

Table I. Analytical Data, Molar Conductance Values, and IR and Raman Bands of $A[V(O_2)_3]$ ($A = Na$ or K)

compd	molar conductance, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	% found (% calcd)			IR, cm^{-1}	Raman, cm^{-1}	assignt
		A	V	O_A^a			
Na $[V(O_2)_3]$	135	13.8	30.4	55.8	855 (s)	850	ν_{-O-O-} (ν_1)
		(13.53)	(29.98)	(56.49)	610 (s)	600	ν_{V-O_2} (ν_3)
					525 (s)	530	ν_{V-O_2} (ν_2)
K $[V(O_2)_3]$	140	21.2	27.8	52.1	855 (s)	860	ν_{-O-O-} (ν_1)
		(21.02)	(27.38)	(51.6)	610 (s)	610	ν_{V-O_2} (ν_3)
					530 (s)	530	ν_{V-O_2} (ν_2)

^a Peroxo oxygen.

Results and Discussion

Albeit there has been a continued interest in the peroxovanadium chemistry, most of the recent reports deal with the aspects of solution chemistry^{3,5-10} while information on synthesis, isolation in the solid state, characterization, and structural assessment of peroxovanadate compounds is rather scanty. The synthesis of blue alkali-metal triperoxovanadates(V), $A[V(O_2)_3]$ ($A = Na$ or K), has been achieved from the reaction of V_2O_5 with 30% H_2O_2 in the presence of a relatively large concentration of alkaline medium with the molar ratio of $V_2O_5:H_2O_2:AOH$ being maintained at 1:42.5:(10-12). A high concentration of AOH is necessary and conducive to the formation and then isolation of $A[V(O_2)_3]$ compounds. Although the $V^{5+}-H_2O_2$ solution assumes a blue color at a relatively lower concentration of AOH, the IR spectrum of the product isolated from it shows a band at ca. 950 cm^{-1} owing to $\nu_{V=O}$ in addition to those expected for the coordinated O_2^{2-} . This suggests that the formation of the triperoxovanadate(V), $[V(O_2)_3]^-$, complex is not complete; thus, it is required to add a further amount of alkali-metal hydroxide after the first appearance of blue color, however, not beyond the stipulated limit (see the Experimental Section). It may be noted that the change of color of $V^{5+}-H_2O_2$ solution, with the increase in concentration of alkaline medium, from yellow to blue clearly indicates that the complex $[VO(O_2)_2]^-$ is first formed and then is ultimately converted to the $[V(O_2)_3]^-$ complex. The complete disappearance of the $\nu_{V=O}$ at ca. 950 cm^{-1} in the IR and laser Raman spectra of the compound ensures completion of the reaction. Thus $A[V(O_2)_3]$ compounds were obtained by the addition of ethanol, which facilitates precipitation. Attempts to synthesize $NH_4[V(O_2)_3]$ were futile. Although a transitory blue solution was obtained by the addition of NH_4OH solution (sp gr 0.9), the color was practically discharged, with brisk evolution of oxygen, during workup. It is worthwhile to mention that the tetraperoxovanadate(V), $[V(O_2)_4]^-$, complex, as opposed to the triperoxo species, is formed^{12,19} only at temperatures below 0 °C presumably in the presence of a relatively higher amount of alkaline medium.

The blue triperoxovanadates(V) $A[V(O_2)_3]$ ($A = Na$ or K) are diamagnetic in line with the occurrence of quinquivalent vanadium and, unlike the $A_2[V(O_2)_3X]$ ($X = F$ or Cl)¹⁵ and $A_3[V(O_2)_4]$ ¹⁹ compounds, are stable in water. Whereas $A_2[V(O_2)_3X]$ ¹⁵ and $A_3[V(O_2)_4]$ ¹⁹ do not permit molar conductance measurements, the values for the $A[V(O_2)_3]$ compounds, at ambient temperatures, were found to lie in the range 130-140 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, suggesting their 1:1 electrolytic nature, in complete agreement with the formulas. The estimation of peroxide content is emphasized to be very crucial in order to fix the number of O_2^{2-} groups bound to the V^{5+} center. The results of peroxide determination, accomplished by redox titrations^{17,18} involving Ce^{4+} and potassium permanganate, conspicuously suggested the occurrence of three peroxide groups per V^{5+} center in each of the new compounds. The UV-vis spectra of the solutions recorded before isolation of the compound and of that obtained by redissolving the compound were similar and showed absorptions at 560 and 192 nm with the molar absorption coefficients being 84.3 and 1.04×10^4 , respectively. This indicates that the complex species formed in solution and that isolated in the solid state are identical. The electronic spectral data for $[V(O_2)_4]^{3-}$ are not available in the

literature, thus precluding comparison with those of $[V(O_2)_3]^-$.

