

(step 1), chemisorption onto the surface (step 2), surface migration (step 3), chemisorption-absorption transition (step 4), solid diffusion (step 5), and phase transformation (step 6). The present investigation might be construed in part as a study of changes in surface properties of the magnesium particles caused by dispersing metal atoms into organic media, because it was confirmed from X-ray diffraction studies of Mg-THF that the hexagonal structure of magnesium was maintained in the bulk after cocondensation reaction. In view of the appearance of the specific activity of transition-metal clusters formed in such a way for catalytic gas-phase reaction,¹³⁻¹⁵ it is further deduced for the present system that the surface process involved in steps 2-4 is concerned with acceleration of the reaction of magnesium with hydrogen. To check this, attempts were made to perform H₂-D₂ equilibrium reactions, because the isotopic-exchange reaction is available as an index of metal surface activity for dissociative adsorption. When

Mg-THF was outgassed at 200 °C and was brought into contact with equimolar amounts of H₂ and D₂ (each 39 torr), rapid formation of HD occurred even at 0 °C and its rate was 1.35×10^{19} molecules·s⁻¹·g⁻¹. On the other hand, the activated pure magnesium was inactive under these conditions and exhibited only a slight activity at 240 °C. In the course of our study on the improvement of sorption properties of metal hydrides using the modification techniques,¹⁶⁻¹⁹ it has been shown that surface-treating the Mg-THF particles with aromatic molecules enhances the hydrogen uptake rate of magnesium as a result of the formation of electron donor-acceptor complexes on the particle surface.⁸ Accordingly, the marked effect of aromatics would appear to eliminate internal steps as rate controlling, i.e., steps 5 and 6, and we can conclude that the surface processes are important in Mg-THF.

Registry No. Magnesium, 7439-95-4; hydrogen, 1333-74-0.

- (13) Klabunde, K. J.; Davis, S. C.; Hattori, H.; Tanaka, Y. *J. Catal.* **1978**, *54*, 254.
 (14) Klabunde, K. J.; Ralston, D.; Zoellner, R.; Hattori, H.; Tanaka, Y. *J. Catal.* **1978**, *55*, 213.
 (15) Klabunde, K. J.; Tanaka, Y. *J. Mol. Catal.* **1983**, *21*, 57.

- (16) Imamura, H.; Tsuchiya, S. *J. Chem. Soc., Chem. Commun.* **1981**, 567.
 (17) Imamura, H.; Takahashi, T.; Tsuchiya, S. *J. Catal.* **1982**, *77*, 289.
 (18) Imamura, H.; Takahashi, T.; Galleguillos, R.; Tsuchiya, S. *J. Less-Common Met.* **1983**, *89*, 251.
 (19) Imamura, H.; Tsuchiya, S. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1461.

Contribution from the Department of Chemistry,
 State University of New York at Buffalo, Buffalo, New York 14214

Electrochemical and Spectroscopic Studies of Polypyridine Complexes of Fe(II/III) and Ru(II/III) in the Aluminum Chloride-*N*-1-Butylpyridinium Chloride Molten Salt

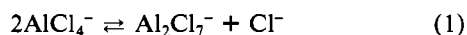
SAEED SAHAMI and ROBERT A. OSTERYOUNG*

Received September 30, 1983

The electrochemical and spectroscopic behavior of Fe(bpy)₃²⁺, Fe(phen)₃²⁺, and Ru(bpy)₃²⁺ in an ambient-temperature molten salt system, aluminum chloride-*N*-1-butylpyridinium chloride (BuPyCl), has been studied as a function of melt composition. The complexes show a single one-electron reversible oxidation wave from melt compositions of 1:1 to 2:1 (AlCl₃:BuPyCl mole ratio). Visible spectroscopic and electrochemical data indicate that these compounds are stable in the neutral (1:1) and acid (mole ratio >1) melts, while Ru(bpy)₃²⁺ is stable in basic melts (mole ratio <1), but Fe(bpy)₃²⁺ and Fe(phen)₃²⁺ decompose to FeCl₄²⁻. Comparison of the formal potentials for M(III/II)-polypyridine couples studied in this melt and in other solvents indicates that the redox properties of these complexes are relatively insensitive to the nature of the solvent. It was shown that oxygen acts as an oxidant in the acid melts to oxidize Fe(bpy)₃²⁺, Fe(phen)₃²⁺, and Ru(bpy)₃²⁺ to their corresponding 3+ forms. The 3+ form of each complex was stable in acid melts for several weeks. Perchlorate is also shown to function as an oxidant in acidic melts.

Introduction

The molten salt system composed of aluminum chloride and *N*-1-butylpyridinium chloride (BuPyCl) is liquid at ambient temperatures (~30 °C) over a wide compositional range varying from ~0.7:1 to 2:1 (mole ratio of AlCl₃ to BuPyCl).^{1,2} The Lewis acid-base properties of these melts change as the mole ratio of AlCl₃ to BuPyCl changes. The melts can be characterized as acidic, basic, or neutral depending on the mole ratio of AlCl₃ to BuPyCl being greater than, less than, or equal to unity.³ In the acidic melts, anionic species are Al₂Cl₇⁻ and AlCl₄⁻, in basic melts AlCl₄⁻ and Cl⁻, and in neutral melts AlCl₄⁻. It has been shown that equilibrium 1 with log *K* = -16.9 ± 2⁴ provides an adequate description of the system throughout the entire range of melt composition.²



In view of their nonlability and extreme stability in the absence of direct illumination, low-spin complexes of Ru(bpy)₃²⁺, Fe(bpy)₃²⁺, and Fe(phen)₃²⁺ (where bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline) were chosen to study in AlCl₃-BuPyCl melts. These complexes were selected for several reasons. Initially we were interested to know whether these compounds are stable in this molten salt media, i.e. whether the reactant's coordination sphere remains intact while the Lewis acid-base properties of the melts are varied. A second aspect of this work was the examination of the possible use of these complexes as internal reference couples. In addition, the use of these melts as solvents for modified-electrode studies, which includes Ru(II)/Ru(III) polymers, suggested such studies.⁵

Spontaneous oxidation of hydrocarbons in highly acidic AlCl₃-BuPyCl melts has been observed by Robinson and Osteryoung.¹ The slow chemical oxidation of iodide in acidic AlCl₃-BuPyCl melts has been suggested to be due to a reaction

(1) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.
 (2) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.
 (3) Lipsztajn, M.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1968.
 (4) Karpinski, Z. J.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 1491.

(5) Pickup, P. G.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *103*, 1965.

with traces of impurity present in the drybox atmosphere, probably molecular oxygen.⁶ To determine the true nature of the oxidizing species in the melt, these polypyridine complexes proved to be useful.

The electrochemistry of these transition-metal complexes has been studied in both protic and aprotic solvents.⁷⁻¹⁷ The oxidation states frequently observed for these complexes are 2+ and 3+. Polypyridine complexes of Ru and Fe with total charges of 1+, 0, and 1- have been observed in solvents with very negative potential windows such as acetonitrile^{7,9} and *N,N*-dimethylformamide.⁸ Recently more highly oxidized species such as Ru(bpy)₃⁴⁺, Fe(bpy)₃⁴⁺, and Fe(bpy)₃⁵⁺ have been reported in liquid sulfur dioxide.¹³ We report here electrochemical and spectroscopic investigations of Fe(bpy)₃^{2+/3+}, Fe(phen)₃^{2+/3+}, and Ru(bpy)₃^{2+/3+} in ambient-temperature AlCl₃-BuPyCl ionic liquids.

