Voltammetry of Terpyridine and Terosine Complexes of Cobalt(II) and Iron(II)

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Received July 24, 1974

The voltammetric behavior of cobalt(II) and iron (II) bis complexes with the tridentate ligands, 2,6-bis (2-pyridyl)pyridine (terpyridine) and 2,6-bis(2-pyrid-yl)-4-phenylpyridine (terosine) is described. Using D.C. and A.C. polarography and cyclic voltammetry the cobalt(II) complexes undergo three one-electron reductions: $Co(L)_2^{2+} \rightarrow Co(L)_2^+$; $Co(L)_2^+ \rightarrow Co(L)_2^0$ and $Co(L)_2^0 \rightarrow Co(L)_2^{-1}$. The iron(II) complexes are reduced to the +1 and zero formal oxidation states. All complexes show a one-electron oxidation to the +3 formal oxidation state. Spectroscopic and magnetic data for the complexes are also given.

Introduction

In recent years several reports concerning the non-aqueous electrochemistry of complexes of cobalt and iron with the imine ligands 1,10-phenanthroline, 2,2'-bipyridine and 2,2',2''-terpyridine have appeared[1–9] with much of the attention centering on the unusual stability of low formal oxidation states of these complexes. The present investigation focuses on the electrochemistry of the bis complexes of iron(II) and cobalt (II) with the ligands 2,6-bis(2-pyridyl)-4-phenyl-pyridine (terosine)[10] and 2,6-bis(2-pyridyl)pyridine (terpyridine).

The visible spectra of the bis(terosine) iron(II) and cobalt(II) complexes have been reported by Wilkins and Smith[11] while the spectra of the terpyridine complexes of these metals have been extensively studied[12–13]. The voltammetric behavior of the bis(terpyridine) complexes of iron(II), cobalt(II) and chromium (II) has been studied in aqueous media where each was shown to reduce in one step to $Fe(terpy)_2^0$, $Co(terpy)_2^+$ and $Cr(terpy)_2^+$, respectively[14–16]. In aqueous media, likewise, $Fe(tero)_2^{2+}$ and $Co(tero)_2^{2+}$ each show one step reductions to $Fe(tero)_2^0$ and $Co(tero)_2^+$, respectively[17]. Musemeci *et al.*[5], report that in acetonitrile $Co(terpy)_2^{2+}$ undergoes only a two step reduction to the +1 and zero formal oxidation states; however, more recently we have noted evidence for a third reduction of this complex to a formal oxidation state of $Co(-1)$[18].

Experimental

Terosine and 2,2',2''-terpyridine were obtained from the G. Frederick Smith Chemical Company. Terpyridine was used as received; terosine was recrystallized three times from nitromethane to a constant melting point of 206° C. *Anal.* Calcd. for terosine, $C_{21}H_{15}N_3$: C, 81.5; H, 4.89; N, 13.6. Found: C, 81.2; H, 4.92; N, 13.8. Electrometric grade tetraethylammonium fluoborate (TEABF$_4$) was obtained from Southwestern Analytical Chemical Company, and spectro grade acetonitrile was purchased from Eastman Organic Chemicals. All other chemicals were reagent grade and were used as received. High purity nitrogen was washed with acetonitrile before use.

The compounds $Co(tero)_2(ClO_4)_2$, $Fe(tero)_2(ClO_4)_2$, $Co(terpy)_2(ClO_4)_2$ and $Fe(terpy)_2(ClO_4)_2$ were prepared by mixing 1.2 milligram-mol of the ligand dissolved in hot absolute ethanol with 0.5 milligram-mol of $CoCl_2 \cdot 6H_2O$ or $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ dissolved in a minimum amount of triply distilled water. The complexes were precipitated with sodium perchlorate, washed with 50% ethanol–water and then recrystallized from ethanol. The recrystallized product was dried at 85° C *in vacuo* over P_2O_5 for 6 hours. *Anal.* Calcd. for $Fe(tero)_2(ClO_4)_2$: C, 57.7; H, 3.46; N, 9.62. Found: C, 56.9; H, 3.64; N, 9.45. Calcd. for $Co(tero)_2(ClO_4)_2$: C, 57.5; H, 3.45; N, 9.59. Found: C. 57.3; H, 3.56; N, 9.63.

