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Dual Role of *Para*-phenyl Substituents in Aromatic Imine Ligand Complexes of Cobalt and Iron

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The voltammetric behavior of bis complexes of Co(II) and Fe(II) with the ligand 2,6-bis-(4-phenyl-2-pyridyl)-4-phenyl-pyridine (terosite) has been studied in acetonitrile using D. C. and A. C. polarography and cyclic voltammetry. The cobalt(II) complex undergoes three one-electron reductions to the +1, 0 and −1 formal oxidation states, respectively, and one-electron oxidation to Co(site)$_2^{3+}$. *The bis(terosite)iron(II) complex is reduced in two steps to the +1 and zero formal oxidation states and also exhibits a one-electron oxidation to* Fe(site)$_2^{3+}$. *Comparison of half-wave potentials with the corresponding complexes of cobalt and iron with the ligands 2,6-bis(2-pyridyl)pyridine (terpyridine) and 2,6-bis(2-pyridyl)-4-phenylpyridine (terosine) shows that the ligand* para *phenyl groups can function as both weak electron donors and acceptors. Spectroscopic and magnetic data is also given.*

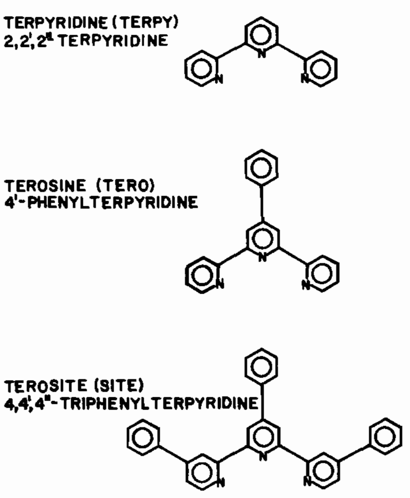

Fig. 1. Ligand Structures.

Introduction

In recent years the use of non-aqueous electrochemistry for the detection of unusual oxidation states in imine ligand complexes of first row transition metals has received considerable attention [1–23]. We have previously reported the non-aqueous polarographic behavior of the bis complexes of Co(II), Fe(II), Mn(II) and Cr(III) with the tridentate imine ligands 2,2'2"-terpyridine and 4'-phenylterpyridine (terosine) [24, 25]. Since then we have extended our investigations to include transition metal complexes formed with phenyl groups fully substituted on the ligand to determine the effect of such phenyl substituents on the redox properties of these complexes. The particular ligand under study is 4,4',4"-triphenylterpyridine (terosite) which was first synthesized by Case and Kasper [26] in 1956. More recently a new synthesis of this compound was reported [27]. Schilt and Smith [28] studied the spectrophotometric constants of the bis complexes of terosite with Fe(II), Co(II) and Cu(I). The few other studies of terosite which have been reported concern its use in the spectrophotometric determination of iron [29–31] and an ESR study of alkaline earth metal terosite complexes [32]. The major difficulty encountered with the use of this ligand is its extreme insolubility in both aqueous and non-aqueous solvents; chloroform and 50–50 chloroform–ethanol mixture being the only solvent systems in which it has been shown to be reasonably soluble [28]. Figure 1 shows the structure of the three ligands: terpyridine, terosine and terosite.

Experimental

Terosite was obtained from the G. Frederick Smith Chemical Company and recrystallized three

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*Present Address: Allied Chemical Corporation, Syracuse Research Laboratory, P.O. Box 6, Syracuse, N.Y. 13209, U.S.A.

TABLE I. Elemental Analysis of Complexes.

