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Further Studies on the Stabilization of High and Low Oxidation States in Aromatic Imine Ligand Complexes of First Row Transition Metals. I. Substituted Bipyridine Complexes of Cobalt and Iron

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Introduction

There have been some reports on the non-aqueous electrochemistry of complexes of 2,2′-bipyridine with cobalt [1–3] and iron [1, 4–8] and of complexes of dimethyl substituted bipyridines with iron and cobalt [1]. The methyl substituent effect on the localizaton of the redox orbital was investigated for the iron and cobalt complexes [1]. All reports have indicated that while bipyridine stabilizes all formal oxidation states of iron from Fe(III) to Fe(–I), the sequence of reduction steps: Co(III)–Co(II), Co(II)–Co(I), and Co(I)–Co(–I) which are found for the cobalt complexes, implies that a different reduction mechanism is extant for the formally low-valent cobalt complexes (*vide infra*). This paper reports an investigation of the oxidative as well as the reductive behavior of methyl and phenyl substituted bipyridine complexes of cobalt and iron using several electrochemical techniques including low frequency in-phase AC polarography.

Experimental

Bipyridine, 4,4′-dimethylbipyridine and 4,4′-diphenylbipyridine were purchased from the G. F. Smith Chemical Company and used as received. Electrometric grade tetraethylammonium fluoborate (TEABF$_4$) was purchased from Southwestern Analytical Chemical Company and dried at 80 °C *in vacuo* for several hours. Spectro grade acetonitrile was obtained from Matheson, Coleman and Bell Manufacturing Chemists. All other chemicals were reagent grade and used as received. High purity nitrogen was washed with acetonitrile before use.

The compounds $Co(L)_3(ClO_4)_2$ and $Fe(L)_3(ClO_4)_2$, where L = bipyridine, 4,4′-dimethylbipyridine and 4,4′-diphenylbipyridine, were prepared by reacting stoichiometric quantities of $CoCl_2 \cdot 6H_2O$ or $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ with the respective ligand in ethanol–water solution. The tris complexes were precipitated with $NaClO_4$, washed, and dried at 80 °C *in vacuo* for several hours.

Voltammetric measurements were carried out in the same manner as described previously [9].

Results and Discussion

The voltammetric data for the free ligands is summarized in Table I. The current to concentration

TABLE I. Voltammetric Data for the Free Ligands.[a]

	D.C. Polarography			Cyclic Voltammetry	
	$E_{1/2}$(V)	$i_l\left(\frac{\mu A}{mM}\right)$	Slope (mV)	Scan Rate $\left(\frac{mV}{sec}\right)$	ΔE_p (mV)
bipy					
1st Reduction	–2.14	7.7	–65	115 Hg	NRP
2nd Reduction	–2.40	6.9	–71	–	–
3rd Reduction	–2.64	7.9	–85	–	–
$\phi_2$bipy					
1st Reduction	–1.96	8.4	–59	120 Hg	120
2nd Reduction	–2.32	16.6	–84	–	–
Me$_2$bipy					
1st Reduction	–2.18	8.0	–55	125 Hg	NRP
2nd Reduction	–2.64	10.0	–88	–	–

[a] NRP = No Reverse Peak. All voltages *vs.* Ag/AgCl sat. NaCl. Solvent = *spectro* acetonitrile. Background electrolyte = 0.1 *M* TERBF$_4$.

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TABLE II. Voltammetric Data for the Iron Complexes.

