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The Dual Role of *Para*-phenyl Substituents in Aromatic Imine Ligand Complexes of Manganese and Chromium

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The voltammetric behavior of the bis complexes of manganese(II) and chromium(III) with the ligand 2,6-bis(4-phenyl-2-pyridyl)-4-phenyl-pyridine (terosite) has been studied in acetonitrile using DC and AC polarography and cyclic voltammetry. The manganese(II) complex undergoes two one-electron reductions to the +1 and zero formal oxidation states, respectively, and a poorly defined one-electron oxidation to the +3 formal oxidation state. The bis(terosite)chromium(III) complex shows four one-electron reductions to the +2, +2, 0, and −1 formal oxidation states, respectively. Comparison of half-wave potentials is made on the corresponding complexes of manganese and chromium with the ligands: 2,6-bis(2-pyridyl)pyridine(terpyridine) and 2,6-bis(2-pyridyl)-4-phenylpyridine (terosine). Redox potentials and comparisons of behavior are also presented for the cobalt and iron complexes with the three ligands mentioned above. All comparisons indicate that the para *phenyl substituent is able to stabilize both the high and low formal oxidation states of the complexes. Spectroscopic and magnetic data are also given.*

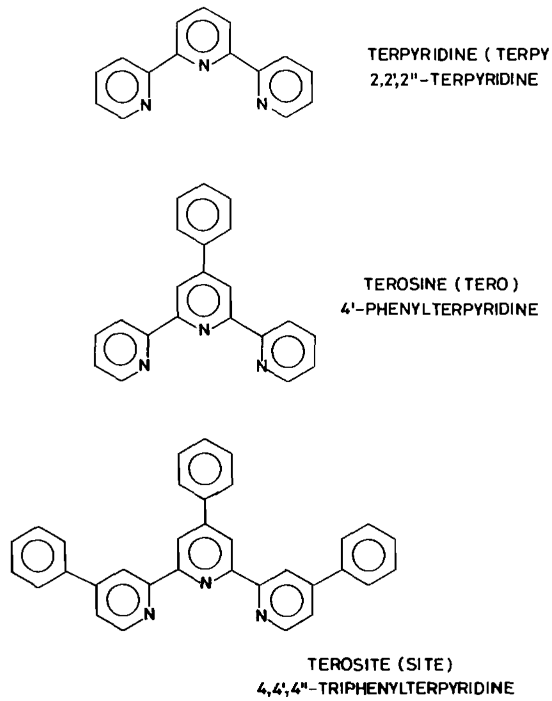

Fig. 1. Ligand structures.

Introduction

Non-aqueous electrochemical measurements have proven to be an excellent technique for the study of reversible multi-membered electron transfer chains in metal coordination compounds. Formal redox potentials obtained from the study of closely related ligand–metal systems can be used to evaluate the relative electron donating or accepting capabilities of either a series of structurally similar ligands or of substituents on a single ligand structure. We have previously reported the effect of *para*-methyl and -phenyl substituents on the stability of high and low oxidation states of aromatic imine ligand complexes of first row transition metals [1–5]. The ligands used in the present study are shown in Fig. 1. These three ligands form an ideal series for the study of the effect of *para*-phenyl substituents. Terpyridine, terosine, and terosite are highly symmetric ligands and all provide the corresponding bis-metal complexes with identical symmetry, *i.e.*, D_{2d}. Terosine and terosite also represent a short series of

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TABLE I. Visible and Ultra-Violet Spectral Information for the Manganese and Chromium Complexes.[a]

	λ (nm)	ϵ	
$Mn(site)^{2+}$	429(sh)	200	2.85×10^{-4} *M*
	343	46,500	
	331	46,000	6.94×10^{-6} *M*
	284	98,700	
	265	99,400	
	239(sh)	87,500	
$Cr(site)^{3+}$	575	648	6.17×10^{-5} *M*
	465(sh)	2,540	
	428(sh)	5,320	
	399(sh)	11,200	
	349(sh)	74,200	
	340	81,700	
	293(sh)	53,500	6.17×10^{-6} *M*
	269	77,800	
	266(sh)	77,500	
	239	72,600	
	218(sh)	79,900	

[a] Solvent = spectro acetonitrile.

varying *para*-phenyl substitution on the terpyridine ligand structure. This report deals with the non-aqueous electrochemistry of the bis(terosite) complexes of manganese(II) and chromium(III), presents data for all three ligands complexed with the first row transition metals chromium, manganese, iron, and cobalt, and discusses the unusual effect of *para*-phenyl substitution on the electrochemistry of aromatic imine ligand complexes of chromium.