The characteristic features of the IR and laser Raman (LR) spectra are the absorption at ca. 850 cm^{-1} owing to ν_{-O-O-} ²⁰ and the two absorptions at ca. 600 and ca. 530 cm^{-1} due to ν_{V-O_2} ²⁰ with all three originating from the coordinated peroxide groups. The typical pattern of the spectra suggests that each of the O_2^{2-} ligands is bonded to the V^{5+} center in a triangular bidentate manner. The $-O-O-$ and metal- O_2 bonds are important spectroscopic probes for molecular structure assessment of peroxometal compounds and are amenable to direct IR and LR spectroscopy. Considering C_{2v} to be the local symmetry of a coordinated O_2^{2-} group, three vibrations, viz. ν_1 (ν_{-O-O-}), ν_2 (ν_{V-O_2}), and ν_3 (ν_{V-O_2}), are expected to be active in both IR and Raman spectra,²⁰ with the ν_1 and ν_2 modes being polarized in the latter and appearing comparatively more sharp and intense than ν_3 mode. Accordingly, the LR signals at ca. 850, ca. 530, and ca. 600 cm^{-1} have been assigned respectively to the ν_1 , ν_2 , and ν_3 modes of the coordinated O_2^{2-} ligands. The solution LR spectra of $A[V(O_2)_3]$ compounds resemble those of the corresponding solids, suggesting that the complex anion $[V(O_2)_3]^-$ possesses the same structure in the solid state as well as in solution. Further, the absence of any band at ca. 950 cm^{-1} due to $\nu_{V=O}$, especially in the LR spectra in which it would be very strong on account of the large polarizability changes involved in the $V-O$ bond, renders it certain that the complex does not contain any $V=O$ group.

It may be inferred that a minimum of three O_2^{2-} groups, coordinated to a V^{5+} center, is required for the formation of a blue color in the $V^{5+}-H_2O_2$ system. The complex $[V(O_2)_3]^-$ ion, unlike the $[V(O_2)_4]^{3-}$ species, retains its identity both in solution as well as in the solid state. The $[V(O_2)_3]^-$ ion may have a hexacoordinated monomeric structure with the O_2^{2-} groups being bonded to the V^{5+} center in a triangular bidentate manner.

Acknowledgment. The authors thank the Council of Scientific and Industrial Research, New Delhi, for awarding fellowships to S.K.G. and N.S.I.

Registry No. Na $[V(O_2)_3]$, 96760-79-1; K $[V(O_2)_3]$, 96760-80-4.

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Electrochemistry and Spectroelectrochemistry in CH_3CN and Aluminum Chloride/ N -(1-Butyl)pyridinium Chloride Molten Salts of Films Prepared by Electrochemical Polymerization of Tris(5-amino-1,10-phenanthroline)iron(II)

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Received July 24, 1984

The incorporation of transition-metal complexes into polymer films on electrodes has received considerable attention in recent

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years.¹⁻³⁴ One of the most satisfactory methods for achieving this is the electrochemical polymerization of suitably substituted transition-metal complexes directly onto the electrode.^{19-23,31,32}

Murray, Meyer, and co-workers²⁰⁻²³ have made extensive studies of a series of electropolymerized transition-metal complexes of the form $[M(L-L)_2(L)_2]^{2+}$, where $M = Fe, Ru, \text{ or } Os$, $L-L = 2,2'$ -bipyridine (bpy), 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy), or 5-amino-1,10-phenanthroline (5-NH₂-phen), and $(L)_2 = vbpy, 5-NH_2\text{-phen}, (vpy)_2, (4\text{-py-cinnamamide})_2, (3-NH_2\text{-py})_2, \text{ or } (4-NH_2\text{-py})_2$. These polymers have proven to be excellent for fundamental studies of polymer film electrochemistry.³⁵⁻⁴⁰ They are generally very stable and homogeneous and exhibit facile electrochemistry. They swell in CH₃CN and are then permeable to small molecules and ions in solution. Thus, the solvated polymers are extremely interesting from a structural point of view. Further interesting and useful properties of this series of polymers are that they are electrochromic, they undergo photochemical reactions, and they are rapid outer-sphere electron-transfer agents.

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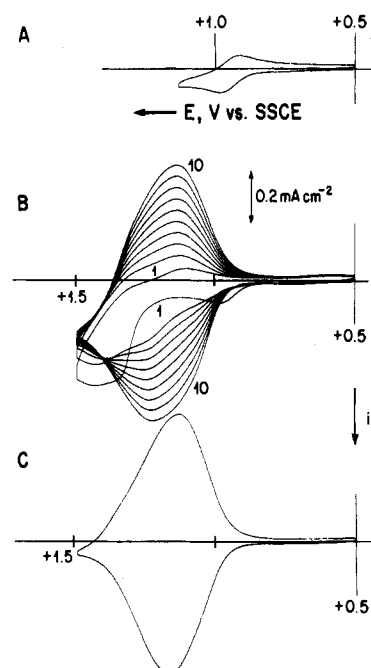
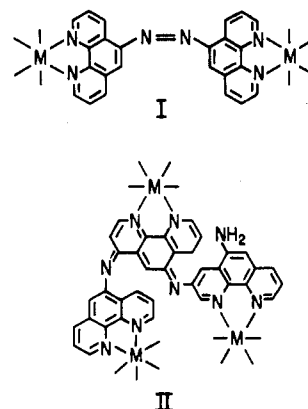


Figure 1. Cyclic voltammograms at 100 mV s⁻¹ of (A and B) ca. 0.5 mM $[Fe(5-NH_2\text{-phen})_3]^{2+}$ in CH₃CN/0.1 M Et₄NClO₄ at a glassy-carbon electrode and (C) the same electrode in CH₃CN/0.1 M Et₄NClO₄ after 10 scans in the solution containing $[Fe(5-NH_2\text{-phen})_3]^{2+}$.

We were interested in investigating the electrochemistry of a previously unreported member of the above series of polymers, poly- $[Fe(5-NH_2\text{-phen})_3]^{2+}$, in ambient-temperature molten salts composed of mixtures of either *N*-(1-butyl)pyridinium chloride (BuPyCl) or 1-methyl-3-ethylimidazolium chloride (ImCl) with AlCl₃.⁴¹⁻⁴⁴ We report here the preparation and characterization of this polymer and the results of preliminary studies of its electrochemistry in molten salts.