Complex Couple	D.C. Polarography			Cyclic Voltammetry		In-Phase A.C. Polarography		
	$E_{1/2}$(V)	$i_d\left(\frac{\mu A}{mM}\right)$	Slope (mV)	Scan Rate $\left(\frac{mV}{sec}\right)$	ΔE_p (mV)	E_p(V)	$I_p\left(\frac{\mu A}{mM}\right)$	Half-width (mV)
Fe(bipy)₃								
II–III^a	+1.087	–	+60	90 Pt	63	–	–	–
II–I	–1.316	2.82	–59	75 Hg	67	–1.30	2.46	92
I–0	–1.491	2.92	–62	125 Hg	65	–1.49	2.12	96
0–(–I)	–1.765	3.19	–61	125 Hg	75	–1.75	1.87	105
Fe(φ₂bipy)								
II–III^a	+1.016	–	+62	95 Pt	60	–	–	–
II–I	–1.240	2.28	–60	75 Hg	63	–1.23	2.29	91
I–0	–1.410	2.67	–53	75 Hg	60	–1.39	2.11	89
0–(–I)	–1.627	2.18	–61	75 Hg	70	–1.62	1.61	106
Fe(Me₂bipy)₃								
II–III^a	+0.935	–	+59	90 Pt	60	–	–	–
II–I	–1.423	2.33	–57	100 Hg	65	–1.42	1.84	89
I–0	–1.617	2.60	–58	100 Hg	65	–1.61	1.64	93
0–(–I)	–1.853	2.58	–59	110 Hg	70	–1.85	1.36	105

[a] Done at the rotating platinum electrode (D.C.). [b] Applied frequency = 27 Hz. Applied potential = 5 mV. IR compensation = 225 ohms. All voltages *vs.* Ag/AgCl sat. NaCl. Solvent = *Spectro* acetonitrile. Background electrolyte = 0.1 *M* TEABF$_4$.

ratios indicate all waves to be due to electron transfers involving more than one electron. All free ligand waves were shown to be irreversible from cyclic voltammetric studies. No oxidation wave for any of the ligands was observed at the rotating platinum electrode out to +1.8 volts *vs.* Ag/AgCl, sat. NaCl.

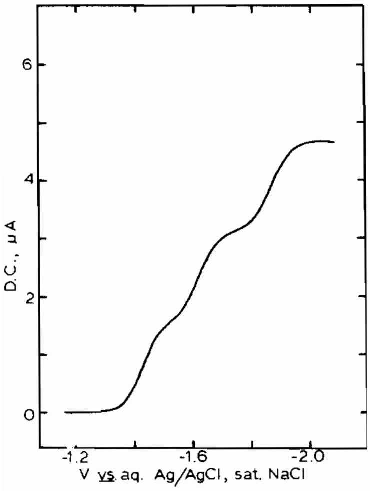

Fig. 1. D. C. polarogram of 0.653 m*M* Fe(4,4′-Me$_2$bipy)$_3$-(ClO$_2$)$_4$ in *spectro* acetonitrile and 0.1 *M* TEABF$_4$.

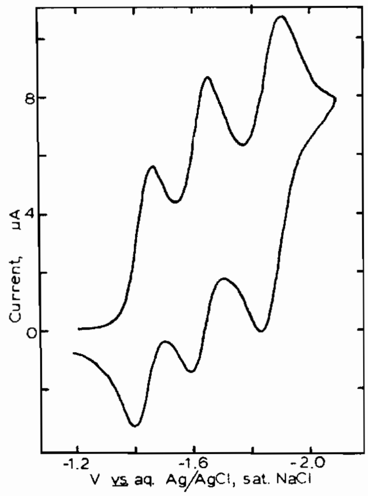

Fig. 2. Cyclic voltammogram on Hg of 0.653 m*M* Fe(4,4′-Me$_2$bipy)$_3$(ClO$_4$)$_2$ in *spectro* acetonitrile and 0.1 *M* TEABF$_4$. Scan rate = 100 mV/sec.

The voltammetric parameters for the iron bipyridine complexes are given in Table II. All of the values are in the range expected for reversible, one electron transfers. Figure 1 shows the D.C. polarogram of the three reduction waves for Fe(Me$_2$bipy)$_3$-(ClO$_4$)$_2$ and Fig. 2, a cyclic voltammogram of these same three waves. Figure 3 shows a cyclic voltammogram on platinum of the II–III oxidation wave for Fe(φ$_2$bipy)$_3$(ClO$_4$)$_2$. Phenyl substitution on the bipyridine ring produces a potential shift toward zero volts relative to the unsubstituted ligand for all redox

TABLE III. Voltammetric Data for the Cobalt Complexes.

