Further Studies on the Stabilization of High and Low Oxidation States in Aromatic Imine Ligand Complexes of First Row Transition Metals. II. Substituted Bipyridine Complexes of Manganese(II) and Chromium(III)

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Introduction

The non-aqueous electrochemistry of tris(bipyridine)chromium(III) has been reported a number of times in the recent literature [1–6]. Some of these

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reports were concerned with electron-transfer rates [4, 6] and one report attempted to correlate the electrochemical behavior of chromium complexes of bipyridine and two dimethyl-substituted bipyridines with their spectroscopic properties [2]. Complexes of the type CrL_3^{3+}, where L = bipy or a dimethyl substituted bipy, all exhibit four reversible one electron reductions, with one exception [3] which reported additional reductions to the formal Cr(−II) and Cr(−III) oxidation states at potentials considerably negative of the normal free ligand reduction. There has been only one report on the non-aqueous electrochemistry of $Mn(bipy)_3^{2+}$ [7]. In this paper we report on the non-aqueous electrochemistry of the bipyridine, 4,4'-dimethylbipyridine (Me$_2$bipy) and 4,4'-diphenylbipyridine (Ph$_2$bipy) complexes of chromium(III) and manganese(II).

Experimental

Chromium(III) complexes were synthesized by procedures previously reported [5]. They were recrystallized once from ethanol–water, and dried at 80 °C in vacuum over P_2O_5 for 24 hours. Manganese(II) complexes were prepared by mixing stoichiometric amounts of $MnSO_4$ and ligand (dissolved in ethanol–water), and adding $NaClO_4$ to precipitate

TABLE I. Voltammetric Data for the Chromium Complexes.

Complex Couple	D. C. Polarography			Cyclic Voltammetry		In-Phase A. C. Polarography [a]		
	$E_{1/2}$ (V)	$i_d \frac{\mu A}{mM}$	slope (mV)	scan rate (mV/sec)	ΔE_p (mV)	E_p (V)	$I_p \frac{\mu A}{mM}$	half-width (mV)
Cr(bipy)$_3$								
III–II	−0.212	2.84	−58	100 Hg	60	−0.20	3.45[b]	92
II–I	−0.720	3.29	−60	100 Hg	60	−0.71	3.40[b]	92
I–0	−1.285	2.96	−56	100 Hg	60	−1.28	3.50[b]	85
0–(−I)	−1.913	2.82	−60	100 Hg	60	−1.89	2.50[b]	96
Cr(Ph$_2$bipy)$_3$								
III–II	−0.245	2.58	−59	110 Hg	65	−0.23	1.71	89
II–I	−0.666	2.68	−60	110 Hg	65	−0.65	1.78	92
I–0	−1.192	2.66	−56	110 Hg	65	−1.18	1.91	90
0–(−I)	−1.738	2.57	−65	110 Hg	70	−1.72	1.56	103
Cr(Me$_2$bipy)$_3$								
III–II	−0.378	2.64	−57	120 Hg	65	−0.36	2.38	90
II–I	−0.875	3.24	−69	120 Hg	75	−0.86	1.86	94
I–0	−1.399	2.82	−56	120 Hg	65	−1.38	2.07	89
0–(−I)	−1.985	2.77	−59	100 Hg	85	−1.97	1.62	90

[a]Applied frequency = 27 Hz. Applied potential = 5 mV. IR compensation = 225 ohms. [b]Maximum currents. All voltages *vs.* Ag/AgCl, sat. NaCl. Solvent = spectro acetonitrile. Background electrolyte = 0.1 *M* TEABF$_4$.

the perchlorate salt of the complex. The manganese-(II) complex perchlorates were recrystallized and dried by the same procedures used for the Cr(III) complexes.