The Ru analogue of this polymer has been described by Meyer and co-workers.²³ It was prepared by electrochemical oxidation of the amino substituents of $[Ru(5-NH_2\text{-phen})_3]^{2+}$ in CH₃CN. The mechanism of the polymerization reaction is not fully understood, but it is thought to involve a -NH radical. Coupling of two such radicals followed by further oxidation and deprotonation can lead to a diazo linkage (structure I). Delocalization of the radical within the ring system can lead to coupling via imine linkages at the 3- or 7-positions of the ring (structure II).



Propagation, and the fact that there are three amine groups per molecule, can lead to a heavily cross-linked polymer with a variety

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of imine, diazo, and unreacted amine sites.

Gillard and Hill⁴⁵ have reported the formation of a polymer by Sn-HCl reduction of $[\text{Ru}(5\text{-NO}_2\text{-phen})_3]^{2+}$. The formation of hydrazo linkages is suggested.

Poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ is of particular interest for use in ambient-temperature molten salts. Sahami and Osteryoung⁴⁶ have shown that $[\text{Fe}(\text{phen})_3]^{2+}$ is oxidized by O_2 in acidic (excess AlCl_3) $\text{AlCl}_3/\text{BuPyCl}$ melts. This is a potentially useful reaction because $[\text{Fe}(\text{phen})_3]^{3+/2+}$ has a high formal potential (+730 mV vs. ferrocenium/ferrocene) in this solvent system. We wanted to determine whether a poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ -coated electrode would electrocatalytically reduce O_2 in these melts.

Another feature of poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ electrochemistry in melts containing AlCl_3 is the possibility of adduct formation between AlCl_3 and the nitrogen atoms of unreacted $-\text{NH}_2$ groups or $-\text{N}=\text{}$ or $-\text{N}=\text{N}-$ bridging groups within the polymer. Such interactions could influence the redox potentials and/or structure of the polymer. Structural changes might influence the permeability and charging rate of the polymer, and the discovery of such effects would be of great significance to our understanding of polymer film electrochemistry. We report here results which suggest that the above effects are indeed in operation in poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ films in acidic (mole ratio of $\text{AlCl}_3:\text{RCl} > 1$) melts. Here R^+ represents either the BuPy^+ or the Im^+ cation.

Experimental Section

Preparation of $[\text{Fe}(5\text{-NH}_2\text{-phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.⁴⁷ A 0.10-mmol sample (20 mg) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Fisher) and 0.50 mmol (100 mg) of 5-NH₂-phen (Polysciences) were stirred together in H_2O (10 mL) for 10 min. An aliquot of 70% HClO_4 (0.5 mL) was added to the resulting red solution, and the precipitate was collected, washed well with water, and dried under vacuum. Anal. Calcd for $[\text{Fe}(5\text{-NH}_2\text{-phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: C, 49.32; H, 3.54; N, 14.39; Fe, 6.37. Found: C, 49.79; H, 3.55; N, 14.65; Fe, 5.87.

Molten Salts The preparation, use, and properties of the melts used here have been described elsewhere.^{42,44} Electrochemical experiments in melts were performed at $40 \pm 2^\circ\text{C}$ (BuPyCl melts) or $26 \pm 2^\circ\text{C}$ (ImCl melts) in a Vacuum Atmospheres Co. drybox under purified argon.

Electrochemistry. Electrochemical experiments were performed in a conventional glass H-cell or in a glass cell with a Luggin capillary between the working and reference electrodes (for voltammetry at high scan speeds, chronoamperometry, and chronocoulometry). For all experiments in CH_3CN , 0.1 M Et_4MClO_4 supporting electrolyte was used and the temperature was $26^\circ \pm 2^\circ\text{C}$. Glassy-carbon sealed in Teflon (area 0.46 cm^2 ; Pine Instruments Co.), glass (area 0.071 cm^2), or Pt sealed in Teflon (area 0.0079 cm^2) working electrodes were used. Reference electrodes were either SSCE or Ag/AgCl (in CH_3CN) or an Al wire in a 1.2:1 melt (for electrochemistry in melts). All potentials in the text are converted to be vs. SSCE in CH_3CN . In the case of melt electrochemistry this is done by taking ferrocenium/ferrocene as a standard.⁴⁸ An E & G PARC 175 universal programmer with a PARC 173 potentiostat, a Houston Omnigraph Model 2000 recorder and a Bascom-Turner 8120 data acquisition, processing, and storage system were used.

Spectroelectrochemistry. A glass H-cell with a square cross-section body was used with a SnO_2 -coated glass-plate working electrode (1 \times 5 cm; PPG Industries; NES 80 Ω/sq). For experiments with melts the cell was filled and sealed with Parafilm in the drybox; otherwise the cell was open. A Perkin Elmer (Coleman 575) spectrometer was used.

Materials. CH_3CN (Burdick and Jackson; UV grade) was used as received. Et_4NClO_4 (Baker) was dried in a vacuum oven before use.

Results

Polymerization of $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ in CH_3CN . Figure 1 shows the cyclic voltammetry of ca. 0.5 mM $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ at a glassy-carbon electrode in CH_3CN . If the anodic scan is reversed before +1.15 V (Figure 1A), then a reversible wave corresponding to the $\text{Fe}^{3+/2+}$ couple is observed at $E^\circ = +0.945$ V. This is close to E° for $[\text{Fe}(\text{phen})_3]^{3+/2+}$ (+1.07 V), as expected. However, if the cyclic scan is extended to +1.5 V (Figure 1B), a large oxidation wave is observed at $E_p \approx +1.4$ V and a smaller reduction wave is observed at $E_p = +1.10$ V on the reverse scan.