Experimental

Terosite (abbreviated, 'site') was purchased from the G. F. Smith Chemical Company and recrystallized three times from chloroform–ethanol to a constant melting point of 259 °C. *Anal.* Calcd. for $C_{33}H_{22}N_3$: C, 85.9; H, 5.02; N, 9.10. Found: C, 85.5; H, 5.24; N, 8.89%. Electrometric grade tetraethylammonium fluoborate, $TEABF_4$, was obtained from Southwestern Analytical Chemical Company and spectrograde acetonitrile was purchased 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 compound $Mn[site]_2[ClO_4]_2$ was prepared by dissolving 0.15 mmol of terosite in 50 ml of hot 50% chloroform–ethanol and reacting with 0.07 mmol of $MnCl_2 \cdot 4H_2O$ dissolved in 15 ml of 50% ethanol–water. Complex formation was ascertained by the appearance of a yellow color. The complex was precipitated with sodium perchlorate and washed with 50% $EtOH–H_2O$. The product was dried at 80 °C *in vacuo* for 24 hours. *Anal.* Calcd. for $Mn[site]_2[ClO_4]_2$: C, 67.3; H, 3.94; N, 7.14. Found: C, 67.2; H, 4.05; N, 7.25%.

$Cr[site]_2[ClO_4]_2$ was prepared in a similar manner from anhydrous $CrCl_2$ using nitrogen deaerated solvents. The Cr(III) product was formed by bubbling chlorine gas into the Cr(II) precipitate–solvent mixture.

Electronic absorption spectra were obtained with a Cary Model 14 and a Cary Model 118 spectrophotometer. Magnetic susceptibilities were determined at room temperature by the Faraday method and elemental analyses were performed by Instranal Laboratories, Renssalear, New York. Voltammetric measurements were carried out in the same manner as described in a previous report [1].

Results and Discussion

Visible and Ultraviolet Spectra

The UV spectrum of the free ligand, terosite, has been reported [2]. Table I summarizes the visible and ultraviolet spectral data for the manganese and chromium complexes. All spectra were run in spectrograde acetonitrile; concentrations indicated in the table are of the perchlorate salt of the respective complex.

Magnetic Susceptibilities

A room temperature magnetic moment of 5.87 B.M. was found for $Mn[site]_2[ClO_4]_2$ indicating an octahedral high spin d^5 configuration [6]. $Mn[terpy]_2[ClO_4]_2$ and $Mn[tero]_2[ClO_4]_2$ also give room temperature moments indicative of a high spin configuration [3]. A diamagnetic correction [$\times 10^6$ cgs] of 317 was measured for terosite and the value of 32 taken for the perchorate anion correction.

Voltammetry

D.C. polarography of the free ligand, terosine, in acetonitrile, has been reported previously [5]. Two irreversible reductions are observed at the DME at −1.92 and −2.18 V *vs.* Ag/AgCl (sat. NaCl). No oxidations are observed at the rotating platinum electrode at potentials up to +1.8 V.

The bis(terosite) manganese(II) complex exhibited two well-defined diffusion controlled, one-electron reduction waves. Fig. 2 shows a DC polarogram and a cyclic voltammogram of the II–I and I–0 reduction processes. Unlike the corresponding terpyridine and terosine complexes of manganese(II), both of which gave evidence of intense adsorption when the techniques of DC polraography and cyclic voltammetry were used [3], the terosite complex

TABLE II. Voltammetric Data for the Complexes.

Complex Couple	D.C. Polarography			Cyclic Voltammetry		A.C. Polarography[b]		
	$E_{1/2}$ (V)	i_d (μA/mM)	slope (mV)	Scan Rate (mV/sec)	ΔEp (mV)	Ep (V)	I_p (μA/mM)	half-width (mV)
Cr(site)$_2$								
III–II	−0.150	2.87	−63	85 Hg	65	−0.147	2.29	89
II–I	−0.486	3.04	−59	85 Hg	65	−0.484	2.29	92
I–0	−0.927	2.68	−59	85 Hg	65	−0.932	2.18	91
0–(–I)	−1.800	2.83	−64	85 Hg	65	−1.80	1.80	91
Mn(site)$_2$								
II–III[a]	+1.19	–	–	–	–	–	–	–
II–I	−1.043	3.19	−58	75 Hg	70	−1.05	1.31	119
I–0	−1.348	2.72	−60	75 Hg	60	−1.35	1.83	93

[a] Done at the rotating platinum electrode (DC). Estimated value (see text). [b] Applied frequency = 23 Hz (Mn complex); 28 Hz. (Cr complex) Applied Potential = 5 mV; IR compensation = 225 ohm. All voltages *vs.* Ag/AgCl sat. Nac. Solvent = spectro acetonitrile. Background electrolyte = 0.1 *M* TEABF$_4$.