Reagent grade acetonitrile, containing less than 0.1% water (Fisher) was further dried and purified by refluxing over and distilling off of P_2O_5 followed by calcium hydride, and stored over molecular sieves. Supporting electrolyte was polarographic grade tetraethylammonium tetrafluoborate (Southwestern Analytical Chemicals) which was used as received.

Data were taken on instrumentation which has been described previously [5]. All potential are *vs.* Ag(AgCl) (saturated NaCl).

Results and Discussions

Table I gives the electrochemical parameters for the chromium complexes. The complex of Me_2bipy shows two minor anomalies in behavior. First, the cyclic voltammetry and AC polarography of the Cr(II)–Cr(I) reductions shows evidence of adsorption (Fig. 1), and the cyclic voltammetry peak separation for the Cr(0)–Cr(–I) reduction wave has a value considerably larger than expected for a reversible, one electron process. The latter behavior is most likely due to the fact that the Cr(0)–Cr(–I) wave occurs very close to the free ligand reduction (due to break-up of the complex) and is distorted by being so close to this large wave. However, the data in the Table show that each complex undergoes four reversible
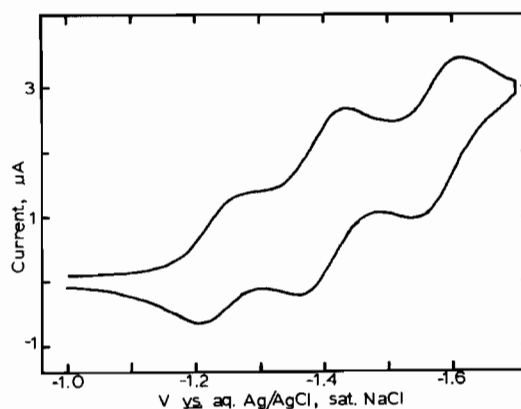

Fig. 1. Cyclic voltammogram of $Cr(Me_2bipy)_3(ClO_4)_3$, 0.64 mM in spectrograde acetonitrile, 0.1 M TEABF$_4$. Scan rate = 120 mV/sec.

one-electron reductions, producing a five-membered redox chain from the formal Cr(III) oxidation state through the formal Cr(–I) oxidation state.

Table II gives the voltammetric data for the manganese complexes. The Mn(II)–Mn(III) oxidation occurred at very positive potentials (*circa* +1.5 *vs.* Ag/AgCl) and waves clear enough for accurate potential determination could not be obtained. The reduction waves of all manganese complexes were deformed by maxima which could be eliminated by adding excess free ligand. All of these manganese(II) complexes showed three well-defined reduction waves with the addition of excess ligand. Figure 2 shows a D. C. polarogram of $Mn(bipy)_3(ClO_4)_2$ and Fig. 3

TABLE II. Voltammetric Data[a] for the Manganese Complexes.

Complex Couple	D. C. Polarography			Cyclic Voltammetry		In-Phase A. C. Polarography[b]		
	$E_{1/2}$ (V)	$i_d \frac{\mu A}{mM}$	slope (mV)	scan rate (mV/sec)	ΔE_p (mV)	Ep (V)	Ip $\frac{\mu A}{mM}$	half-width (mV)
$Mn(bipy)_3$								
II–I	−1.314	2.68	−59	110 Hg	68	−1.30	2.24	93
I–0	−1.496	3.07	−58	110 Hg	63	−1.48	2.37	92
0–(−I)	−1.722	3.18	−60	125 Hg	70	−1.70	2.10	99
$Mn(Ph_2bipy)_3$								
II–I	−1.228	–	−66	125 Hg	70			
I–0	−1.393	–	−61	125 Hg	70		c	
0–(−I)	−1.579	–	−59	125 Hg	65			
$Mn(Me_2bipy)_3$								
II–I	−1.424	2.53	−58	95 Hg	67	−1.42	2.12	94
I–0	−1.607	2.91	−59	95 Hg	67	−1.60	2.09	92
0–(−I)	−1.807	2.89	−60	95 Hg	65	−1.79	1.92	92