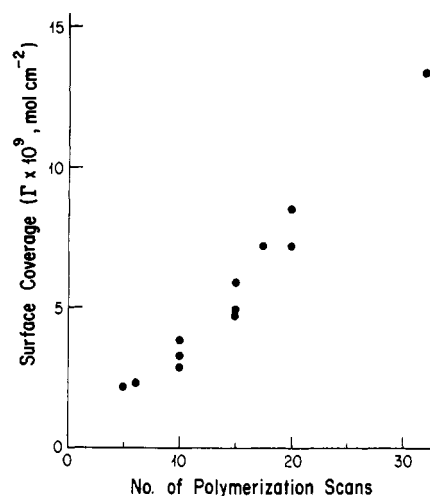


Figure 2. Surface coverage of polymer vs. number of cyclic scans between +0.50 and +1.50 V at 100 mV s^{-1} in a 0.16 mM $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ solution for glassy-carbon electrodes.

When the potential is continually cycled between +0.5 and +1.5 V the voltammogram develops into a growing reversible wave at $E^\circ \approx +1.2$ V. When, after 10 cycles, the electrode was removed from the cell, washed well with acetone, and transferred to a cell containing $\text{CH}_3\text{CN}/0.1 \text{ M Et}_4\text{NClO}_4$ with no Fe complex, the voltammogram shown in Figure 1C was obtained.

The interpretation of these results is that, as with the Ru analogue of this complex,²³ the oxidation of the amino groups at $E_p \approx +1.4$ V leads to polymerization. An electroactive (via the $\text{Fe}^{3+/2+}$ couple now at $E^\circ = +1.16$ V) polymer deposits upon the electrodes and becomes thicker with further cycles through the amine oxidation wave of the monomer. That a film is formed on the electrode can be confirmed by inspection (most easily observed on Pt). The reduced film is red and pale green electrochemically oxidized. The smooth, homogeneous appearance of the film is notable.

Figure 2 shows a plot of surface coverage (estimated from the area under a voltammogram) vs. the number of scans used to prepare films of poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ from a 0.16 mM solution of $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ in CH_3CN . The linear relationship is useful for estimating surface coverages. Most of the films used in this work were prepared under the conditions of Figure 2.

We have not further investigated the polymerization of $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ in CH_3CN , and we assume that it follows a mechanism similar to that outlined above for the Ru analogue.

Electrochemistry of Poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ in CH_3CN . The voltammogram shown in Figure 1C demonstrates that oxidation of poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{2+}$ films in CH_3CN is facile and reversible. The formal potential for the $\text{Fe}^{3+/2+}$ couple of the polymer is +1.16 V, which represents a +210-mV shift from the formal potential of the monomer complex. This potential shift is compatible with the hypothesis that many of the amino substituents of the monomer have become imine or diazo groups during the polymerization. These better electron-withdrawing groups should lower the ligand π^* orbitals and stabilize the Fe^{2+} state relative to the Fe^{3+} state.²³

A second notable aspect of the poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{3+/2+}$ voltammetric wave is its broadness ($E_{\text{fwhm}} \approx 240$ mV). Theoretically, for an ideal polymer-coated electrode, E_{fwhm} should be 90 mV.¹ Generally, larger values than this (≈ 150 mV) are found experimentally. This broadening has been attributed to interactions between the redox sites in the polymer^{38,49} or to the existence of many different redox sites with slightly different formal potentials.^{50,51} The extreme broadening with poly- $[\text{Fe}(5\text{-NH}_2\text{-phen})_3]^{3+/2+}$

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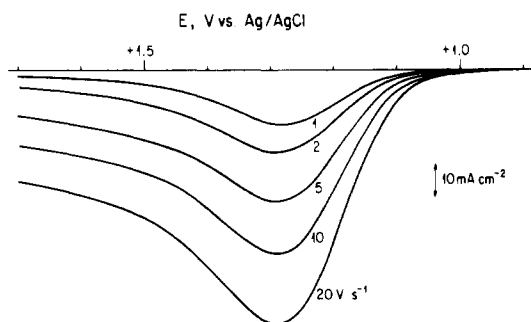


Figure 3. Linear-sweep voltammetry of a Pt/poly-[Fe(5-NH₂-phen)₃]²⁺ ($\Gamma = 5.2 \times 10^{-8}$ mol cm⁻²) electrode in CH₃CN/0.1 M Et₄NClO₄. IR compensation was used.

NH₂-phen)₃]²⁺ must be, at least in part, due to a mixture of Fe sites with various combinations of amino-, imino-, and diazo-substituted phen ligands. This is a reasonable consequence of the proposed polymerization mechanism and the shift in potential caused by the polymerization.