Electronic absorption spectra were taken with a Cary Model 14 recording spectrophotometer. Infra-red spectra were run as Nujol mulls on KBr discs (2000 to 600 cm^{-1}) and polyethylene plates (600 to 200 cm^{-1}) using a Perkin–Elmer Model 521 spectrophotometer. Magnetic susceptibilities were determined at room temperature by the Faraday method and elemental analyses were performed by Instranal Laboratories, Rensselear, New York.

DC polarograms and cyclic voltammograms were obtained with an instrument assembled from solid state operational amplifiers and standard electronic components.[19,20] AC polarograms were run on an instrument which employs a standard operational ampli-

fier potentiostat in conjunction with a Princeton Applied Researches Model 121 Lock-In Amplifier. Positive feedback IR compensation was employed to minimize the effect of cell resistance. All polarograms were recorded on a Hewlett–Packard Model 7001-A XY recorder. A conventional polarographic H-cell was used and all electrochemical potential measurements were referred to an aqueous silver/silver chloride saturated sodium chloride electrode. An ultrafine fritted glass disc was used to separate the aqueous reference electrode from the polarographic background solution ($0.1M$ TEABF$_4$ in acetonitrile) which in turn was isolated from the depolarizer solution by another fritted glass disc contained in the H-cell. A platinum wire served as the counter electrode. All measurements were made at ambient temperature ($24° \pm 2°$C).

Results and Discussion

IR Spectra

Table I gives the principal infra-red absorption bands for terosine and the bis terosine complexes. The assignments are made by comparison with those reported for 2,2′,2″-terpyridine.[21,22] The changes in the ligand spectrum in the 1500 to 1600 cm^{-1} region upon complexation parallel those observed for other imine ligand complexes;[23,24] however, there are no absorption bands in the 300 to 500 cm^{-1} region which can be unambiguously assigned to v(M–N).

Visible Spectra

Visible spectral data for Co(tero)$_2$(ClO$_4$)$_2$ and Fe(tero)$_2$(ClO$_4$)$_2$ are summarized in Table II. The

TABLE I. Infra-Red Spectra.

Terosine	Co(tero)$_2$(ClO$_4$)$_2$	Fe(tero)$_2$(ClO$_4$)$_2$	
1600 (m)	1599 (m)	1603 (m)	
1583 (st)	1580 (m)		C=C and C=N stretch
1565 (m)	1547 (m)	1530 (m)	
1546 (m)			
1500 (w)			
1260 (w)	1297 (w)	1290 (w)	ring vibration
	1240 (w)	1240 (w)	
	1070 (st br)	1070 (st br)	ClO$_4^-$
1065 (w)			ring vibration and
1035 (w)			C–H deformation
985 (w)			pyridine ring breathing
890 (m)	873 (w)	870 (w)	
792 (m)	787 (w)	788 (m)	ring hydrogens
755 (st)	760 (st)	760 (st)	
730 (m)	723 (m)	722 (m)	
678 (m)	685 (w)	690 (w)	
655 (w)	655 (w)	652 (w)	
611 (m)			
	615 (st)	617 (st)	ClO$_4^-$
490 (m)	490 (m)	501 (m)	
443 (w)	395 (w)	458 (m)	
355 (w)			

individual molar extinction coefficients were determined at different concentrations of the perchlorate salt of the respective complex in 50% ethanol–water solution. The molar extinction coefficients presented in Table II are considerably greater than the values reported previously by Wilkins and Smith.[11] More care in the purification of the terosine ligand and the metal complexes is probably the reason for the higher value.

Magnetic Susceptibilities

Room temperature magnetic moments of 4.15 and 4.00 B.M. were found for $Co(tero)_2(ClO_4)_2$ and Co $(terpy)_2(ClO_4)_2$, respectively. These values correspond to a high spin d^7 octahedral configuration.[25] Both $Fe(tero)_2(ClO_4)_2$ and $Fe(terpy)_2(ClO_4)_2$ were observed to be diamagnetic at room temperature indicating a low spin d^6 octahedral configuration. Diamagnetic corrections ($\times 10^6$ cgs) of 233 and 298 were measured for terpyridine and terosine, respectively, and 32 was taken for the perchlorate anion correction.