Compound	C%		H%		N%	
	Calc.	Found	Calc.	Found	Calc.	Found
Co(terpy)$_2$(ClO$_4$)$_2$	49.7	49.0	3.06	2.99	11.6	11.6
Co(tero)$_2$(ClO$_4$)$_2$	57.5	57.3	3.45	3.56	9.59	9.63
Fe(tero)$_2$(ClO$_4$)$_2$	57.7	56.9	3.46	3.64	9.62	9.45

TABLE II. Ultraviolet and Visible Spectra of Terosite and its Complexes. (Solvent = Spectrograde Acetonitrile)

Terosite	9.89 x 10^{-6} *M*	294 nm (sh) (1.88 x 10^4) 250 nm (7.19 x 10^4)
Co(site)$_2^{2+}$	9.86 x 10^{-6} *M*	235 nm (sh) (7.98 x 10^4) 241 nm (8.30 x 10^4) 275 nm (sh) (9.88 x 10^4) 280 nm (9.91 x 10^4) 327 nm (6.12 x 10^4)
	2.07 x 10^{-4} *M*	460 nm (1.37 x 10^3) 475 nm (sh) (3.00 x 10^3) 521 nm (3.39 x 10^3) 565 nm (1.37 x 10^3)
Fe(site)$_2^{2+}$	9.04 x 10^{-6} *M*	237 nm (sh) (7.56 x 10^4) 245 nm (8.42 x 10^4) 269 nm (8.93 x 10^4) 285 nm (9.31 x 10^4) 327 nm (sh) (5.68 x 10^4) 337 nm (7.12 x 10^4)
	2.02 x 10^{-5} *M*	378 nm (1.98 x 10^4) 505 nm (sh) (9.46 x 10^3) 538 nm (sh) (1.34 x 10^4) 562 nm (sh) (1.83 x 10^4) 576 nm (2.85 x 10^4) 623 nm (sh) (6.63 x 10^3)

times from chloroform–ethanol to a constant melting point of 259 °C. *Anal.* Calcd. for $C_{33}H_{23}N_3$: 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 spectro grade acetonitrile was purchased from Matheson, Coleman and Bell Manufacturing Chemists. All other chemicals were reagent grade and were used as received. High purity nitrogen was washed with acetonitrile before use.

The compounds Co(site)$_2$(ClO$_4$)$_2$ [site = terosite] and Fe(site)$_2$(ClO$_4$)$_2$ were prepared by dissolving 0.21 mmol of terosite in 50 ml of hot 50% chloroform–ethanol and reacting with 0.10 mmol of $CoCl_2 \cdot 6H_2O$ or $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ dissolved in 15 ml of 50% ethanol–water. With this particular ratio of $CHCl_3$:EtOH:H_2O, the reaction solution was completely miscible. Complex formation was ascertained by the appearance of a deep red and intense violet color for the Co(II) and Fe(II) complexes, respectively. The complexes were precipitated with sodium perchlorate and washed with 50% $CHCl_3$/EtOH and 50% EtOH/H_2O and then recrystallized from 2-methoxyethanol. The recrystallized products were dried at 85 °C *in vacuo* for 15 hours and characterized by their absorption spectra [28]. Elemental analyses were also obtained (Table I); as all compounds were prepared and purified by the same methods, results for several representative compounds are listed in Table I. Solutions for the absorbance and voltammetric measurements were prepared from the perchlorate salt of the appropriate complex.

Electronic absorption spectra were taken with a Cary Model 14 recording spectrophotometer using Norell 10 mm Spectrosil cells. Magnetic susceptibilities were determined at room temperature by the Faraday method. Voltammetric measurements were carried out in the same manner as described previously [24].

Results and Discussion

Magnetic Susceptibilities

A room temperature magnetic moment of 4.88 B.M. was found for $Co(site)_2(ClO_4)_2$ which would indicate an octahedral high spin d^7 configuration [33]. $Co(terpy)_2(ClO_4)_2$ (terpy = terpyridine) and $Co(tero)_2(ClO_4)_2$ (tero = terosine) also gave room temperature moments indicative of the high-spin configuration [24]; it should be noted that a detailed temperature magnetic study of $Co(terpyridine)_2(ClO_4)_2$ indicates that the terpyridine complex is close to the cross-over point [34]. $Fe(site)_2(ClO_4)_2$ gave a diamagnetic moment indicating low spin d^6 octahedral configuration which is not unexpected since both $Fe(terpy)_2(ClO_4)_2$ and $Fe(tero)_2(ClO_4)_2$ also exhibited diamagnetic moments [24]. A measured diamagnetic correction ($\times 10^6$ cgs) of 317 was measured for terosite and 32 was taken for the perchlorate anion correction.