At 100 mV s⁻¹ the 1.3×10^{-8} mol cm⁻² (ca. 80 nm) film of Figure 1C is continually in Nernstian equilibrium with the applied potential, and the charge under the voltammogram represents the full amount of Fe in the polymer film. Thus, charge transport through the ca. 160 monolayer equivalents of this film must be rapid on the time scale of the experiment. However, with thicker films and higher scan rates it is possible to obtain diffusion-controlled voltammograms and hence to measure the charge-transport diffusion coefficient (D_{ct}) of the polymer.⁵²⁻⁵⁵

Figure 3 shows linear-sweep voltammograms for oxidation of a 5.2×10^{-8} mol cm⁻² film of poly-[Fe(5-NH₂-phen)₃]²⁺ on Pt at scan rates of up to 20 V s⁻¹. At scan rates of 5 V s⁻¹ or more, semiinfinite linear diffusional behavior is observed. IR compensation was used here to compensate for the solution resistance. Unfortunately, this also compensates for resistance effects in the film due to charge-transport limitations by counterion movements.⁵⁶⁻⁵⁹ Thus the diffusion coefficient obtained from this experiment represents the exchange rate between redox sites in the polymer but does not necessarily represent the true charging rate of the polymer, which may be limited by counterion movement.

Plots of i_p vs. $\nu^{1/2}$ and Q vs. $\nu^{-1/2}$ (where Q is the charge under the voltammogram up to +1.5 V) for the voltammograms of Figure 3 (plus results at 50, 100, and 200 V s⁻¹) are linear for $\nu > 2$ V s⁻¹. $D_{ct}^{1/2}C_{Fe}$ (where C_{Fe} is the concentration of Fe sites in the film) can be obtained from the slopes of these plots by using the Randles-Sevcik equation (1) and the treatment of Osteryoung

$$i_p = (2.72 \times 10^5)_n^{3/2} A D_{ct}^{1/2} C_{Fe} \nu^{1/2} \quad (1)$$

and co-workers,⁶⁰ respectively. In the latter case the charge under the voltammogram is given by eq 2, where $f(E_F, E_1, T)$ is a

$$Q = nFA C_{Fe} D_{ct}^{1/2} (RT/nF\nu)^{1/2} f(E_F, E_1, T) \quad (2)$$

function that depends upon the initial and final potentials and in this case is equal to 3.71.

The values of $D_{ct}^{1/2}C_{Fe}$ evaluated by these two methods are 5.2×10^{-8} and 7.9×10^{-8} mol cm⁻² s^{-1/2}, respectively. A value of

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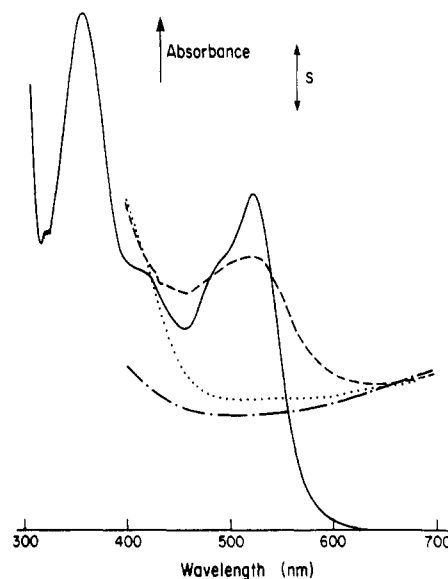


Figure 4. Electronic absorption spectra of 0.16 mM [Fe(5-NH₂-phen)₃]²⁺/CH₃CN/0.1 M Et₄NClO₄ (—; 1-mm path length; $S = 0.03$ A cm⁻²) and of the electrochemical cell containing CH₃CN/0.1 M Et₄NClO₄ with a naked SnO₂ working electrode (---) or a SnO₂/poly-[Fe(5-NH₂-phen)₃]^{3+/2+} ($\Gamma = 8.0 \times 10^{-9}$ mol cm⁻²) working electrode at either +0.50 V (- -) or +1.70 V (· · ·) ($S = 0.05$ A cm⁻²).

8.2×10^{-8} mol cm⁻² s^{-1/2} was obtained by both chronoamperometry and chronocoulometry for the same electrode (IR compensation was used). Thus, it appears that linear-sweep voltammetry is a valid technique for polymer film D_{ct} measurements if the charge under the voltammogram is used. However, the peak-current method seems to underestimate $D_{ct}^{1/2}C_{Fe}$, presumably because the voltammetric wave is broader and therefore lower than it would be ideally. Measurements of $D_{ct}^{1/2}C_{Fe}$ for reduction of the polymer from Fe³⁺ to Fe²⁺ yielded essentially the same results as for oxidation (7.8×10^{-8} mol cm⁻² s^{-1/2} by chronoamperometry and 6.6×10^{-8} mol cm⁻² s^{-1/2} by linear-sweep voltammetry). Measurements on a C/poly-[Fe(5-NH₂-phen)₃]²⁺ electrode also gave $D_{ct}^{1/2}C_{Fe}$ values (average 5.2×10^{-8} mol cm⁻² s^{-1/2}) that agree reasonably with the values obtained for the Pt electrode.

It should be noted that all attempts to measure D_{ct} in fact yield $D_{ct}^{1/2}C_{Fe}$ (or $D_{ct}C_{Fe}^2$). The concentration of redox sites in the polymer is very difficult to estimate, and so accurate values of D_{ct} cannot be obtained. Murray and co-workers²¹ have tried to estimate C_{Ru} for a polymer similar to the one used here, namely poly-[Ru(vbpy)₃]²⁺, from density measurements ($C_{Ru} = 1.6$ M) and from measurements of film thickness by XPS ($C_{Ru} = 0.4$ M).