Experimental Section

Preparation of *N*-1-butylpyridinium chloride and purification of aluminum chloride have been described elsewhere.¹ Ru(bpy)₃Cl₂·6H₂O, Fe(bpy)₃(ClO₄)₂, and Fe(phen)₃(ClO₄)₂ (G. F. Smith Chemical Co.), FeCl₂ (Alfa Products), FeCl₃ (Fisher), 2,2'-bipyridine (Baker), and 1,10-phenanthroline were used without further purification. Tetraethylammonium perchlorate (TEAP, Baker) was dried in a vacuum oven and used for experiments testing the ability of perchlorate to function as an oxidant. Aluminum wire (Alfa Products) was cleaned in a 30:30:40 volume mixture of H₂SO₄-HNO₃-H₃PO₄, rinsed with water, and dried. Chemicals were stored and all electrochemical experiments performed under argon atmosphere in a Vacuum Atmospheres Co. drybox.

A Metrohm glass cell covered with a Teflon lid that had several holes for reference electrode and counterelectrode compartments, working electrode, and thermometer was used for the electrochemical measurements. The entire cell assembly was placed in a furnace and the temperature controlled at 40 ± 1 °C by a Thermo Electric Selector 800 temperature controller. Reference electrode and counterelectrode compartments were aluminum wires dipped into the 2:1 AlCl₃:BuPyCl melt, and both were separated from the working compartment by fine glass frits. A glass-carbon-disk (GC) electrode obtained from Pine Instrument Co. was used as the working electrode. The GC (with the area of 0.196 or 0.454 cm²) was polished with successively finer grades of 1.0-, 0.3-, and 0.05-μm alumina (Buehler) and then rinsed with water and air-dried prior to transfer to the drybox.

All voltammograms were obtained with a EG&G PARC 175 universal programmer with a PARC 173 potentiostat and a Houston Omnigraph Model 2000 recorder. A pine Instrument Co. electrode rotator (Model ASR2) was used for rotating-disk electrode (RDE) studies.

UV and visible absorption spectra were recorded in either 0.1 or 1.0 cm path length quartz cells fitted with airtight Teflon caps with a Perkin-Elmer (Coleman 575) spectrophotometer. The cells were filled and sealed in the drybox.

- (6) Karpinski, Z. J.; Osteryoung, R. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *164*, 281.
- (7) Tokel, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.
- (8) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 401.
- (9) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 1.
- (10) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *63*, 31.
- (11) Tanaka, N.; Sato, Y. *Electrochim. Acta* **1968**, *13*, 335.
- (12) Mayer, U.; Kotocova, A.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 409.
- (13) Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373.
- (14) Ogura, K.; Miyamoto, K. *Electrochim. Acta* **1978**, *23*, 509.
- (15) Samec, Z.; Nemeč, I. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *31*, 161.
- (16) Sahami, S.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 155.
- (17) (a) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. (b) Yee, E. L.; Weaver, M. J. *Inorg. Chem.* **1980**, *19*, 1077.

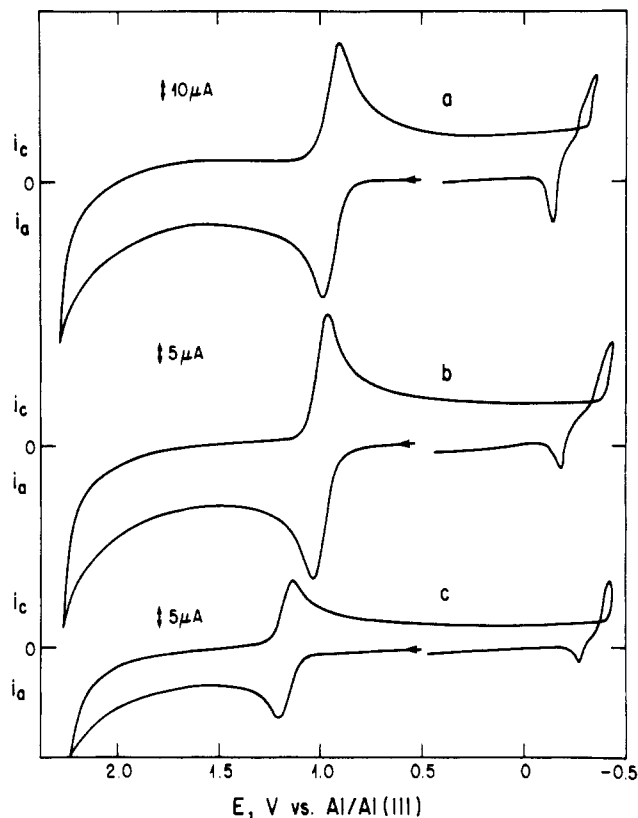


Figure 1. Cyclic voltammograms in 1.05:1 AlCl₃-BuPyCl melts (scan rate 50 mV/s; *T* = 40 °C): (a) 3.2 mM Fe(bpy)₃²⁺, GC electrode with *A* = 0.454 cm²; (b) 1.8 mM Fe(phen)₃²⁺, GC electrode with *A* = 0.454 cm²; (c) 2.8 mM Ru(bpy)₃²⁺, GC electrode with *A* = 0.196 cm².

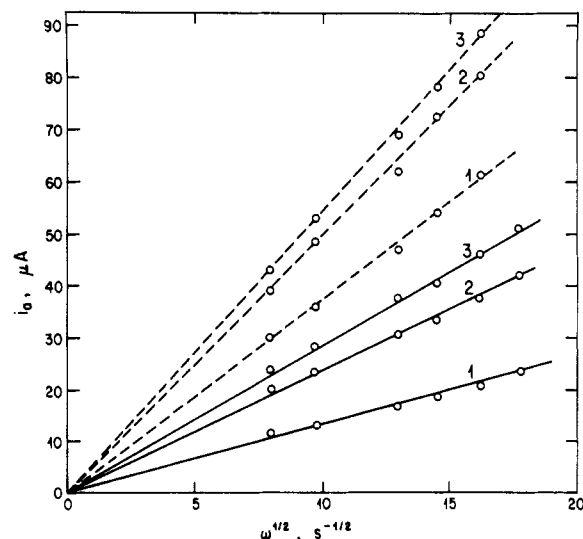


Figure 2. Plots of current at various potentials vs. $\omega^{1/2}$ for the oxidation of Fe(bpy)₃²⁺ (dashed lines) and Fe(phen)₃²⁺ (solid lines) in 1.0:1.0 AlCl₃-BuPyCl. *E* in mV: (1) 1000; (2) 1050; (3) 1300.