Complex Couple	D.C. Polarography			Cyclic Voltammetry		In-Phase A.C. Polarography		
	$E_{1/2}$(V)	$i_d\left(\frac{\mu A}{mM}\right)$	Slope (mV)	Scan Rate $\left(\frac{mV}{sec}\right)$	ΔE_p (mV)	E_p(V)	$I_p\left(\frac{\mu A}{mM}\right)$	Half-width (mV)
Co(bipy)₃								
II–III	+0.351	2.95	+57	90 Hg	70	+0.358	2.47	91
II–I	−0.938	2.97	−61	110 Hg	67	−0.925	3.13	91
I–(−I)^a	−1.580	6.36	−37	100 Hg	40	−1.57	7.11	54
Co($\phi_2$bipy)₃								
II–III	+0.263	2.98	+66	35 Pt	80	+0.274	1.76	97
II–I	−0.873	2.56	−63	110 Hg	67	−0.868	1.98	90
I–(−I)^b	−1.446	4.41	−36	110 Hg	40	−1.43	3.89	57
Co(Me₂bipy)₃								
II–III	+0.216	2.82	+59	85 Hg	67	+0.228	2.53	89
II–I	−1.078	2.89	−65	85 Hg	67	−1.06	2.56	91
I–(−I)^a	−1.694	5.46	−36	110 Hg	43	−1.68	5.72	53

^{a}All values reported are in the presence of excess ligand. ^{b}Slight amount of excess ligand (very low solubility of ligand). ^{c}Applied frequency = 27 Hz. Applied potential = 5 mV. IR compensation = 225 ohms. All voltages *vs.* Ag/AgCl sat. NaCl. Solvent = *spectro* acetonitrile. Background electrolyte = 0.1 *M* TEABF$_4$.

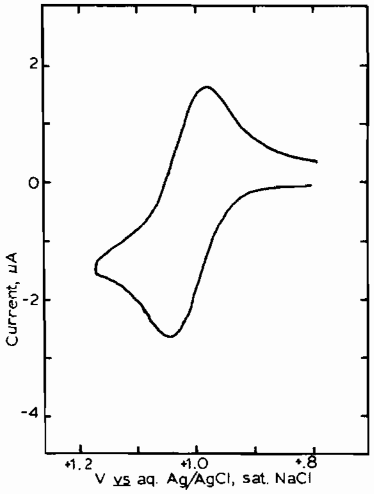

Fig. 3. Cyclic voltammogram on Pt of 0.377 m*M* Fe(4,4′-$\phi_2$bipy)$_3$(ClO$_4$)$_2$ (II–III) in *spectro* acetonitrile and 0.1 *M* TEABF$_4$. Scan rate = 95 mV/sec.

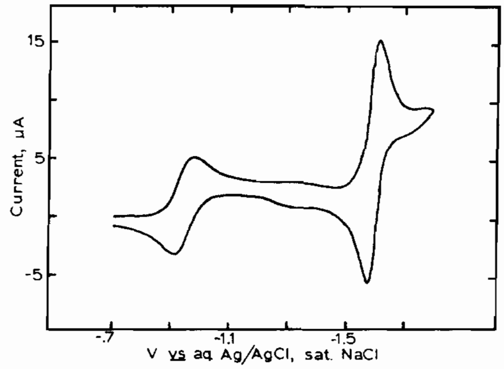

Fig. 4. Cyclic voltammogram on Hg of 0.799 m*M* Co(bipy)$_3$(ClO$_4$)$_2$ with excess ligand (II–I and I–(−I)) in *spectro* acetonitrile and 0.1 *M* TEABF$_4$. Scan rate = 100 mV/sec.

couples indicating that the *para* phenyl substituent contributes to the stability of both the high and low oxidation states of iron. This same effect has been reported for tridentate imine ligand complexes [9–12] of iron, cobalt, manganese and chromium, phenanthroline complexes of iron [13], and bipyridine complexes of chromium and manganese [14].