The values of $D_{ct}^{1/2}C_{Fe}$ obtained here fall in the middle of the range of $D_{ct}^{1/2}C_M$ values that have been measured for other [M-(L-L)₂(L)₂]²⁺ polymers.³⁹ D_{ct} for this type of polymer is thought to be controlled by the energy barrier to electron exchange between the redox sites within the polymer.³⁹ If we assume that the homogeneous electron self-exchange rate for [Fe(phen)₃]^{3+/2+} (ca. 10^7 M⁻¹ s⁻¹)⁶¹ approximates the exchange rate in poly-[Fe(5-NH₂-phen)₃]²⁺ and we convert this to a D_{ct} value using the Smoluchowski equation (3) as described by Murray and co-

$$D_{ct} = 20k_{ex}^{homo}/Nr \quad (3)$$

workers,³⁹ where r is the collision radius (ca. 0.7 nm), we obtain $D_{ct} = 4.8 \times 10^{-9}$ cm² s⁻¹. Comparing this with the experimentally determined $D_{ct}^{1/2}C_{Fe}$ value of 8.2×10^{-8} mol cm⁻² s^{-1/2}, we obtain $C_{Fe} = 1.2$ M. This is a very reasonable value for the Fe concentration in the solvent-swollen polymer, and it falls within the range estimated by Murray and co-workers for the similar Ru-containing polymer. It should be noted that the flotation density measurement used by Murray and co-workers³⁷ would overestimate the density of a porous material and that these polymers

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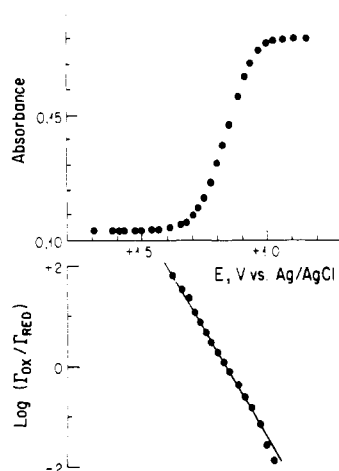


Figure 5. Absorbance at 520 nm vs. potential (top) and $\log(\Gamma_{\text{ox}}/\Gamma_{\text{red}})$ vs. potential (bottom) plots for the cell described in Figure 4.

could well be extremely porous.

The above treatment demonstrates that the charge-transport rate in poly-[Fe(5-NH₂-phen)₃]²⁺ is close to that predicted by assuming an electron-exchange-rate limitation. It seems that polymer rigidity does not limit charge transport significantly and that there is no faster route for charge transport through the polymer linkages.

Spectroelectrochemistry. An underlying assumption in the discussion so far has been that the voltammetric wave of poly-[Fe(5-NH₂-phen)₃]²⁺ at $E^{\circ'} = +1.16$ V corresponds solely to the Fe^{3+/2+} couple. The large shift in potential from the monomer E° , the large peak width, and the results described later for experiments in molten salts suggest that this might be an oversimplification. We have therefore used spectroelectrochemistry to confirm the nature of the electrochemical reaction.

Figure 4 shows the visible-region spectrum of the monomer and of a poly-[Fe(5-NH₂-phen)₃]^{3+/2+}-coated SnO₂ electrode in an electrochemical cell. The spectrum of the reduced polymer is very similar to that of the monomer, with a negligible shift in the maximum at 522 nm. The spectrum of the oxidized polymer is also as expected by comparison with that of [Fe(phen)₃]²⁺,⁶² with no significant peaks in the region investigated and with little absorbance at 522 nm. The extinction coefficient ($\epsilon_s = (A/1000)\Gamma$) at 524 nm of the reduced form of the polymer is ca. 15 000 L mol⁻¹ cm⁻¹, which is in reasonable agreement with the solution value of ca. 10 000 L mol⁻¹ cm⁻¹ (or 12 060 L mol⁻¹ cm⁻¹ according to ref 47).

Figure 5 shows plots of A_{520} and $\log(\Gamma_{\text{ox}}/\Gamma_{\text{red}})$ vs. potential for the polymer-coated electrode. The Γ_{ox} and Γ_{red} values were calculated by assuming a background absorbance given by an electrode with no polymer and by accounting for a slight decrease in surface coverage during the experiment by estimating the final surface coverage from the absorbance of the reduced polymer at 524 nm at the end of the experiment. The slight instability of the oxidized polymer observed in this experiment was probably due, at least in part, to moisture from the air, which was not excluded.

The results in Figures 4 and 5 confirm that the Fe^{3+/2+} couple is responsible for the observed electrochemistry of poly-[Fe(5-NH₂-phen)₃]²⁺. The spectroelectrochemically determined $E^{\circ'}$ of 1.16 V agrees with that obtained by cyclic voltammetry, and the Nernstian slope of 120 mV is compatible with the voltammetric peak width. Again, the considerable deviation from the ideal value of 59 mV is probably due to a combination of activity effects^{38,49} and multiple oxidation states^{50,51}.

Electrochemistry in AlCl₃/BuPyCl and AlCl₃/ImCl Molten Salts. [Fe(5-NH₂-phen)₃]²⁺ can be reversibly oxidized in neutral or acidic AlCl₃/BuPyCl melts at $E^{\circ'} = +1.42$ V (vs. SSCE in CH₃CN,