Visible and Ultraviolet Spectra

Terosite showed one peak and a shoulder in the U.V. region using spectro grade acetonitrile as solvent (Table II). The ultraviolet and visible spectral data for the complexes are also summarized in Table II. Molecular orbital calculations for iron complexes of phenanthroline (35) and bipyridine (36) have shown that the intense absorbance observed in the 500 nm region, corresponding to the maximum absorbance in the visible region of the spectrum, is due to the change transfer transition of an electron from the 3dπ orbital (primarily metal localized) to the lowest vacant MO of the ligand. In view of the structures of the present ligands, it seems reasonable to conclude that the maximum absorbance bands found in the 550 to 575 nm region for the iron complexes (Table III) correspond to this same charge transfer transition. This conclusion is supported by the shift in λ_{max} towards lower energy in the order $Fe(terpy)_2^{2+} > Fe(terosine)_2^{2+} > Fe(site)_2^{2+}$. Bathochromic shifts in metal-to-ligand charge transfer bands indicate increased stability [37], and therefore such a shift in the series of complexes where the formal oxidation state is +2 can be ascribed to the effect of the addition of equivalent *para* phenyl groups onto the complex.

TABLE III. Comparison of λ_{max} in the Iron(II) Complexes.

	λ_{max} (χω)	ϵ
$Fe(terpyridine)_2^{2+}$	552	11.900
$Fe(terosine)_2^{2+}$	565	22.600
$Fe(terosite)_2^{2+}$	576	28.500

Solvent = Spectrograde Acetonitrile

Voltammetry

D. C. polarography of the free ligand, terosite, shows two reduction waves at −1.92 and −2.18 volts *vs.* the Ag/AgCl, sat. NaCl electrode, respectively. Plots of E *vs.* log $[i/(i_d - i)]$gave slopes of 65 and 91 mV for the first and second wave with a current-to-concentration ratio for the first wave of 5.7 μA/m*M* and that of the second wave about three times larger. Cyclic voltammetry of the second wave at scan rates greater than 100 mV/sec, however, shows a shoulder midway up the cathodic portion of the cyclic voltammogram. At CV scan rates of from 25 to 250 mV/sec no anodic peaks were evident for any of the reduction steps of terosite indicating that all the reduction processes are irreversible. No oxidation wave was observed for terosite out to a potential of +1.8 volts.

the cobalt complex. Four well-defined waves are evident: one oxidation and three reductions. The first-wave has been assigned to the oxidation: $Co(site)_2^{2+} \rightarrow Co(site)_2^{3+}$ and the second, third and fourth waves to the reductions, seriatim: $Co(site)_2^{2+} \rightarrow Co(site)_2^{+}$; $Co(site)_2^{+} \rightarrow Co(site)_2^{0}$ and $Co(site)_2^{0} \rightarrow Co(site)_2^{-1}$. All four waves were shown to be diffusion controlled by a column height study, *i.e.*, $i_d/h^{1/2}$ is constant at varying mercury column height. Plots of E *vs.* log $[i/(i_d - i)]$from the D. C. polarograms gave straight lines with slopes close to 59 mV indicating all waves to be reversible one-electron charge transfers. A cyclic voltammogram of the bis(terosite)-cobalt(II) complex appears in Fig. 3. The cyclic voltammetric peak splittings for the four electrochemical processes of the cobalt complex gave values close to 60 mV and low frequency in-phase A.C.