Results

1. Electrochemistry. a. Oxidation of Fe(bpy)₃²⁺ and Fe(phen)₃²⁺. Fe(bpy)₃(ClO₄)₂ and Fe(phen)₃(ClO₄)₂ both dissolve in the neutral (mole ratio 1.0) and acid (mole ratio >1) melts and give intense red solutions. The solubility of Fe(phen)₃(ClO₄)₂ is less than that of Fe(bpy)₃(ClO₄)₂, especially in the neutral melt. In Figure 1, typical cyclic voltammograms at a GC electrode are shown for Fe(bpy)₃²⁺ and Fe(phen)₃²⁺, respectively. Cyclic and rotating-disk electrode voltammograms for oxidation of polypyridine complexes of iron(II) were

Table I. Summary of Voltammetric Parameters for Fe(bpy)₃^{2+/3+} in AlCl₃-BuPyCl Melts^a

melt composition ^b	cyclic voltammetric data							RDE data	
	scan rate (ν), mV/s	E _p ^c , mV	E _p ^a , mV	E _f , mV	ΔE _p , mV	i _p ^a /i _p ^c	i _p ^a /ν ^{1/2} , mA cm ⁻² V ^{-1/2} s ^{1/2}	rotation rate, rpm	E _{1/2} , mV
1:1	10	927	992	960	65	1.00	0.507	600	957
	20	927	992	960	65	1.01	0.510	900	959
	50	922	996	959	74	1.01	0.514	1600	960
	100	920	998	959	78	1.00	0.515	2000	959
									2500
1.05:1	10	935	1000	968	65	1.01	0.413	400	965
	20	935	1000	968	65	1.02	0.420	600	965
	50	936	1002	969	66	1.01	0.428	900	967
	100	931	1005	968	74	1.00	0.430	1600	970
	200	930	1010	970	80	1.00	0.433	2000	972
1.2:1	10	950	1015	982	65	1.01	0.451	600	980
	20	950	1015	982	65	1.01	0.478		
	50	948	1015	981	67	1.00	0.480		
	100	945	1020	982	75	1.01	0.494		
1.4:1	10	963	1025	994	62	1.01	0.407	600	990
	20	963	1025	994	62	1.00	0.412		
	50	960	1028	994	68	0.99	0.414		
	100	960	1030	995	70	1.02	0.414		
1.7:1	10	990	1055	1022	65	1.02	0.385	600	1020
	20	990	1055	1022	65	1.04	0.389		
	50	990	1057	1023	67	1.01	0.379		
	100	985	1060	1022	75	1.00	0.383		
1.9:1	10	1007	1073	1040	66	0.98	0.363	600	1038
	20	1007	1073	1040	66	0.99	0.358		
	50	1007	1075	1041	68	1.00	0.364		
	100	1005	1075	1040	70	0.99	0.369		

^a All potentials are in mV vs. Al/Al(III) in 2:1 AlCl₃-BuPyCl, at T = 40 °C. ^b Mole ratio of AlCl₃:BuPyCl.

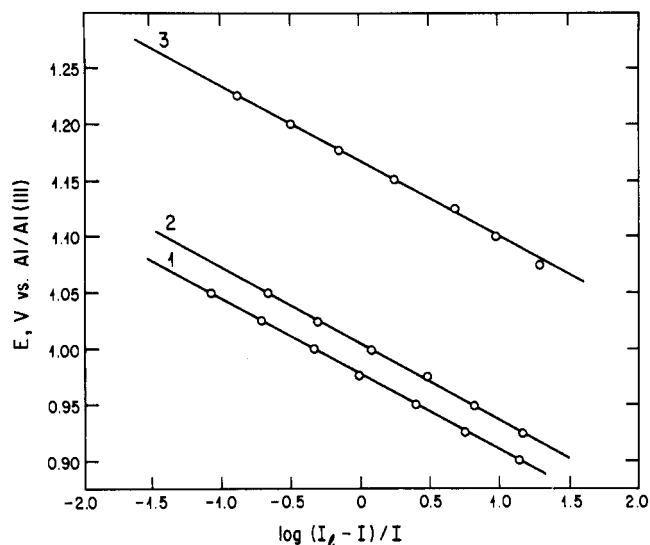


Figure 3. Plots of E vs. $\log(I_1 - I)/I$ for the oxidation of (1) Fe(bpy)₃²⁺, (2) Fe(phen)₃²⁺, and (3) Ru(bpy)₃²⁺ in 1.05:1 AlCl₃-BuPyCl.

recorded as a function of melt acidity. Tabulations of cyclic and RDE voltammetric parameters, anodic to cathodic peak current ratios i_p^a/i_p^c , the difference between the anodic and cathodic peak potentials $\Delta E_p = E_p^a - E_p^c$, and $i_p^a/\nu^{1/2}$ for Fe(bpy)₃^{2+/3+} and Fe(phen)₃^{2+/3+} are presented in Tables I and II, respectively. As shown in Figure 2, plots of the current vs. the square root of the electrode rotation rate at potentials on the rising portion of the waves and on the plateaus for oxidation of both complexes in the neutral melt were linear and passed through the origin, indicating that the oxidation is reversibly convective diffusion controlled.¹⁸ Plots of E vs.

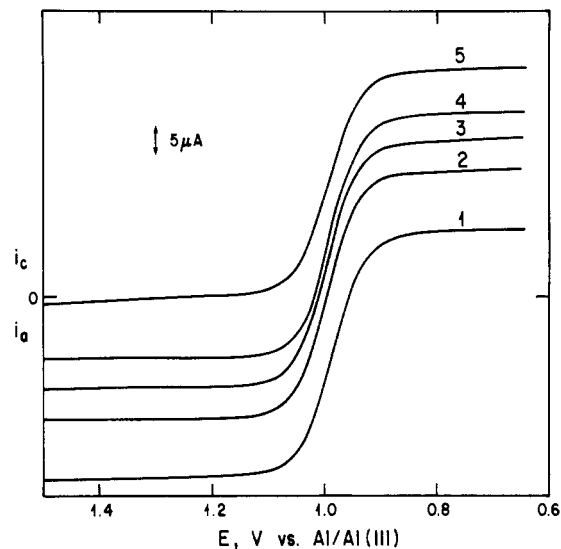


Figure 4. RDE voltammograms for a 1.2:1 AlCl₃-BuPyCl melt with initial concentration of 3.8 mM Fe(bpy)₃(ClO₄)₂, recorded as a function of time (scan rate 5 mV/s; rotation rate 600 rpm; T = 40 °C; GC electrode with A = 0.454 cm²). Time in minutes: (1) 0; (2) 35; (3) 65; (4) 110; (5) 300.

$\log(I_1 - I)/I$, constructed from RDE data for oxidation of both polypyridine complexes of Fe(II), were linear with slopes of 65 ± 1 mV ($2.3RT/F = 62$ mV at 40 °C) (see Figure 3). Solutions of Fe(bpy)₃²⁺ and Fe(phen)₃²⁺ in the neutral melt were found to be stable for a period of over 1 week. There was no change in the color of the solutions or their visible spectra. RDE voltammograms were recorded daily for polypyridine complexes of Fe(II) in the neutral melt. The values of $E_{1/2}$ and anodic limiting current, I_1^a , were found to be constant within experimental error for at least 7 days. When a neutral melt containing either of the polypyridine complexes of iron was made acidic by addition of AlCl₃, RDE voltam-

(18) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; p 288.