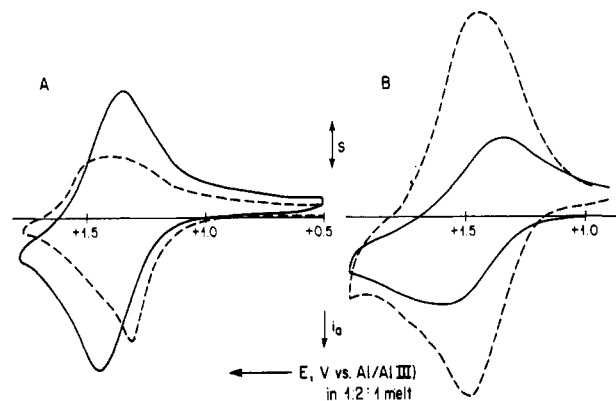


Figure 6. Cyclic voltammograms at 100 mV s⁻¹ (—) and 10 mV s⁻¹ (---) of C/poly-[Fe(5-NH₂-phen)₃]²⁺ electrodes in the 1.00:1 (A; $\Gamma = 5.5 \times 10^{-9}$ mol cm⁻²; $S = 28$ (—) or 7.0 (---) A cm⁻²) or 1.20:1 (B; $\Gamma = 1.1 \times 10^{-8}$ mol cm⁻²; $S = 43$ (—) or 4.3 (---) A cm⁻²) AlCl₃/BuPyCl melts.

assuming that ferrocenium/ferrocene has the same formal potential in both solvents).⁴⁸ No amine-oxidation and no polymerization were observed. Basic melts could not be used in this work because of the instability of Fe complexes in such melts⁴⁶ and the anodic solvent cutoff at ca. +1 V.

The formal potential of [Fe(phen)₃]^{3+/2+} in the neutral melt is +1.11 V on our reference scale,⁴⁶ so there is a large positive shift (310 mV) caused by the amino substituents. As such a shift is not observed in CH₃CN we believe that the shift in the melts is due to formation of an adduct between AlCl₃ and the amino groups of the complex. We believe that this is also responsible for the absence of any amino oxidation wave and therefore the lack of any polymerization in the melts. Because the polymer could be prepared in any of the melts used here, it was prepared in CH₃CN as described above and then used in the melts.

Polymer-coated electrodes in AlCl₃/RCl melts generally exhibit a break-in period during cyclic voltammetry, in which the voltammetric response gradually increases as the melt permeates into the polymer.^{63,64} Poly-[Fe(5-NH₂-phen)₃]²⁺ exhibits this in both acidic and neutral melts. Break-in of these films requires continual cycling through the Fe^{3+/2+} wave (at ca. +1.5 V) and is not accomplished merely by soaking the polymer or by trying to exhaustively oxidize the polymer. The number of cycles required to produce the full steady-state response depends upon the film thickness and the potential limits.

Figure 6 shows voltammograms of poly-[Fe(5-NH₂-phen)₃]²⁺ films on C in neutral and acidic AlCl₃/BuPyCl melts after break-in (ca. 100 scans between +0.4 and +1.7 V for film A; ca. 300 scans between +0.9 and +1.9 V for film B). The voltammogram at 100 mV s⁻¹ of the 5.5 × 10⁻⁹ mol cm⁻² film in the neutral melt is fairly normal with $E^{\circ'} = +1.30$ V. The cathodic shift from the formal potential of the monomer is compatible with the hypothesis that many of the amino groups have become the less basic imino and diazo groups, which do not form adducts with AlCl₃ as readily. It is also clear from this voltammogram that charge transport in the polymer is much slower in the melt than it is in CH₃CN. This conclusion is supported by the voltammogram at 10 mV s⁻¹ when the charge under the voltammogram is much higher and approaches the value obtained in CH₃CN. However, at the slower scan rate the voltammogram is severely distorted, and we have no explanation for this (see below).

The voltammogram of poly-[Fe(5-NH₂-phen)₃]²⁺ in the acidic melt is very similar to that in the neutral melt. $E^{\circ'}$ is +1.35 V, and the charge under the voltammogram is much larger at lower scan rates. Even at 10 mV s⁻¹ this 1.1 × 10⁻⁸ mol cm⁻² film is not quantitatively oxidized. A plot of charge under the voltammogram (anodic portion integrated to +1.7 V) vs. $\nu^{-1/2}$ for this electrode was linear for scan rates above 50 mV s⁻¹ and gave a $D_{\text{ct}}^{1/2}C_{\text{Fe}}$ value of 1.6 × 10⁻⁹ mol cm⁻² s^{-1/2}. Similar measurements

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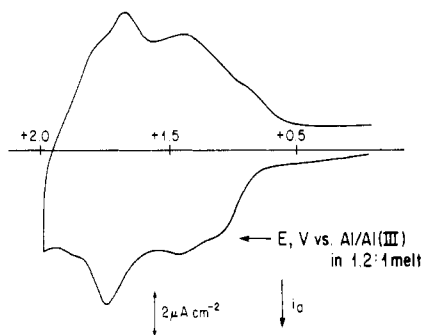


Figure 7. Cyclic voltammogram at 20 mV s^{-1} of a C/poly-[Fe(5-NH₂-phen)₃]²⁺ ($\Gamma = 2.3 \times 10^{-9} \text{ mol cm}^{-2}$) electrode in the 1.20:1 AlCl₃/BuPyCl melt.

on two other electrodes in the 1.2:1 melt gave values of 1.6×10^{-9} and $1.0 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1/2}$. The electrode of Figure 6A in the neutral melt gave a $D_{\text{ct}}^{1/2}C_{\text{Fe}}$ value of ca. $2 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1/2}$.