TABLE IV. 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)	Ip (μA/mM)	half-width (mV)
Co(site)$_2$								
II–III	+0.245	2.94	63	45 Hg	60	+0.249	3.48	93
II–I	–0.707	2.72	61	45 Hg	60	–0.696	3.35	92
I–0	–1.498	3.00	60	120 Hg	65	–1.485	2.90	92
0–(–I)	–1.789	3.20	58	120 Hg	65	–1.775	2.52	96
Fe(site)$_2$								
II–III[a]	+1.055	–	60	130 Pt	57	–	–	–
II–I	–1.145	2.51	59	130 Pt	65	–1.142	2.29	92
I–0	–1.272	2.48	61	130 Pt	65	–1.266	2.24	90

[a] Done at the rotating platinum electrode (DC). [b] Applied Frequency = 28 Hz; Applied Potential = 5 mV; IR compensation = 225 ohms. All voltages *vs.* Ag/AgCl sat. NaCl. Solvent = spectroacetonitrile. Background electrolyte = 0.1 M TEABF$_4$.

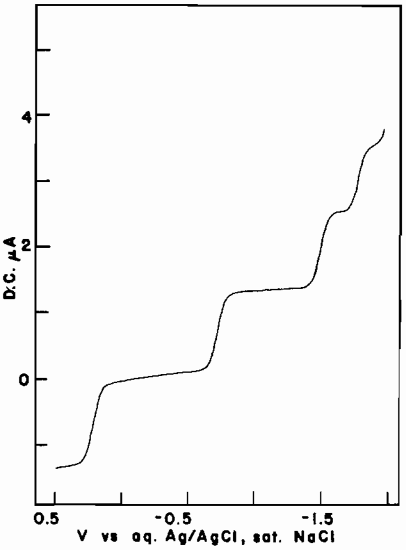

Fig. 2. D. C. polarogram of 0.325 mM Co(site)$_2$(ClO$_4$)$_2$.

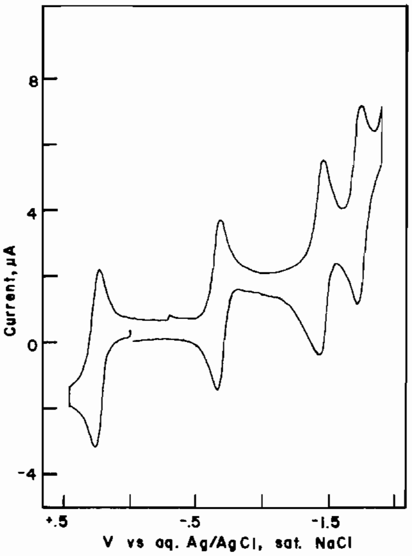

Fig. 3. Cyclic voltammogram on Hg of 0.325 mM Co(site)$_2$-(ClO$_4$)$_2$. Scan rate = 125 mV/sec.

polarograms showed half peak widths close to 92 mV indicating all four waves to be reversible one-electron charge transfers.

The bis(terosite)iron(II) complex exhibited two closely spaced diffusion controlled reduction waves (Fig. 4). The voltammetric results are consistent with reversible one-electron charge transfers to Fe(site)$_2^+$ and Fe(site)$_2^0$, respectively. At the rotating platinum electrode, Fe(site)$_2^{2+}$ shows a one-electron oxidation to the +3 formal oxidation state (Fig. 5). Both E *vs.* log[i/(i$_d$ – i)] plots and cyclic voltammetric data indicate this wave to be due to a reversible, one-electron charge transfer. Table IV summarizes the voltammetric data observed for the cobalt and iron bis terosite complexes.

In Table V are listed the values of the half-wave potentials for the bis complexes of cobalt and iron with the ligands terpyridine, terosine and terosite. Comparing the potentials for each complex couple of a given metal shows a shift toward lower energy in the order: terpyridine complex > terosine complex > terosite complex for all couples. Note that the shift is in the same direction and order as that observed for the spectrophotometric data taken on the divalent iron complexes. Comparisons of redox potential data with spectrophotometric data for the cobalt(II) complexes is impossible since no definitive theoretical or experimental characterizations of cobalt(II)–imine ligand complex spectra have been reported. Reference to Table V shows that

TABLE V. Comparison of the Half-Wave Potentials for the Phenyl Substitued Terpyridine Complexes.