Voltammetry

DC polarography of the free ligands showed a well-defined reduction wave at –2.07 and –1.98 volts *vs.* Ag/AgCl sat. NaCl for terpyridine and terosine, respectively. Voltammetric data for the ligands is summarized in Table III. Cyclic voltammetry at scan rates similar to those used for the complexes showed no anodic peak for terpyridine. Terosine, on the other hand, exhibited both cathodic and anodic peaks with peak potential separations greater than that corresponding to a reversible process. No oxidation wave could be observed for either ligand out to a potential as positive as +1.8 volts *vs.* Ag/AgCl, sat. NaCl, at the rotating

platinum electrode; however, at the D.M.E. a reversible one electron oxidation at +0.161 and +0.177 volts was observed for terpyridine and terosine, respectively. This wave is attributed to the oxidation of mercury and its subsequent complex formation with the ligand.

Table IV summarizes the voltammetric data observed for the bis complexes. Both $Co(tero)_2^{2+}$ and Co $(terpy)_2^{2+}$, each exhibit three diffusion controlled reduction waves and one diffusion controlled oxidation wave, *i.e.*, $i_d/h^{1/2}$ is constant at varying mercury column height. Figure 1 shows a typical DC polarogram for 0.4 mM $Co(tero)_2^{2+}$ in acetonitrile. Plots of E *vs.* $\log[i/(i_d-i)]$ for all waves gave straight lines with slopes very close to the value of 59.2 mV expected for a reversible one-electron charge transfer. Cyclic voltammetric data for the oxidation wave and the first two reduction waves of each complex show peak potential separations of 60–65 mV and identical anodic and cathodic peak currents indicating that these waves

TABLE II. Visible Spectra.[a]
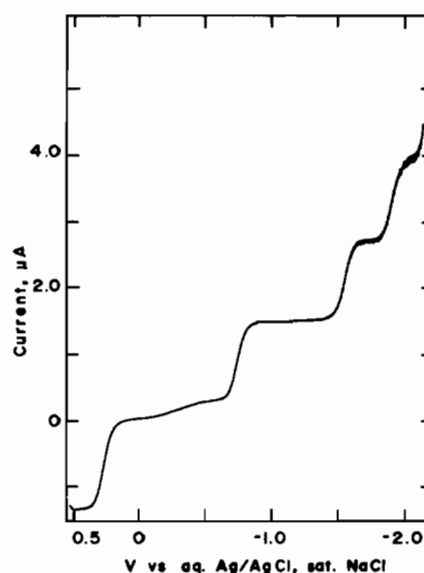
	λ_{max} (nm)	ε
$Fe(tero)_2(ClO_4)_2$	565	$24,700 \pm 100$
$Co(tero)_2(ClO_4)_2$	514	2790 ± 20
	447	2730 ± 20

[a]Solvent = 50% EtOH–H₂O.

Figure 1. D. C. polarogram of 0.382 mM $Co(tero)_2(ClO_4)_2$ in spectro acetonitrile and 0.1 M TEABF₄.

TABLE III. Comparison of the First Ligand Reduction with the Third Cobalt Complex Reduction.[a]

	$E_{1/2}$ (V)	Slope (mV)	$i_1 \dfrac{\mu A}{mM}$	C.V. ΔEp(mV)	A.C. half-width (mV)
Terpy	–2.07	–47	4.74	NRP	90
Co(terpy)₂	–1.99	–59	3.24	100	86
Tero	–1.98	–88	4.36	175	140
Co(tero)₂	–1.90	–55	3.32	120	91

[a]NRP = no reverse peak. All voltages *vs.* Ag/AgCl sat. NaCl. Solvent = spectro acetonitrile. Background electrolyte = 0.1 M TEABF₄.

TABLE IV. Voltammetric Data for the Complexes.