Table II. Summary of Voltammetric Parameters for $\text{Fe}(\text{phen})_3^{2+/3+}$ in AlCl_3 -BuPyCl Melts^a

melt composition ^b	scan rate (ν), mV/s	cyclic voltammetric data						RDE data	
		E_p^c , mV	E_p^a , mV	E_f , mV	ΔE_p , mV	i_p^a/i_p^c	$i_p^a/\nu^{1/2}$, $\text{mA cm}^{-2} \text{V}^{-1/2} \text{s}^{1/2}$	rotation rate, rpm	$E_{1/2}$, mV
1:1	10	965	1033	999	68	1.00	0.242	600	1002
	20	965	1035	1000	70	1.02	0.230	900	1005
	50	965	1035	1000	70	1.01	0.226	1600	1007
	100	962	1040	1001	78	1.01	0.233	2000	1005
								2500	1007
							3000	1007	
1.05:1	10	976	1040	1008	64	1.02	0.268	600	1008
	20	975	1042	1008	67	1.00	0.288	900	1008
	50	973	1045	1009	72	1.01	0.293		
	100	973	1047	1010	74	1.01	0.293		
1.2:1	10	990	1052	1021	62	1.03	0.341	600	1020
	20	990	1055	1022	65	1.02	0.343	900	1021
	50	990	1058	1024	68	1.01	0.335	1600	1022
	100	988	1060	1024	72	1.00	0.338	2000	1025
1.4:1	10	1007	1070	1038	63	1.02	0.319	600	1038
	20	1007	1070	1038	63	1.02	0.323	900	1040
	50	1005	1072	1038	67	1.01	0.320		
	100	1000	1075	1037	75	1.00	0.314		
1.7:1	10	1035	1100	1067	65	1.01	0.270	600	1065
	20	1035	1100	1067	65	1.01	0.276	900	1065
	50	1032	1102	1067	70	1.00	0.280		
	100	1032	1105	1068	73	1.00	0.275		
1.9:1	10	1052	1118	1085	66	1.00	0.264	600	1083
	20	1052	1120	1086	68	1.01	0.261	900	1083
	50	1050	1120	1085	70	0.98	0.261		
	100	1050	1120	1085	70	0.98	0.260		

^a All potentials are in mV vs. Al/Al(III) in 2:1 AlCl_3 -BuPyCl, at $T = 40^\circ\text{C}$. ^b Mole ratio of AlCl_3 :BuPyCl.

mograms showed both cathodic and anodic current, indicating the presence of both the reduced and oxidized forms of $(\text{bpy})_3$ and $(\text{phen})_3$ complexes of iron in the solution. Indeed in the 1.05:1 melt the cathodic limiting current, I_1^c , is $<5\%$ of the total limiting current, $I_1^t = I_1^c + I_1^a$. As the acidity of the melt increased, the I_1^c/I_1^a ratio also increased and the color of the solution changes from red to dark brown and finally to blue. When the melt composition approached 1.9:1, almost all the complex was in the oxidized form. This oxidation of $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ occurred not only when the melt acidity was increased (i.e., increase in AlCl_3 concentration) but also, as shown in Figure 4, even when a 1.2:1 melt containing 3.8 mM $\text{Fe}(\text{bpy})_3^{2+}$ was kept in the drybox, where I_1^c increased with time while I_1^a decreased. After about 2 h I_1^c was ~ 3 times larger and I_1^a ~ 3 times smaller than their initial values. Thus, $\sim 75\%$ of the $\text{Fe}(\text{bpy})_3^{2+}$ was oxidized to $\text{Fe}(\text{bpy})_3^{3+}$ in less than 2 h and eventually almost all of it was oxidized. It has been suggested that the slow chemical oxidation of I^- (with $E_{1/2} \approx 1 \text{ V}$), in an acidic AlCl_3 -BuPyCl melt, resulted from a reaction with traces of impurity present in the drybox atmosphere, possibly molecular oxygen.⁶ Although the drybox atmosphere had an oxygen level of ≤ 5 ppm, it may have been enough to slowly oxidize both $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ complexes to their corresponding 3+ forms, although perchlorate can also function as an oxidant (see below). The formation of the oxidized forms of these complexes was proved by both RDE experiments and the visible spectra of the complexes (see below). Neither the reduction of oxygen nor the electrochemistry from its reduction product could be seen directly by the electrochemical techniques. To show that O_2 was an oxidizing species, several other experiments were performed. Acidic AlCl_3 -BuPyCl melts with various compositions (1.07:1, 1.2:1, and 1.9:1) were prepared, and $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ was dissolved in them. These solutions were taken outside the drybox in sealed tubes. When these solutions were purged with oxygen, their color changed from red to blue (although the color change in the less acidic melt,

1.07:1, was slower than in the other melts). The spectra of these solutions were identical with those for acidic solutions of $\text{Fe}(\text{phen})_3^{2+}$, which were oxidized slowly to $\text{Fe}(\text{phen})_3^{3+}$ in the drybox. These results clearly indicate that oxygen in the acid melts can oxidize $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ to $\text{Fe}(\text{bpy})_3^{3+}$ and $\text{Fe}(\text{phen})_3^{3+}$, respectively. The rate of the oxidation of these complexes appears to depend on both the amount of oxygen present in the drybox atmosphere and the melt acidity (see below, however). It is obvious from our results that the oxidation of any of these complexes in a given melt by traces of oxygen or perchlorate (see below) does not affect the E_f or $E_{1/2}$ values. The only changes were in the values of I_1^c and I_1^a . In any case the sum of $I_1^c + I_1^a$ (i.e., I_1^t) remained unchanged within experimental error. The oxidized forms of these polypyridine complexes of iron, i.e., $\text{Fe}(\text{bpy})_3^{3+}$ and $\text{Fe}(\text{phen})_3^{3+}$, were stable in acid melts for at least 2 weeks.

The possibility that perchlorate could function as an oxidant in these systems was examined. As mentioned above, both $\text{Fe}(\text{phen})_2^{2+}$ and $\text{Fe}(\text{bpy})_2^{2+}$ were added to the melts as perchlorate salts and underwent slow oxidation in the acidic melts, some of which, as demonstrated above, was due to oxygen but some of which might have been due to the presence of perchlorate. As described below, although the oxidation of the $\text{Ru}(\text{bpy})_2^{2+}$ complex was observed in very acidic (1.7:1) melts, it appeared much slower than that of the corresponding $\text{Fe}(\text{II})$ complexes. Since the $\text{Ru}(\text{bpy})_2^{2+}$ salts were chlorides, they were used in experiments to ascertain the effect of perchlorate as an oxidant. If a 40-fold excess of TEAP was added to a 1.7:1 AlCl_3 -BuPyCl melt containing ca. 1 mM $\text{Ru}(\text{bpy})_2^{2+}$, the orange solution took about 30 min to change to green. This compares to much longer periods of time in the absence of perchlorate (see below). In a 1.1:1 melt, visible changes in color took place much more slowly; this was under conditions where, in the absence of perchlorate, no change in the solution color or electrochemistry was noted. In both basic and neutral (i.e., 1.0:1.0) melts, no indication of the oxidation of $\text{Ru}(\text{bpy})_2^{2+}$

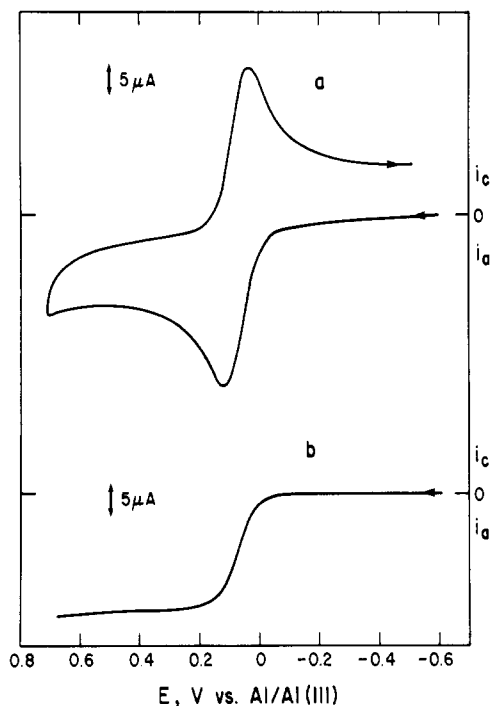


Figure 5. Voltammograms for 3.1 mM $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$ dissolved in a 0.95:1 AlCl_3 -BuPyCl melt (which actually corresponds to 3.1 mM FeCl_4^{2-} , see text) ($T = 40^\circ\text{C}$; GC electrode with $A = 0.454\text{ cm}^2$): (a) cyclic voltammogram with scan rate 100 mV/s; (b) RDE voltammogram with scan rate 5 mV/s and rotation rate 600 rpm.