	II–III	II–I	I–0	0–(–I)
Co(terpyridine)$_2$	+0.303	–0.747	–1.630	–1.985
Co(terosine)$_2$	+0.281	–0.726	–1.545	–1.896
Co(terosite)$_2$	+0.245	–0.707	–1.498	–1.789
Fe(terpyridine)$_2$	+1.130	–1.208	–1.364	–
Fe(terosine)$_2$	+1.105	–1.176	–1.302	–
Fe(terosite)$_2$	+1.055	–1.145	–1.272	–

Voltages *vs.* Ag/AgCl sat. NaCl. Solvent = Spectrograde Acetonitrile. Background Electrolyte = 0.1 *M* TEABF$_4$.

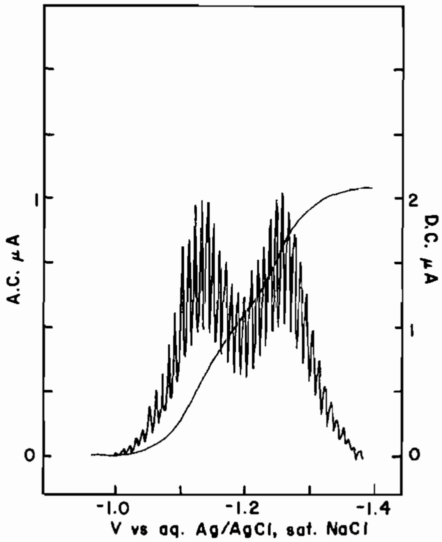

Fig. 4. D. C. and A. C. Polarograms of 0.346 m*M* Fe(site)$_2$-(ClO$_4$)$_2$ showing the II → I and I → 0 reduction waves.

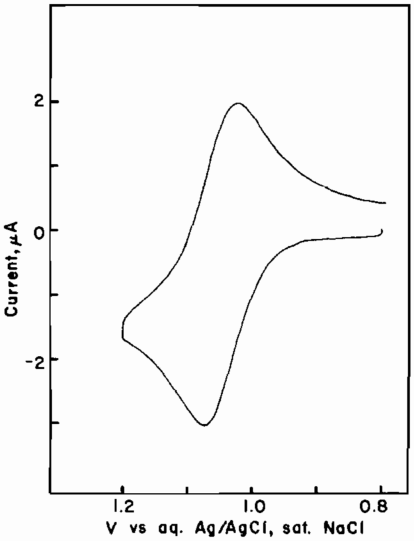

Fig. 5. Cyclic Voltammogram on platinum of 0.346 m*M* Fe(site)$_2$(ClO$_4$)$_2$ for the II–III couple. Scan rate = 130 mV/sec.

the redox behavior of the cobalt complexes gives a pattern identical to that of the iron complexes. On this basis, it seems reasonable to assume that the stabilization effects discussed in detail below for the iron complexes are equally valid for the cobalt complexes. Assuming that the values of the free energies of formation of the divalent species are all equal or in the order: M(terosite)$_2^{2+}$ more negative than M(terosine)$_2^{2+}$ more negative than M(terpyridine)$_2^{2+}$, then the observed half-wave potential shifts indicate that all oxidation states of each complex are stabilized with M(site)$_2^n$ more stable than M(tero)$_2^n$ and M(tero)$_2^n$ more stable than M(terpy)$_2^n$. This assumption is supported by comparing reported values for log β_3, the overall formation constant, of 21.3 and 21.8 for Fe(phenanthroline)$_3^{2+}$ and Fe(4,7-diphenylphenanthroline)$_3^{2+}$, respectively [38] The four and seven positions in the phenanthroline complexes are symmetrically para to the central metal atom just as the 4, 4′ and 4″ positions in the terpyridine complexes. This evidence along with the increased stability noted for the divalent species in the order M(terpyridine)$_2^{2+}$ < M(terosine)$_2^{2+}$ < M(terosite)$_2^{2+}$ from a comparison of the charge transfer bands in the visible spectra suggests that it is reasonable to conclude that in these complexes the para phenyl groups are playing a dual role, *i.e.*, electron accepting in the case of the lower oxidation states and electron donating in the higher oxidation states.

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