Complex Couple	D.C. Polarography				Cyclic Voltammetry			A.C. Polarography[c]	
	$E_{1/2}$(V)	$i_d\left(\dfrac{\mu A}{mM}\right)$	Slope (mV)	$i_d/h^{1/2}$ [b]	Scan Rate $\left(\dfrac{mV}{sec}\right)$	ΔEp (mV)	Ep (V)	$lp\left(\dfrac{\mu A}{mM}\right)$	half-width (mV)
Co(tero)$_2$									
II→III	+ .281	−3.04	+59	.19±.00	35 Hg	60	+ .292	−2.65	90
II→I	− .726	2.70	−60	.16±.00	35 Hg	60	− .713	2.54	93
I→0	−1.545	2.64	−56	.16±.00	35 Hg	65	−1.532	2.11	94
0→−I	−1.896	3.32	−55	.17±.01	35 Hg	120	−1.880	1.88	91
Co(terpy)$_2$									
II→III	+ .303	−2.87	+59	.40±.00	125 Hg	65	+ .310	−2.50	89
II→I	− .747	2.74	−57	.38±.00	125 Hg	60	− .735	2.47	91
I→0	−1.630	2.93	−60	.39±.00	125 Hg	65	−1.615	2.05	91
0→−I	−1.985	3.24	−59	.37±.00	125 Hg	100	−1.970	1.83	86
Fe(tero)$_2$									
II→III[a]	+1.105	–	+65	–	100 Pt	60	–	–	–
II→I	−1.176	2.62	−60	.27±.00	50 Pt	65	−1.170	1.90	98
I→0	−1.302	2.70	−58	.23±.01	50 Pt	65	−1.298	2.03	91
Fe(terpy)$_2$									
II→III[a]	+1.130	–	+60	–	125 Pt	62	–	–	–
II→I	−1.208	3.17	−61	.35±.00	125 Pt	60	−1.197	2.36	92
I→0	−1.364	3.19	−55	.33±.01	125 Pt	67	−1.354	2.27	94

[a] Done at the rotating platinum electrode (DC). [b] Data taken at 4 different column heights. [c] Applied frequency = 22 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$_4$.

are due to reversible one-electron charge transfer processes. Low frequency AC polarograms (Figure 2) show half-peak widths close to the value of 92 mV[26] expected for a one-electron reversible charge transfer.

It has been reported[5] that the third reduction wave of Co(terpy)$_2^{2+}$ in acetonitrile is a reduction of the free ligand produced by the breakup of the complex after the reduction Co(terpy)$_2^+ \rightarrow$ Co(terpy)$_2^0$ occurs. This conclusion was based on the fact that the addition of excess terpyridine to a solution of the Co(terpy)$_2^{2+}$ complex resulted in a large increase in the height of the third reduction wave. This effect has been observed by us as well for both the terpyridine and terosine complexes of cobalt(II); however, our interpretation is that the third reduction wave of the complex is being masked by the very large first reduction wave of the free ligand. Evidence for this interpretation is obtained from a study of polarograms taken on a series of solutions in which the ratio of metal ion to free ligand was systematically varied from essentially 0 to over 0.5. At the exact stoichiometric ratio of the bis complex, *i.e.*, a metal ion to ligand ratio of 0.500, a third one-electron wave appears at −1.896 and −1.985 volts *vs.* Ag/AgCl, sat. NaCl for the terosine and terpyridine cobalt complexes, respectively. At all metal to ligand ratios lower than 0.5 a much larger wave with a half-wave potential

close to that for the first reduction wave of the free ligand can only be discerned.
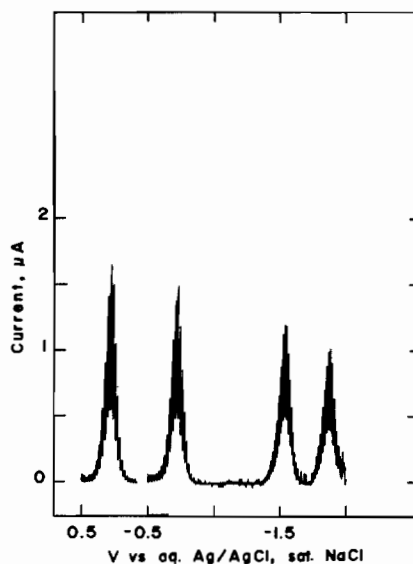

Figure 2. A. C. polarogram of 0.382 mM Co(tero)$_2$(ClO$_4$)$_2$ in spectro acetonitrile and $0.1 M$ TEABF$_4$.

The voltammetric behavior of the third reduction wave corresponding to a formal 0→−1 reduction in both cobalt complexes (Tables III and IV) cannot at this time be unambiguously interpreted. With the exception of the cyclic voltammetric results the data presented for the third reduction wave of both cobalt complexes show voltammetric behavior with respect to reversibility which is much more characteristic of complex reductions than that of the free ligand reduction (Table III). The large peak potential separation in the cyclic voltammetric data for the 0→−I wave could be due to either a slow chemical reaction following the reduction or to distortion of the cyclic voltammogram by the large free ligand wave which immediately follows the third reduction wave. The appearance of this large fourth reduction wave (free ligand) for the cobalt terosine complex can be seen in Figure 1. In this regard, the authors have since observed normal reversible behavior of the formal 0→−I reduction in a cobalt complex with a different phenyl substituted terpyridine for which this third reduction wave and following free ligand reduction were more clearly separated.[27]