was noted from spectroscopic measurements. These observations indicate that perchlorate, like oxygen, can act as an oxidant only in the acidic melt, that, qualitatively, the oxidation rate increases with increasing melt acidity, and that there is no oxidation by perchlorate in the basic or neutral melt. Further experiments on this are in progress.¹⁹

As in the case in other solvents, it was not possible to generate $\text{Fe}(\text{bpy})_3^{3+}$ or $\text{Fe}(\text{phen})_3^{3+}$ simply by adding ligands to an acidic solution of AlCl_3 -BuPyCl containing FeCl_3 . However, the polypyridine complexes of Fe(II) were easily obtained in acid melts by mixing FeCl_2 and ligands.

In basic AlCl_3 -BuPyCl melts (mole ratio <1), it was found that complexes of both $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ decompose and form FeCl_4^{2-} .²⁰ When either of these complexes was dissolved in the basic melt, a red solution was obtained initially, which changed within minutes to a light yellow. Cyclic and RDE voltammograms for $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$ in a 0.95:1 AlCl_3 -BuPyCl melt are shown in Figure 5. These voltammograms actually correspond to the oxidation of FeCl_4^{2-} to FeCl_4^- . There is excellent agreement between these results and those obtained by Nanjundiah et al., who studied the $\text{FeCl}_4^{2-/-}$ couple in basic AlCl_3 -BuPyCl melts.²⁰ In the "neutral" melt, i.e., mole ratio 1.0, where the concentration of Cl^- is negligible, both $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ are stable. We found, however, that the addition of even 20 mM BuPyCl (i.e., Cl^-) to a neutral melt containing a 3–4 mM concentration of either of the polypyridine complexes of Fe(II) was sufficient to cause their dissociation to FeCl_4^{2-} . Although Cl^- is a relatively poor nucleophile in aqueous solutions, it seems to be highly reactive toward charged ions in aprotic solvents.²¹ An investigation of decomposition of tris(phenanthroline)-iron(II) in dimethyl sulfoxide (Me_2SO) showed that $\text{Fe}(\text{phen})_3^{2+}$ reacts rapidly with chloride.^{21,22} The reaction was

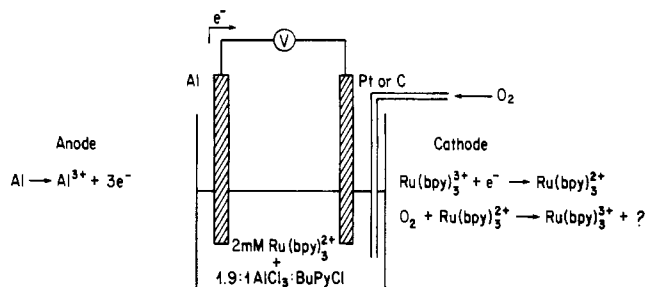


Figure 6. Aluminum-oxygen cell configuration.

assumed to be due to anation by chloride, leading to the formation of the blue $\text{Fe}(\text{phen})_2\text{Cl}_2$ complex.²¹ Thus, the complete dissociation of $\text{Fe}(\text{L})_3^{2+}$ (where $\text{L} = \text{bpy}$ or phen) to FeCl_4^{2-} (see eq 2) in basic AlCl_3 -BuPyCl is not surprising.



b. Oxidation of $\text{Ru}(\text{bpy})_3^{2+}$. $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ dissolves throughout the entire range of melt composition, giving highly colored orange solutions. The electrochemical oxidation of this complex has been studied by cyclic and rotating-disk voltammetry. A typical cyclic voltammogram at a GC electrode is shown in Figure 1. Cyclic and rotating-disk electrode voltammograms for oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ were examined as a function of melt composition from 0.8:1 to 2:1. Data obtained from these voltammograms are listed in Table III. $\text{Ru}(\text{bpy})_3^{2+}$ showed no oxidation or reduction in the basic melt. In acidic or neutral melts only a single oxidation wave was obtained. Table III shows scan rate dependencies of peak potentials and peak currents for the $\text{Ru}(\text{bpy})_3^{2+/3+}$ couple. The ratio of 1 for i_p^a/i_p^c indicates that the electron transfer is reversible over the entire acidic melt composition. For a diffusion-controlled process, $i_p^a/\nu^{1/2}$ should be constant and independent of scan rate; this is true for the present case. Although ΔE_p increases slightly with the scan rate, it does not change with variation in the melt composition. The experimental peak separations (64–70 mV) correspond closely to the theoretical value for a one-electron process of 62 mV at 40°C . Plots of E vs. $\log [(I_1 - I)/I]$ in all melt compositions studied were linear with slopes of 65 ± 1 mV (see Figure 3).

As with the polypyridine complexes of Fe(II), RDE voltammograms showed that when the acidity of $\text{Ru}(\text{bpy})_3^{2+}$ -containing melt increased there was a small cathodic current due to the reduction of $\text{Ru}(\text{bpy})_3^{3+}$ present in solution. This cathodic current could only be observed when the melt acidity (mole ratio) was greater than $\sim 1.7:1$. Apparently the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ is slower than that of the polypyridine complexes of Fe(II). The initial I_1^c in a solution of 1.9:1 AlCl_3 -BuPyCl containing $\text{Ru}(\text{bpy})_3^{2+}$ was about 5% of the I_1^a . Even after 2 weeks I_1^c was less than 55% of I_1^a , indicating that $\sim 55\%$ of $\text{Ru}(\text{bpy})_3^{2+}$ was oxidized to $\text{Ru}(\text{bpy})_3^{3+}$. On going from the reduced to the oxidized form of tris(bipyridine)ruthenium the color of the solution changed from orange to dusty brown and finally to green. As before, the nature of the oxidant (i.e., traces of O_2 in the drybox atmosphere) was confirmed by purging acidic solutions of AlCl_3 -BuPyCl containing $\text{Ru}(\text{bpy})_3^{2+}$ with oxygen. Although it was possible to oxidize these solutions (in sealed tubes) over the melt compositions of 1.2:1 to 1.9:1 by oxygen, the time needed to convert $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$ (i.e., change of color from orange to green) was longer as the acidity decreased. The green solutions of $\text{Ru}(\text{bpy})_3^{3+}$ were found to be stable for months.

c. An Aluminum-Oxygen Cell. In view of the observed oxidation of the polypyridine complexes of Fe(II) and Ru(II)

(19) Sahami, S.; Osteryoung, R. A., unpublished results.
 (20) Nanjundiah, C.; Shimizu, K.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2474.
 (21) Gillard, R. D. *Inorg. Chim. Acta* **1979**, *37*, 103.

(22) Farrington, D. J.; Jones, J. G.; Twigg, M. V. *Inorg. Chim. Acta* **1977**, *25*, L75.