Table III summarizes the voltammetric data for the cobalt complexes. Figure 4 and 5 show a cyclic voltammogram and A. C. polarogram of the tris(bipyridine) cobalt(II) complex, respectively. For the Co(II)–Co(III) and Co(II)–Co(I) couples the data again indicate reversible, one electron transfers. The second reduction step yields DC polarographic diffusion currents and AC polarographic peak current values which correspond to a two electron reduction step, *i.e.*, Co(I) to Co(−I). In the presence of excess free ligand, the DC logplot slopes, cyclic voltammetric peak splittings and AC polarographic half-peak widths all have values approaching those expected for a reversible two-electron change. In the absence of excess free ligand the half-wave potential shifts in the positive direction and the other electrochemical parameters change considerably. For example, those

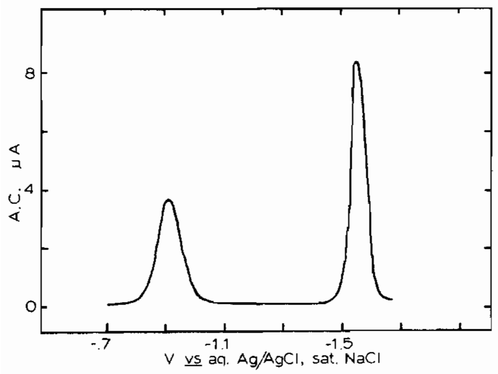

Fig. 5. In-phase A.C. polarogram of 0.799 m*M* Co(bipy)$_3$-(ClO$_4$)$_2$ with excess ligand (II–I and I–(–I)) in *spectro* acetonitrile and 0.1 *M* TEABF$_4$. Frequency = 27 Hz.

for the Co(Me$_2$bipy)$_3^{2+}$ complex (without excess ligand) are given below:

D. C. Polarography: $E_{1/2} = -1.634$ V
$i_d/C = 4.76$ µA/m*M*
logplot slope = 48 mV
Cyclic Voltammetry: $\Delta E_p = 55$ mV
AC Polarography: $E_p = -1.63$ V
half-width = 83 mV

The negative half-wave and peak potential shifts with added excess free ligand (Table III) suggest that there is a chemical reaction involving the free ligand following the charge-transfer. It seems most reasonable to assume that this would be dissociation of the electrode reaction product. The data do not permit any further characterization of this reaction, except to suggest that it is rapid.

Musumeci, *et al.* [15] have reported that Co(terpy)$_2^{2+}$ can only be reduced in two one-electron steps to the formal Co(0) oxidation state, in contrast to the behavior of Co(bipy)$_3^{2+}$, in which a formal oxidation state of Co(–I) appears to be reached via one two-electron reduction step described above. The Co(phen)$_3^{2+}$ complex shows the same behavior as Co(bipy)$_3^{2+}$ [16, 17]. These authors explained this contrasting behavior by noting that tetragonal distortion to D_{4h} symmetry will take place in an octahedral complex in which π back donation occurs, and the bipyridine and phenanthroline cannot accommodate this distortion as well as terpyridine. They claim that the splitting of the e_g metal orbitals into a_{1g} and b_{1g} produced by the distortion in the terpyridine complex accounts for the single reduction to Co(0) (a d^9 system) because the energy difference, $(a_{1g} - b_{1g})$, is too great to allow for a second reduction. Finally, Musumeci and coworkers conclude that two electrons are added simultaneously to the degenerate e_g orbitals in the bipyridine and phenanthroline complexes to give the observed Co(I) (d^8) to Co(–I) (d^{10}) reduction.