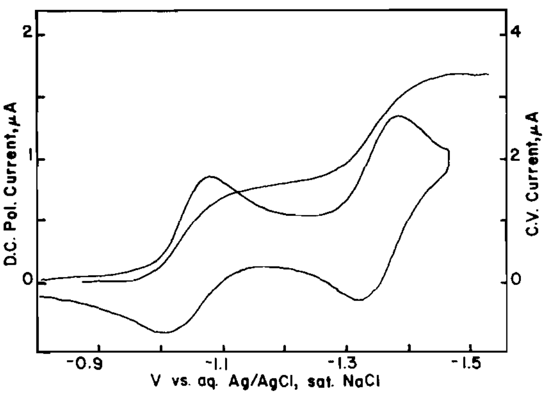

Fig. 2. D.C. polarogram and cyclic voltammogram of 0.30 m*M* Mn(site)$_2$(ClO$_4$)$_2$ in acetonitrile/0.1 *M* TEABF$_4$. C.V. scan rate = 75 mV/sec.

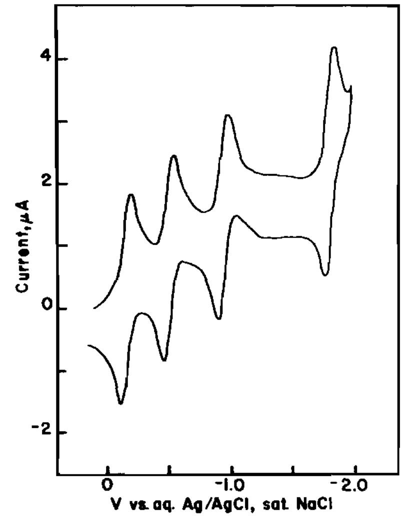

Fig. 3. Cyclic voltammogram on Hg of 0.22 m*M* Cr(site)$_2$-(ClO$_4$)$_3$. Scan rate = 130 mV/sec.

showed no evidence of such surface activity. Cyclic voltammetric peak splittings and DC polarographic log plot slope values for the two reduction processes were in the range expected for reversible one-electron charge transfers (see Table II). Low frequency in-phase AC polarograms exhibited reversible half-width values for the I–0 reduction; however, the II–I wave appears somewhat quasi-reversible. Unlike the compounds, Mn[terpy]$_2$[ClO$_4$]$_2$ and Mn[tero]$_2$[ClO$_4$]$_2$, Mn[site]$_2$[ClO$_4$]$_2$ does not exhibit a well-defined oxidation process at the rotating platinum electrode. Instead the terosite complex shows a poorly-defined oxidation wave which seems to be affected by electrode poisoning probably caused by the oxidation product Mn[site]$_2^{3+}$. It is well known that surface effects on solid electrodes can produce significant changes in recorded current-potential curves [7]. Here the wave definition becomes increasingly poor as repetitive runs are made on the same electrode without electrode treatment. When the platinum electrode was pretreated before each measurement by 15 seconds of oxidation, then 15 seconds of reduction at 1.75 volts in 0.1 *M* HCl, followed by drying and immersion in the acetonitrile solution at +0.8 V for 5 to 10 seconds, a satisfactory oxidation wave was obtained at both the stationary and rotating platinum electrodes. From the current-potential curves obtained, a value of

TABLE III. Formal Redox Potentials for the Cobalt, Iron, Manganese and Chromium Complexes (V).[a]

	II–III	II–I	I–0	0–(–I)
$Co(terpy)_2$	+0.303	−0.747	−1.630	−1.985
$Co(tero)_2$	+0.281	−0.726	−1.545	−1.896
$Co(site)_2$	+0.245	−0.707	−1.498	−1.789
$Fe(terpy)_2$	+1.130	−1.208	−1.364	–
$Fe(tero)_2$	+1.105	−1.176	−1.302	–
$Fe(site)_2$	+1.055	−1.145	−1.272	–
$Mn(terpy)_2$	+1.278	−1.115	−1.455	–
$Mn(tero)_2$	+1.223	−1.071	−1.344	–
$Mn(site)_2$	+1.19	−1.043	−1.348	–
$Cr(terpy)_2$	−0.118	−0.519	−1.027	−1.950
$Cr(tero)_2$	−0.120	−0.487	−1.001	−1.912
$Cr(site)_2$	−0.150	−0.486	−0.927	−1.800
$Cr(bipy)_3$[b]	−0.212	−0.720	−1.285	−1.913
$Cr(\phi_2bipy)_3$[b]	−0.245	−0.666	−1.192	−1.738

[a] Voltages *vs.* Ag/AgCl sat. NaCl. Solvent = spectro acetonitrile. Background electrolyte = 0.1 *M* $TEABF_4$. [b] From ref. (2).

+1.19 volts *vs.* Ag/AgCl (Sat. NaCl) was determined for this II–III oxidation process.