Table III. Summary of Voltammetric Parameters for $\text{Ru}(\text{bpy})_3^{2+/3+}$ in $\text{AlCl}_3\text{-BuPyCl}$ Melts^a

melt composition ^b	cyclic voltammetric data							RDE data	
	scan rate (ν), mV/s	E_p^c , mV	E_p^a , mV	E_f , mV	ΔE_p , mV	i_p^a/i_p^c	$i_p^a/\nu^{1/2}$, $\text{mA cm}^{-2} \text{V}^{-1/2} \text{s}^{1/2}$	rotation rate, rpm	$E_{1/2}$, mV
1:1	10	1130	1198	1164	68	1.00	0.308	600	1163
	20	1130	1198	1164	68	1.03	0.300	900	1163
	50	1127	1202	1165	75	1.02	0.329	1600	1163
	100	1127	1204	1165	77	1.01	0.327	2000	1163
1.05:1	10	1140	1204	1172	64	1.00	0.357	400	1170
	20	1140	1204	1172	64	1.02	0.360	600	1170
	50	1138	1206	1172	68	1.03	0.364	900	1170
	100	1138	1208	1173	70	1.03	0.359	1600	1170
	200	1136	1210	1173	74	1.03	0.353	2000	1170
								2500	1172
								3600	1175
1.2:1	10	1152	1216	1184	64	1.04	0.331	600	1183
	20	1152	1216	1184	64	1.06	0.329		
	50	1150	1218	1184	68	1.05	0.322		
	100	1150	1220	1185	70	1.05	0.321		
1.4:1	10	1170	1234	1202	64	1.02	0.344	600	1202
	20	1170	1234	1202	64	1.03	0.352		
	50	1170	1238	1204	68	1.03	0.343		
	100	1168	1240	1204	72	1.04	0.339		
1.7:1	10	1198	1262	1230	64	1.02	0.332	600	1230
	20	1198	1262	1230	64	1.03	0.338		
	50	1195	1265	1230	70	1.02	0.339		
	100	1195	1265	1230	70	1.04	0.340		
1.9:1	10	1220	1284	1252	64	1.02	0.331	600	1255
	20	1220	1284	1252	64	1.01	0.333		
	50	1220	1288	1254	68	1.02	0.325		
	100	1222	1290	1256	68	1.03	0.327		

^a All potentials are in mV vs. Al/Al(III) in 2:1 $\text{AlCl}_3\text{-BuPyCl}$, at $T = 40^\circ\text{C}$. ^b Mole ratio of $\text{AlCl}_3\text{:BuPyCl}$.

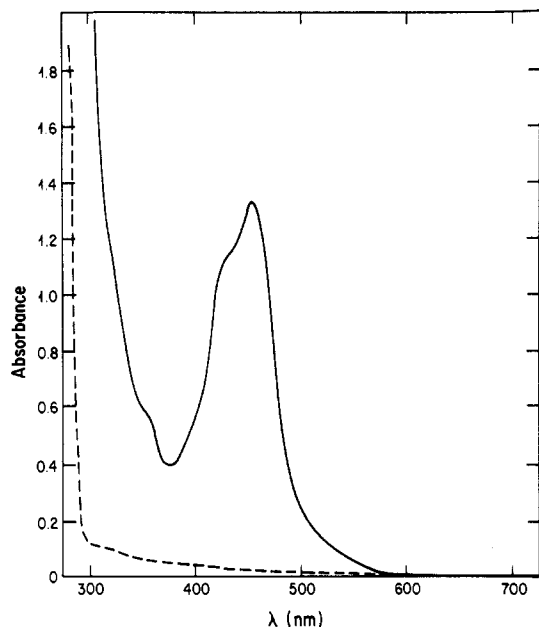


Figure 7. Absorption spectra of a 1.05:1 $\text{AlCl}_3\text{-BuPyCl}$ (dashed line) and 0.96 mM $\text{Ru}(\text{bpy})_3^{2+}$ in 1.05:1 $\text{AlCl}_3\text{-BuPyCl}$ melt (cell thickness 0.1 cm).

by oxygen in acidic melts, an attempt was made to see if a cell using oxygen as an oxidant could be made. The reduction of O_2 by $\text{Ru}(\text{bpy})_3^{2+}$ is potentially a useful reaction for batteries since $\text{Ru}(\text{bpy})_3^{3+}$ is a strong and facile oxidizing agent. We have made a preliminary investigation²³ of this possibility by constructing the cell shown in Figure 6. Aluminum oxidation occurs at the anode and $\text{Ru}(\text{bpy})_3^{3+}$ reduction occurs at the cathode. $\text{Ru}(\text{bpy})_3^{3+}$ is regenerated in the acid melt

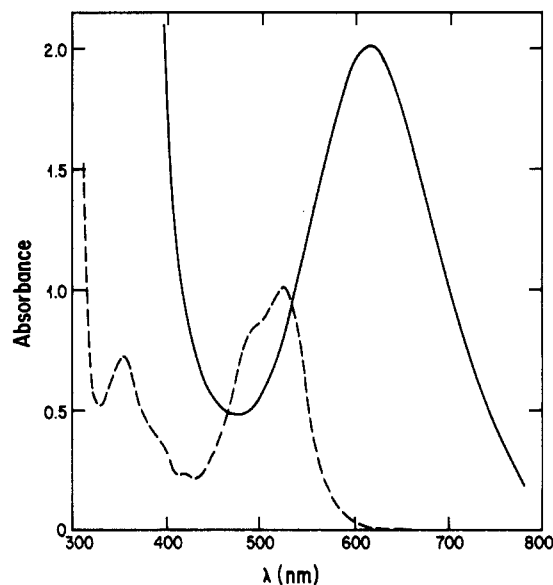


Figure 8. Absorption spectra of 1.17 mM $\text{Fe}(\text{bpy})_3^{2+}$ in a 1:1 melt, with cell thickness 0.1 cm (dashed line), and 2.5 mM $\text{Fe}(\text{phen})_3^{3+}$ in a 1.9:1 melt, with cell thickness 1 cm (solid line).

by oxygen, and so $\text{Ru}(\text{bpy})_3^{2+}$ acts as a mediator for O_2 reduction at the cathode. Thus the net cell reactions are Al oxidation and O_2 reduction; the product of O_2 reduction in the melt is not known at present but is probably AlOCl_2^- . Reduction of $\text{Ru}(\text{bpy})_3^{3+}$ by aluminum is extremely slow so no separator was necessary. The cell of Figure 6 gave an open-circuit potential of ~ 1.4 V and passed a charge corresponding to 400 turnovers of the ruthenium complex with no significant deterioration. The potential is that which is expected on the basis of the $\text{Ru}(\text{bpy})_3^{3+/2+}$ voltammogram (see Figure 1c). The current was limited by mass transport of $\text{Ru}(\text{bpy})_3^{3+}$ to the cathode.

(23) Pickup, P. G.; Sahami, S.; Osteryoung, R. A., unpublished work.