These results are more than an order of magnitude smaller than the results obtained in CH₃CN. Since C_{Fe} is unlikely to have changed considerably D_{ct} must be at least 100 times less in the melts than in CH₃CN. This is contrary to the results obtained for poly-[Ru(bpy)₂(vpy)₂]²⁺ in these melts, where $D_{\text{ct}}^{1/2}C_{\text{Ru}}$ is only 2-3 times smaller in the melts than in CH₃CN.⁶⁵

We can offer two reasonable explanations for the slowness of charge transport in poly-[Fe(5-NH₂-phen)₃]²⁺ in the melts. One possibility is that this polymer is heavily cross-linked (see above), and so it cannot absorb enough melt to allow facile movements of the redox centers. Hence, charge transport is limited by a low collision rate between the redox sites. This fits in with the hypothesis that the lower charge-transport rate of poly-[Ru(bpy)₂(vpy)₂]²⁺ in the melt compared to that in CH₃CN is due to a larger degree of swelling (smaller C_{Ru}).⁶⁵ Because the molar volumes of the melts are about 4.5 times that of CH₃CN, it seems reasonable that facile charge transport would require a higher degree of swelling in the melts than in CH₃CN.

A second possible explanation for the slow charge transport in poly-[Fe(5-NH₂-phen)₃]²⁺ in the melts is that adduct formation between AlCl₃ and free nitrogen sites in the polymer reduces the electron-exchange rate between the Fe sites by either steric or electrostatic hinderance. A third explanation, that charge transport is limited by counterion movements, is ruled out by the fact that, although voltammetric peak currents are more than 3 times lower in the melts than in CH₃CN, there is no significant increase in peak separation. Slow counterion movement implies a high resistance in the polymer film and so should result in increased peak separations in cyclic voltammetry. Obviously, further work is required to resolve the correct explanation for the very interesting differences in charging rates observed in this work.

The results shown in Figure 6 show that in the melts relatively thick films of poly-[Fe(5-NH₂-phen)₃]²⁺ exhibit the behavior of a normal redox polymer with slow charge-transport kinetics. There appear to be no significant differences between the results in the neutral and acidic melts. However, the slow charge transport simplifies the voltammetric response in these cases and obscures the details of the electrochemistry. If thinner films and lower scan rates are used, then more complicated behavior is observed.

Figure 7 shows the voltammetry (after break-in) of a $2.3 \times 10^{-9} \text{ mol cm}^{-2}$ film in the 1.2:1 AlCl₃/BuPyCl melt. There are four oxidation waves and four reduction waves, all of different height, in the region of the Fe^{3+/2+} waves. The positions and relative heights of these waves depend on the scan rate and are poorly reproducible. Similar results were also obtained in AlCl₃/ImCl melts. We believe that two major factors are responsible for this behavior, but we have not been able to rationalize the results completely. The oxidation peak at +1.74 V in Figure 7 and the reduction peak at +1.67 V appear to be related to an impurity

in the melt (possibly HCl).⁶⁶ Secondly, adduct formation between AlCl₃ and some of the nitrogen atoms of the substituents of the phenanthroline rings could create a series of Fe sites with significantly different formal potentials.

We have used a spectroelectrochemical experiment similar to that described above for CH₃CN to further investigate the multiple peaks observed in Figure 7. The results were similar to those obtained in CH₃CN, but experimental difficulties prevented sufficiently accurate results from being obtained. Further useful investigation of this system does not seem feasible until methods for preparing purer melts are devised.

One of the reasons for using poly-[Fe(5-NH₂-phen)₃]²⁺ in AlCl₃/RCl melts was to determine if this polymer would be useful for oxygen reduction in these systems. Unfortunately, the formal potential of the polymer in these solvents (ca. +1.3 V) is considerably higher than that of [Fe(phen)₃]²⁺ (1.11 V), on which we based our initial expectations. We could measure no catalytic current for oxygen reduction in acidic melts at poly-[Fe(5-NH₂-phen)₃]²⁺-coated electrodes.

Conclusions

The preparation, electrochemistry, and spectroelectrochemistry of poly-[Fe(5-NH₂-phen)₃]²⁺ in CH₃CN are entirely predictable by analogy with similar polymers. However, its electrochemistry in AlCl₃/RCl molten salts is significantly different from its electrochemistry in CH₃CN and is also different from that of poly-[Ru(bpy)₂(vcpy)₂]²⁺ in these molten salts. The potential shifts, the multiple redox potentials, and the slow charge transport of poly-[Fe(5-NH₂-phen)₃]²⁺ in the molten salts have not been fully explained, but there is good evidence that adduct formation between AlCl₃ and nitrogen-containing groups in the polymer is at least partly responsible. These results are significant because they show that in situ chemical modification of redox polymers can be used to significantly change the electrochemistry and, presumably, the structure of the polymer. Further work of this type, both in molten salts and in more conventional solvents, will greatly increase our understanding of the structure of solvent-swollen redox polymers.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research and the Office of Naval Research.

Registry No. [Fe(5-NH₂-phen)₃]²⁺, 15053-62-0; BuPyCl, 1124-64-7; CH₃CN, 75-05-8; AlCl₃, 7446-70-0; Et₄NClO₄, 2567-83-1.

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Synthesis of the Heptahydrobis(trimethylphosphine)tetraboron(1+) Cation

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Received December 11, 1984

The triboron complex cation B₃H₆·2P(CH₃)₃⁺ represents the first example of Lewis base attached boron cluster cations, and some novel reactions involving this cation were reported recently.^{2,3} While its reaction chemistry continues to be an intriguing subject of study, the search for other members of the polyboron complex cation family is of natural interest. Several members are known to exist in each of the related, neutral (B_nH_{n+4}·L, L = Lewis base) and anionic (B_nH_{n+5}⁻) boron hydride families.⁴

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