The bis(terosite) chromium(III) complex, and the corresponding terpyridine and terosine complexes, all show four diffusion controlled, one-electron reduction processes to the +2, +1, 0, and −1 formal oxidation states, respectively. Figure 2 shows a cyclic voltammogram of these four reduction waves of $Cr[site]_2[ClO_4]_2$. DC polarographic log plot slopes and cyclic voltammetric peak splitting for all four waves indicate reversible one-electron charge transfers. AC polarographic data also indicate that all four reduction processes are reversible. The electrochemical data are summarized in Table II.

Table III lists values of the formal redox potentials of the various redox couples observed for the complexes of terpyridine, terosine and terosite with Co, Fe, Mn and Cr. As the ligand structure varies in the order given, the metal (III–II) couples all show a negative shift in E^f, indicating a more difficult reduction and an apparently increasing stability of the M(III) oxidation state relative to M(II). For all other couples the E^f values show a positive shift for the same variation in ligand structure, indicating an easier reduction and an apparent stabilization of the lower oxidation state of each couple with respect to the higher. This behavior parallels that reported for a number of other *p*-phenyl substituted aromatic imine ligand complexes [1–5], and has been interpreted to indicate that the *p*-phenyl substituent can function both as a weak electron donor or acceptor depending upon the formal oxidation state of the complex.

For chromium, formal redox potential data is available for a much wider range of imine ligands than for any of the other metals used in this study. We have previously observed that with major changes in ligand structure (*i.e.,* in the series of unsubstituted ligands phenanthroline, bipyridine, terpyridine) [8] and with wide-ranging substitution on the phenanthroline structure [9] the formal redox potential of the Cr(III–II) couple becomes more positive, As the ligand or ligand substituent becomes a better electron acceptor, the formal redox potential of the Cr(III–II) couple becoms more positive, indicating an apparent increasing stabilization of Cr(II) oxidation state relative to Cr(III). Similar data are, unfortunately, lacking for the other metals, but the chromium complex data may be discussed in more detail.

Comparison of standard or formal redox potentials of metal complexes is best done in terms of the electron affinity of the oxidized species [10]:

$$nF(E_1^f - E_2^f) = \epsilon_1 - \epsilon_2 \qquad (1)$$

For a series of complexes of essentially identical structure which show reversible electron transfer with retention of configuration, the electron affinity will be primarily determined by the energy required to effect the electron transfer and by any changes in orbital energies required to accomodate the added electron. Thus, ϵ is a function of the properties of both the oxidized and reduced forms of the complex, and it may be difficult or impossible to discuss changes in formal redox potential with changes in ligand structure or substitution on the basis of the effects on only one member of the couple.

The redox potential behavior reported previously for chromium complexes with imine ligands [8, 9] may be interpreted as indicating that increasing metal–ligand interaction (increasing ligand character of the redox orbital) increases the electron affinity of the Cr(III) complex in a regular fashion. In a series of ligands or substituted ligands, strong electron acceptors then produce a positive shift in E^f relative to weak electron acceptors. In view of this obvious and direct correlation observed between the ligand structure and the Cr(III–II) formal redox potential, and the clearly defined differences between the electronic structures of Cr(II) and Cr(III), it appears that the dominant term governing the value of E^f should be the degree of stabilization of the spin-paired Cr(II) complex.

Where *p*-phenyl substitution on an imine ligand (terpyridine or bipyridine) is concerned, the effect of the substituent becomes ambiguous for all of the cases studied. The *p*-phenyl group is normally regarded as being a weak electron donor ($\sigma_p = -0.010$) [11] and appears to behave in this fashion in all of the M(III–II) couples; in contrast, where low formal oxidation states are involved, *p*-phenyl substitution appears to have pronounced electron withdrawing effect. Table III shows this clearly and gives additional data for the *p*-phenyl substituted bipyridine complex of chromium from reference 2. The formal redox potential of the Cr(III–II) couple becomes increasingly negative with increasing *p*-phenyl substitution on both terpyridine and bipyridine indicating a decreasing electron affinity of the Cr(III) complex, and that *p*-phenyl substitution is influencing the energy of the redox orbital in a way that is quite different from other substituents.

The behavior exhibited by the Cr(III–II) couple in the presence of *p*-phenyl substitution cannot be completely explained using electrochemical data alone. In view of the considerations outlined above, it is not possible to localize the effect of the *p*-phenyl substitution as being primarily on the Cr(II) or the Cr(III) complex, although one would speculate that the major influence of the *p*-phenyl substitution is most likely to be on the Cr(II) complex. It does appear that behavior of the Cr(III–II) couple discussed here provides the clearest example yet found on the dual effect of *p*-phenyl substitution in aromatic imine ligands on the properties of the redox orbitals of such complexes.

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