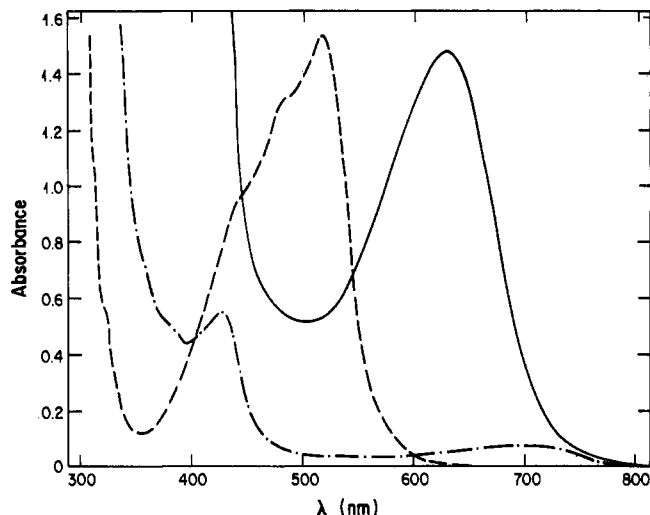


Figure 9. Absorption spectra of 1.45 mM $\text{Fe}(\text{phen})_3^{2+}$ in a 1:1 melt, with cell thickness 0.1 cm (---), 1.7 mM $\text{Ru}(\text{bpy})_3^{3+}$ in a 1.9:1 melt, with cell thickness 0.1 cm (-.-.), and 3.87 mM $\text{Fe}(\text{bpy})_3^{3+}$ in a 1.2:1 melt, with cell thickness 1 cm (—).

Table IV. Spectroscopic Data for Polypyridine Complexes of Ru and Fe in AlCl_3 -BuPyCl Melts^a

complex	color	$\lambda_{\text{max}}, \text{nm} (\epsilon, \text{M}^{-1} \text{cm}^{-1})^b$	
		this work	lit. values
$\text{Ru}(\text{bpy})_3^{2+}$	orange	454 (14 000)	453 (13 800), ^c 450 (14 000) ^d
$\text{Ru}(\text{bpy})_3^{3+}$	green	424 (3200)	418 (~3000) ^c
$\text{Fe}(\text{bpy})_3^{2+}$	red	523 (8700)	522 (8740), ^e 520 (8240) ^f
$\text{Fe}(\text{bpy})_3^{3+}$	greenish blue	627 (380)	618 (284), ^g 613 (289) ^h
$\text{Fe}(\text{phen})_3^{2+}$	red	512 (10 800)	510 (11 300), ⁱ 510 (11 100) ^j
$\text{Fe}(\text{phen})_3^{3+}$	blue	~610 (800)	590 (600), ^j 602 (870) ^k

^a These spectra were obtained in either the neutral or acidic melts (see text for details). ^b Molar absorptivities are accurate to $\pm 5\%$. ^c Reference 24. ^d Reference 25. ^e Reference 26. ^f Reference 27. ^g Reference 13. ^h Reference 28. ⁱ Reference 29. ^j Reference 30. ^k Reference 31.

2. Spectroscopy. UV-visible absorption spectra for both the bivalent and the trivalent complexes of tris(bipyridine)-complexes of iron and ruthenium and tris(phenanthroline)iron in the neutral and acidic AlCl_3 -BuPyCl melts are shown in Figures 7-9. The trivalent compounds were obtained by the chemical oxidation of the respective divalent complexes in acid melts either by bubbling with oxygen or by trace of O_2 impurity present in the drybox atmosphere. The spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ did not change as the melt composition varied from basic to acidic. Thus $\text{Ru}(\text{bpy})_3^{2+}$, unlike $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ complexes, does not decompose in the basic melt. The spectra of $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ in the neutral melt are identical with their respective spectra in the slightly acidic melt. In Table IV the molar absorptivities and maxima wavelengths obtained in this work was summarized and compared with those reported in other solvents.²⁴⁻³¹ There is good

Table V. Formal Potentials for Polypyridine Complexes of Ru(II/III) and Fe(II/III) in Various Solvents vs. Ferrocene/Ferrocenium Couple

solvent	E_f^a		
	Fe- (phen) ₃ ^{2+/3+}	Fe- (bpy) ₃ ^{2+/3+}	Ru- (bpy) ₃ ^{2+/3+}
water	743 ^b	718 ^b	921 ^b
acetonitrile	686 ^c	670 ^d	900 ^e
1:1 AlCl_3 - BuPyCl	730 ^f	690 ^f	894 ^f
nitromethane	721 ^c	727 ^d	

^a The formal potential for each redox couple is quoted in mV vs. E_f for the ferrocene/ferrocenium couple in the same solvent: i.e., $E_f = E_f(\text{redox couple}) - E_f(\text{ferrocene/ferrocenium})$. ^b Reference 17. ^c Reference 12. ^d Reference 16. ^e Reference 37. ^f This work.

agreement between positions of the absorption maxima determined here and those from the literature. The intense bands in the visible regions of these compounds are due to the transfer of electronic charge between the d orbital of the metal ion and the π orbitals of the ligand. For the bivalent complexes charge transfer takes place from the metal to the ligand, i.e., $t_{2g} \rightarrow \pi^*$ (MLCT).^{24,25,30} In the case of trivalent complexes the charge transfer is from the ligand to the metal, i.e., $\pi \rightarrow t_{2g}$ (LMCT).^{27,31} In addition to these bands, there are other bands in the shorter wavelength portions of all spectra, which because of their higher intensities are outside the spectrum range. Due to the melt UV cutoff at ~ 280 nm, the UV absorption bands of these compounds could not be recorded.

Discussion

Spectroscopic and electrochemical results show that all the complexes studied here are stable (i.e., have fixed coordination spheres) in the melt compositions of 1.0:1.0 to 2:1 AlCl_3 -BuPyCl. Although $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ decompose in the basic melts to form FeCl_4^- , $\text{Ru}(\text{bpy})_3^{2+}$ is stable and does not dissociate, perhaps due to the significantly greater lability of the Fe(II)-tris(polypyridine) complexes over that of ruthenium.

On the basis of the foregoing observations and results presented in Tables I-III, we conclude that in the entire region from neutral to 2:1 melts the oxidation of $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$, and $\text{Ru}(\text{bpy})_3^{2+}$ corresponds to a Nernstian one-electron electrochemically reversible process. Reversible behavior for these couples has been found in other solvents.^{8,12,13} Consideration of E_f or $E_{1/2}$ from Tables I-III indicates that although these values shift slightly toward more positive potentials with increasing melt acidity, the variation in E_f or $E_{1/2}$ in going from 1:1 to 1.9:1 mole ratio for all of these redox couples is less than 90 mV (the reproducibility of the Al/Al(III) reference electrode is ± 10 mV). This indicates that the influence of variation in the melt composition on the redox properties of these polypyridine complexes is relatively small, but not as small as for the ferrocene/ferrocenium couple. Robinson and Osteryoung reported that the formal potential value of ferrocene/ferrocenium in AlCl_3 -BuPyCl melts was independent of melt acidity (with the E_f value of 0.27 V vs. Al/Al(III)).¹ This is understandable since the compact "sandwich" structure of ferrocene/ferrocenium compared to the open structure of polypyridine complexes should prevent the close approach of the solvent molecules to the metal redox center. A possible explanation of the observed variation in E_f for the polypyridine complexes with the melt acidity is the formation of ion pairs, most probably with AlCl_4^- . As the acidity of the melt increases, the concentration of AlCl_4^- de-

(24) Braddock, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 3158.

(25) Staniewicz, R. J.; Sympson, R. F.; Hendrick, D. G. *Inorg. Chem.* **1977**, *16*, 2166.

(26) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. *J. Aust. J. Chem.* **1971**, *24*, 257.

(27) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(28) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275.

(29) Nord, G.; Pederson, B.; Bjergbakke, E. *J. Am. Chem. Soc.* **1983**, *105*, 1913.