It has recently been reported [9], however, that complexes of cobalt with terpyridine and phenyl substituted terpyridines do show a formal Co(0) to Co(–I) reduction which occurs at potentials considerably negative of the potential of the two electron reduction of Co(I) to Co(–I) in the phenanthroline and bipyridine complexes. This fact suggests an alternate mechanism for the two electron reductions in the cobalt bipyridine and phenanthroline complexes which is similar to that proposed for chromium complexes of bipyridine, phenanthroline and terpyridine. In this scheme an apparently anomalous stabilization of the Cr(–I) formal oxidation state by phenanthroline and bipyridine relative to terpyridine was inferred [18]. This mechanism requires that the electron initially added to Co(L)$_3^+$ (where L = phen or bipy) reduces the complex to one containing a ligand anion and a +1 oxidation state cobalt. If the cobalt central atom is capable of acting as a Lewis acid towards the ligand anion it could induce behavior characteristic of a ligand free radical in the coordinated ligand anion. It has been shown that such a ligand free radical will reduce much more easily than the free ligand [19] with the result that the second reduction takes place immediately after the first one, giving an effective two-electron reduction step.

While the mechanism proposed is somewhat speculative, it does appear to fit the overall observed electrochemical behavior of the cobalt imine ligand complexes. The interaction between ligand and metal required by this process will vary with the properties of both the ligand and the metal. If it can be assumed that reduction to such unusual low formal oxidation states as M(0) and M(–I) take place in molecular orbitals which are primarily ligand centered [18], then in both the chromium and cobalt complexes terpyridine appears to be able to undergo reduction on the complex with the least amount of interaction with the metal. In the chromium complexes, phenanthroline exhibits the strongest apparent interaction with the metal, but the effect is not as extreme as that exhibited by both pyridine and phenanthroline with cobalt, reflecting a significant difference in the properties of the two metal atoms in their low-valent complexes. In this context it should be noted that the anti-bonding metal e_g orbitals are not occupied in the chromium complexes until the formal Cr(–I) oxidation state is reached, whereas in the cobalt complexes the redox orbital in all couples observed involves a metal e_g orbital.

The half-wave potentials, *i.e.*, formal redox potentials, in Table II and III can be viewed as a relative measure of the electron donating or accepting capabilities of the *para* substituents studied in this report. Considering first the *para* phenyl complex *vs.* the unsubstituted complex it was observed that the formal redox potentials for the oxidation of

$M(\phi_2bipy)_3^{2+} \rightarrow M(\phi_2bipy)_3^{3+}$ are shifted toward lower energy compared to the corresponding potentials for $M(bipy)_3^{2+} \rightarrow M(bipy)_3^{3+}$. This behavior indicates that the *para* phenyl group is functioning as a weak electron donor which is expected from the value of $\sigma_p = -0.01$ reported by Swain and Lupton [20]. Comparison of the reduction couples for these same complexes *also* shows a shift toward lower energy for the phenyl substituted complex which indicates that the *para* phenyl group can also act as a weak electron acceptor. It must be noted here, however, that this argument is valid if the assumption is made that the free energy of the formation of the phenyl complex, *i.e.*, $M(\phi_2bipy)_3^{2+}$, is equal to or more negative than the unsubstituted complex $M(bipy)_3^{2+}$. This increase in stability of the +2 formal oxidation state for a similar *para* phenyl complex *vs.* the unsubstituted complex has been shown to be valid from consideration of stability constant data and has been previously reported [13]. The bifunctional nature of the *para* phenyl substituent has also been found numerous times in tridentate imine ligand complexes of first row transition metals [9–12]. Comparison of the formal redox potentials for the methyl complex *vs.* the unsubstituted complex, on the other hand, shows that this substituent can function only as an electron donor. Finally, inspection of the data for all complexes studied shows an increase in stability in the order unsubstituted complex < diphenyl complex < dimethyl complex for the high, *i.e.* +3, formal oxidation state and dimethyl complex < unsubstituted complex < diphenyl complex for the lower formal oxidation states.

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