[a] All data taken in the presence of excess ligand. [b] Applied frequency = 27 Hz. Applied potential = 5 mV. IR compensation = 225 ohms. [c] Data not obtained due to the poorly-defined nature of the A.C. polarographic waves of this complex. All voltages *vs.* Ag/AgCl, sat. NaCl. Solvent = spectro acetonitrile. Background electrolyte = 0.1 M TEABF$_4$.
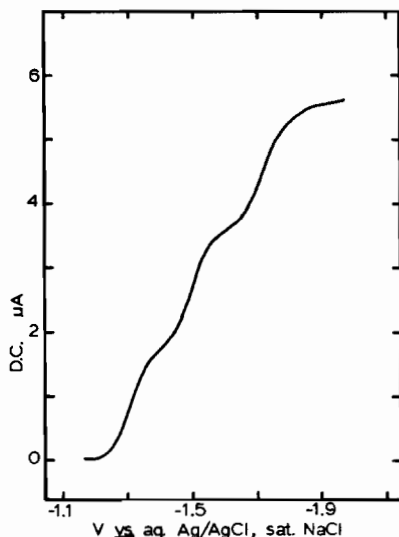
Fig. 2. D. C. polarogram of 0.50 m*M* Mn(bipy)$_3$(ClO$_4$)$_2$ in spectrograde acetonitrile, 0.1 *M* TEABF$_4$; excess free ligand added.
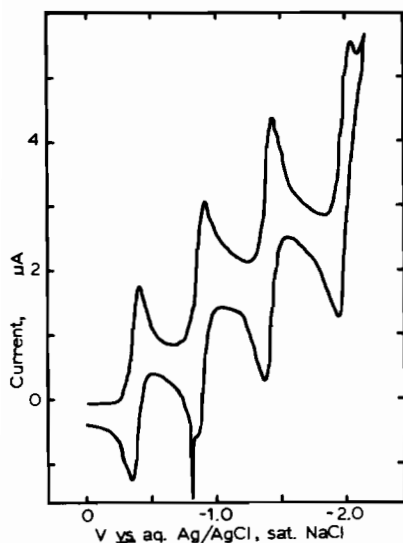

Fig. 3. Cyclic voltammogram of Mn(Ph$_2$bipy)$_3$(ClO$_4$)$_2$ in spectrograde acetonitrile, 0.1 *M* TEABF$_4$; excess free ligand added. Scan rate = 1.25 mV/sec.

shows a cyclic voltammogram of Mn(Ph$_2$bipy)$_3$-(ClO$_4$)$_2$. The Ph$_2$bipy complex gave well-defined DC polarograms and cyclic voltammograms, but gave very poorly defined AC polarographic waves. Several different handling procedures were tried, all with the same result. Because of this, no AC polarographic data for this complex is included in Table II; the other data characterize its behavior sufficiently. In general, it can be seen that all of the complexes give a well-defined redox chain of one electron reversible reductions from the Mn(II) down to the formal Mn(−I) oxidation state.

A comparison of the redox potentials of the bipy and Ph$_2$bipy complexes with both metals shows the same ability of the *p*-phenyl substituent to stabilize both high and low oxidation states which has been observed in tridentate imine ligand complexes of iron, cobalt and manganese [8, 9].

Vlček [10], and more recently Saji and Aoyagui [2, 11] have suggested that for reductions in which the redox orbital is localized primarily on the ligand of a coordination complex, there should exist a direct relationship between the reduction potential of the complex and that of the free ligand which would be of the form

$$E_{1/2}^C = E_{1/2}^L + A$$

where the superscripts C and L stand for complex and ligand, respectively, and A is a constant. Saji and Aoyagui [2] have shown plots of $E_{1/2}^C$ *vs.* $E_{1/2}^L$ for chromium complexes of bipyridine and two dimethyl substituted bipyridines. They interpreted the approximately linear relationships obtained for the 2–1, 1–0 and 0–(−1) couples to indicate that the reduction was primarily localized on the ligands, while a definitely non-linear relationship for the 3–2 couple was taken to indicate metal localization.