(30) Schilt, A. A. "Analytical Applications of 1,10-Phenanthroline and Related Compounds"; Pergamon Press: London, 1969; p 36.

(31) Burgess, J.; Haines, R. J. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1705.

(32) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428.

Table VI. Diffusion Coefficients (at $T = 40^\circ\text{C}$) and Radii of Polypyridine Fe(II) and Ru(II) Complexes in $\text{AlCl}_3\text{-BuPyCl}$ Melts^a

melt compositn	Ru(bpy) ₃ ²⁺		Fe(bpy) ₃ ²⁺ 10 ⁷ <i>D</i> , cm ² /s	Fe(phen) ₃ ²⁺ 10 ⁷ <i>D</i> , cm ² /s
	10 ⁷ <i>D</i> , cm ² /s	10 ⁸ <i>D</i> <i>η</i> , g cm/s ²		
1:1	2.75	6.05	2.61	2.43
1.05:1	2.88	6.06		
1.2:1	2.99	6.00		
1.4:1	3.35	6.04		
1.7:1	3.67	6.05		
1.9:1	4.07	6.11		
		av 6.04 ± 0.04		
calcd radius of complex, nm		0.57	0.60	0.64

^a Values of the viscosity (η) and density used in the calculation of D , $D\eta$, and radius are taken from ref 20.

creases and E_f becomes more positive. In other words, with increasing acidity of the melt the extent of ion pairing between the polypyridine complexes of iron and ruthenium with AlCl_4^- decreases and the overall positive charge of the complex increases, making it more difficult to oxidize.

Comparison of the E_f values for $\text{Fe}(\text{bpy})_3^{2+/3+}$, $\text{Fe}(\text{phen})_3^{2+/3+}$, and $\text{Ru}(\text{bpy})_3^{2+/3+}$ (quoted vs. ferrocene/ferrocenium) in different solvents with those in the neutral melt is shown in Table V. It is obvious from this table that indeed the redox properties of these couples are relatively insensitive to the nature of the solvent. This is expected since the polypyridine ligand should somewhat shield the solvent from the metal cation. Although the redox properties of these polypyridine couples appear to be largely independent of the solvent, indicating that they might be used as internal reference redox couples, they apparently do not offer any advantage over the ferrocene, particularly in $\text{AlCl}_3\text{-BuPyCl}$ melts.

In Table VI values of diffusion coefficients for the polypyridine complexes of iron and ruthenium are given. The values of D were obtained from RDE experiments with use of the Levich equation (eq 3), where I_1 is the limiting current

$$I_1 = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_0 \quad (3)$$

in amperes, n the number of electrons transferred, F the Faraday constant, A the area of the electrode in cm^2 , ω the rotation rate in rad/s , ν the kinematic viscosity, and C_0 the concentration of the electroactive species in mol/cm^3 .¹⁸ Diffusion coefficients for $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ were only determined in the neutral melt, where there was no chemical oxidation of the Fe(II) complex and its concentration was known accurately. The observed change in the D value for $\text{Ru}(\text{bpy})_3^{2+}$ in Table VI can be attributed to changes in the viscosity (η) of the melt. The values of D and η are related by the modified Stokes-Einstein equation³³ (eq 4), where κ

$$D = \frac{\kappa T}{4\pi\eta r} \quad (4)$$

is the Boltzmann constant and r is the radius of the diffusing species. The ηD values for $\text{Ru}(\text{bpy})_3^{2+}$ (tabulated in Table VI) are constant throughout the entire range of melt compositions studied here. Values of r calculated from eq 4 for polypyridine complexes are also listed in Table VI. These radii

are in reasonable agreement with their corresponding crystallographic values,^{34,35} indicating that solvation is not very important in this medium for these compounds.

Although the "spontaneous" oxidation of some aromatic hydrocarbons (with $E_{1/2}$ of less than ~ 1.4 V) in highly acidic $\text{AlCl}_3\text{-BuPyCl}$ melts has been observed by Robinson and Osteryoung, the nature of the oxidizing species was not speculated upon.¹ It is clear from this work that oxygen is an oxidant that oxidizes species with the $E_{1/2}$ of ~ 1.3 V and less in acidic $\text{AlCl}_3\text{-BuPyCl}$ melts. Considering our results and those observed previously for oxidations of aromatic hydrocarbons¹ and iodide,⁶ we conclude that O_2 can oxidize any species with an $E_{1/2}$ of 1.4 V or less in the acidic melts regardless of its chemical nature. In other words, the oxidation process is insensitive to the nature of the reductant and only depends on its formal potential, presumably according to the reaction



with $E_f(\text{O}_2/\text{reduced O}_2) > E_f(\text{Red/Ox})$. Since neither the reduction of oxygen nor the electrochemistry from its reduction product can be seen, it is not known whether the decrease in the rate of oxidation with decreasing melt acidity results from slow kinetics or unfavorable thermodynamics. One possible explanation is that, by decreasing melt acidity, the value of E_f for $\text{O}_2/\text{reduced O}_2$ shifts to negative potentials. Indeed the absence of chemical oxidation of these compounds in the neutral or basic melts is a good indication of such an explanation. The other possibility is that the solubility of O_2 decreases drastically as the acidity decreases, making the oxidation more difficult.

It should also be pointed out that O_2 impurity in the drybox may not be the sole trace oxidant present in these melts. Perchlorate, as indicated above, also functions as an oxidant in acidic melts. Recent work on the reduction of proton arising from the addition of water to the melt indicates that the potential for evolution of hydrogen moves in the positive direction with increasing melt acidity, suggesting that the "proton", which may arise from HCl or an $-\text{Al}-\text{O}-\text{H}$ entity formed as a result of water addition, is a stronger oxidant in acidic than in basic melts.³⁶ However, experiments at a platinum electrode in a melt containing both water and the Ru complex indicated that the ruthenium reduction takes place at more positive potentials than does hydrogen evolution. Nevertheless, the ability of proton to act as an oxidant in these melts at the trace levels should not be overlooked.

Acknowledgment. We wish to thank Dr. Peter G. Pickup for helpful discussions and assistance. Helpful suggestions by other members of the molten salt research group, particularly T. Zawodzinski and Drs. Z. Karpinski and M. Lipsztajn, are appreciated. This work was supported by the Air Force Office of Scientific Research and the Office of Naval Research.

Registry No. $\text{Fe}(\text{bpy})_3^{2+}$, 15025-74-8; $\text{Fe}(\text{phen})_3^{2+}$, 14708-99-7; FeCl_4^{2-} , 17611-27-7; $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $\text{Fe}(\text{bpy})_3^{3+}$, 18661-69-3; $\text{Fe}(\text{phen})_3^{3+}$, 13479-49-7; $\text{Ru}(\text{bpy})_3^{3+}$, 18955-01-6; $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$, 15388-48-4; AlCl_3 , 7446-70-0; BuPyCl , 1124-64-7; Al , 7429-90-5; O_2 , 7782-44-7; perchlorate, 14797-73-0.

(34) Rillema, D. P.; Jones, D. S. *J. Chem. Soc., Chem. Commun.* **1979**, 849.

(35) Zalkin, A.; Templeton, D. H.; Ueki, T. *Inorg. Chem.* **1973**, *12*, 1641.

(36) Sahami, S.; Osteryoung, R. A. *Anal. Chem.* **1983**, *55*, 1970.

(37) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.