All of the above considerations point to the conclusion that the third reduction wave in both of these complexes is a complex reduction to a formal oxidation state of Co(−I). That this complex has no long term stability in solution is indicated by the presence of a free ligand reduction wave following the formal Co(0) →Co(−I) reduction step of the complex. This formal Co(0)→Co(−I) complex reduction most likely falls into the same category as that described for the Cr (0)→Cr(I) reduction in chromium diimine complexes in that the redox orbital is localized primarily on the ligand instead of the metal.[28] This could account for the behavior of the Co(0)→Co(−I) reduction, where the current-to-concentration ratio is larger than that of the other complex reduction waves, while at the same time reduction occurs at lower energy and more reversibly than that of the free ligand.

The corresponding iron complexes, $Fe(tero)_2^{2+}$ and $Fe(terpy)_2^{2+}$, each exhibit two poorly separated diffusion controlled reduction waves which are better defined with AC than with DC polarography (see Figures 3, 4). As shown in Table III, however, the voltammetric data are consistent with reversible, one-electron charge transfers to formal oxidation states of $Fe(L)_2^+$ and $Fe(L)_2^0$, respectively. At the rotating platinum electrode both $Fe(tero)_2^{2+}$ and $Fe(terpy)_2^{2+}$ show an oxidation wave which occurs at very positive potentials. Both E *vs.* $\log[i/(i_d−i)]$ plots and cyclic voltammetric data indicate that these oxidation waves are also due to reversible, one electron charge transfers.

Comparing the half-wave potentials for each complex couple of a given metal makes it appear that terosine stabilizes all oxidation states of both the iron and cobalt complexes better than terpyridine. This may be due to the ability of the phenyl group to func-
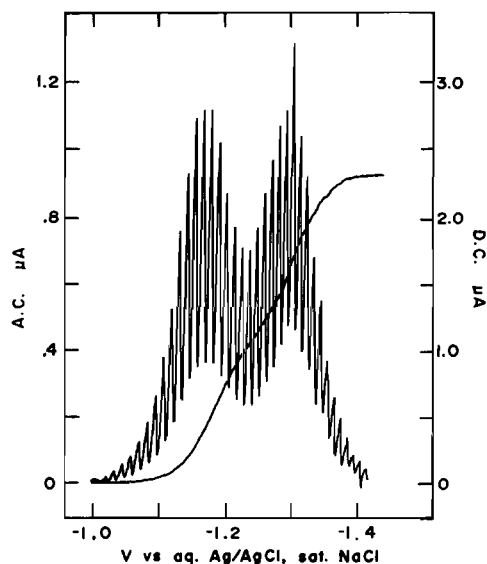

Figure 3. A. C. and D. C. polarograms of 0.366 mM Fe(tero)$_2$ (ClO$_4$)$_2$ in spectro acetonitrile and 0.1M TEABF$_4$.
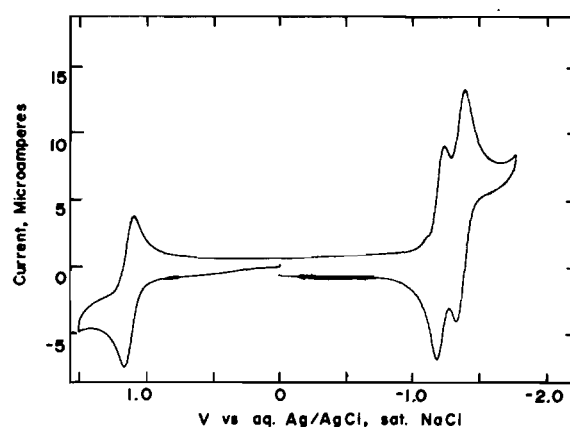
Figure 4. Cyclic voltammogram on platinum of 0.984 mM Fe(terpy)$_2$(ClO$_4$)$_2$ in spectro acetonitrile and 0.1M TEABF$_4$.

tion both as a weak electron donor *and* acceptor *via* resonance coupling to the terpyridine ring system. The validity of this conclusion depends on the values of the formation constants and thermodynamic parameters for the various complexes. This work is presently being done at this laboratory.

Acknowledgement

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