions. We observed, for example, an increase in N (presumably ammonium cation) following electrolyte soaking.

(16) It should be noted that films which have been subjected to (partial) counterion exchange continue to display stable electrochemistry in fresh CH_3CN–TEAP solutions. Also, films can be grown easily in propylene carbonate as solvent. Furthermore, in this solvent we find that $Fe(5\text{-}Cl\text{-}phen)_3Cl_2$ is extremely soluble, even with tetraethylammonium chloride present in large excess. ($[Fe(5\text{-}Cl\text{-}phen)_3]Cl_2$ is also reasonably soluble in CH_3CN but becomes less so in the presence of excess chloride ions.) These three observations are important because they enable us to exclude a possible (albeit, unlikely) alternative explanation for electroactive film formation—namely, that electrochemically induced halide loss leads to monomeric halide salt surface precipitate formation.

Scheme I



plex, also show a negative shift (see Figure 1). Although such decreases for film vs solution must be interpreted with caution,[17] they do imply a loss of the chloro substituent. (4) Cyclic voltammograms for ruthenium-based films generally exhibit, on the first scan following reductive electropolymerization, a large oxidative peak at +1.4 V (see Figure 3) with a shoulder at ca. +1.2 V. The shoulder becomes a well-defined peak when excess chloride is intentionally added to the working-compartment solution. Presumably it arises from Cl^- oxidation.

The available detailed mechanistic observations, admittedly, are few. The mechanistic possibilities, however, are likewise few. A mechanism that does satisfy most of the experimental observations is given in Scheme I. It should be noted that there is a general precedent for Scheme I from a number of studies by Saveant and co-workers of halo–aromatic systems.[12] With monohalogenated reactants, for example, they have sometimes observed electrochemically induced carbon–carbon coupling (albeit, via solvent intermediates).[12a] Their work also suggests ways of elaborating on the basic mechanism.

The single observation that is inconsistent with Scheme I is film formation from $Ru(5\text{-Cl-phen})(phen)_2^{2+}$. One explanation, given the very low efficiency, is that polymer formation occurs from $Ru(5\text{-Cl-phen})_2(phen)^{2+}$ or $Ru(5\text{-Cl-phen})_3^{2+}$ present as a minor impurity. A simple statistical argument appears to rule out that possibility.[18] Consider, for example, a 10% contamination with $Ru(5\text{-Cl-phen})_2(phen)^{2+}$. The chances are essentially 1 in 100 for linking two impurity molecules, 1 in 1000 for linking three, and so on. Formation of polymers in this fashion would appear to be effectively forbidden.

Alternatively, film formation could involve a second electropolymerization pathway. One candidate pathway would be direct attack by radical ligands at *unsubstituted* phenanthroline.[19] To check that possibility, we carried out an electropolymerization experiment involving $Os(5\text{-Cl-phen})_3^{2+}$ in the presence of $Ru(phen)_3^{2+}$. Both metal centers were found to polymerize. On the other hand, control experiments with $Ru(bpy)_3^{2+}$ led to electropolymerization of only the osmium complex.

Returning to Scheme I, we feel some structural implications are worth noting. Synthetic methodoligies now exist that appear to lead to four-carbon,[8k] two-carbon,[8i] and zero-carbon spacers for metallopolymeric repeat units.[20] One might speculate that, within the series, electronic factors would lead to increasing site-to-site communication and enhanced redox conductivity as the spacer is shortened. On the other hand, factors such as counterion motion and collective polymer motions might tend to favor longer spacers for conductivity enhancement. Resolution of issues like these, however, will require that the linkage structures be unambiguously proven—perhaps by solid-state NMR or other nontraditional methods.

In any case we intend to utilize the chlorophenanthroline electropolymerization chemistry in our ongoing studies of metallopolymer microstructure assembly and applications.[9] There are two points at which the new chemistry might favorably impact. The first is redox switching times. If these are controlled by rates of electron hopping, they might be improved by eliminating the carbon spacer, for reasons such as those mentioned above in the discussion of conductivity. (Conversely, switching times could be diminished if ion transport proved to be rate determining.) The second point is the enhancement of resolution in the assembly of small polymeric structures. Our current route to polymeric microstructures is based on a photoelectrochemically triggered vinyl polymerization. The assembly of very small structures relies upon high-resolution focusing of a photolysis beam. Invariably we find, however, that the polymer dimensions exceed the photolysis dimensions by 2 to 10, or even 100, times. The difficulty has been traced in part to uncontrolled dark propagation,[9] presumably by a vinyl-radical chain-reaction mechanism.[8k] The potential key advantage of the chlorophenanthroline systems would be the absence of this mechanism. From Scheme I, each increment of polymerization would appear to require direct electrochemical initiation.

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(17) Redepenning, J.; Anson, F. C. *J. Phys. Chem.* **1987**, *91*, 4553.
(18) We thank a reviewer for suggesting this argument.
(19) It should be noted that a precedent exists from vinylbipyridine chemistry.[8i]
(20) The mechanism involving attack at unsubstituted phenanthroline should also yield zero-carbon spacers.