The ligands used in this study give a wider range of substituent effects and potentials than those reported previously. Figures 4a and 4b show plots of $E_{1/2}^C$ *vs.*
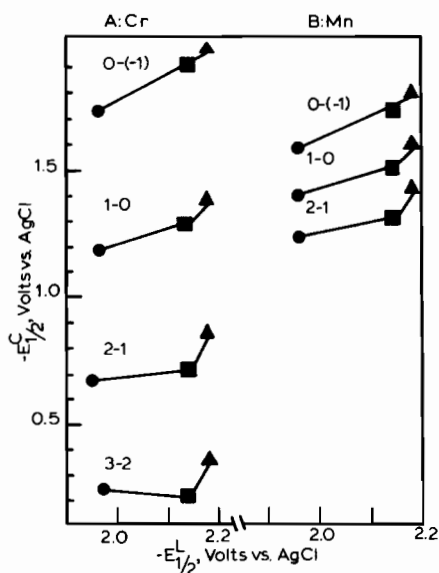

Fig. 4. Redox potential of first ligand reduction *vs.* redox potential for various metal complex couples. See text for discussion.

$E_{1/2}^L$ for the complexes of chromium and manganese, respectively. The plots for the chromium complexes are particularly interesting. If the redox potential for the unsubstituted ligand is taken a reference point on the line for each couple, it can be seen that the

potentials for the methyl and phenyl substituted ligand complexes move positive relative to the unsubstituted ligand complex as the formal oxidation states in the couple become lower. The changes that take place are larger in magnitude for the Ph$_2$bipy complex but are more striking for the Me$_2$bipy complex, which has a redox potential approximately 150 mV negative of the reduction potential of the bipyridine complex for the 3–2 and 2–1 couples. In the 1–0 and 0–(−1) couples, the reduction potential of the Me$_2$bipy complex moves much closer to that of the bipyridine complex. The potential shifts are summarized in Table III. We have reported the

TABLE III. Formal Potential Shifts of the Cr Complexes Relative to $Cr(bipy)_3^{n+}$–$Cr(bipy)_3^{(n-1)+}$.

Couple	Ligand	
	Ph$_2$Bipy	Me$_2$Bipy
Cr(III)–Cr(II)	−32 mV	−166 mV
Cr(II)–Cr(I)	+52 mV	−155 mV
Cr(I)–Cr(0)	+94 mV	−144 mV
Cr(0)–Cr(−I)	+175 mV	−72 mV

aqueous electrochemistry of a much larger series of chromium complexes with substituted phenanthroline ligands [12]. The 3–2 and 2–1 couples are the only ones accessible in aqueous media, and for those couples the effects of electron acceptor substituents became increasingly important as the formal oxidation state of the complex decreased, while the effect of electron donating methyl substituents were apparently offset by the overall electron accepting character of the ligands, and increasing metal–ligand interaction in the lower oxidation states. The data on chromium bipyridine complexes reported here which includes fewer compounds but a more extended series of formal oxidation states, confirms these observations.

From Fig. 2b it can be seen that the manganese bipyridine complexes show the same general behavior as the chromium complexes, but the changes which take place in going to increasingly low oxidation states are much less pronounced than those for the chromium complexes. The nominal location of the redox orbital (on the basis of simple ligand field theory) changes from t_{2g} to e_g at Cr(0) and Mn(I), but it does not appear that any meaningful interpretation of the different behavior of the complexes of the two metals can be made on this basis. Rather, it seems that this difference is further indication that, although redox changes in formally low-valent complexes take place primarily on the ligands, the metal continues to exert a strong influence on the redox behavior of the complexes which cannot be explained on the basis of any simple mechanism.

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