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Redox Behavior of Aromatic Tridentate Imine Ligand Complexes of Manganese and Chromium[1]

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The voltammetric behavior of bis complexes of 2,6-bis(2-pyridyl)pyridine (terpyridine) and 2,6-bis(2-pyridyl)-4-phenylpyridine (terosine) with manganese-(II) and chromium(III) have been studied in acetonitrile using D.C. and A.C. polarography and cyclic voltammetry. The bis complexes of chromium(III) each undergo four one-electron reductions to the +2, +1, 0 and –1 formal oxidation states, respectively. The divalent manganese complexes each are reduced in two steps to the +1 and zero formal oxidation states and also each exhibit a one-electron oxidation to $Mn(L)_2^{3+}$*. Spectroscopic and magnetic data are also given.*

Introduction

The electrochemistry of aromatic tridentate imine ligand complexes of manganese and chromium has received little attention when compared to similar complexes of iron and cobalt. The voltammetric behavior of the bis(terpyridine)chromium(III) cation has been studied in aqueous media where it was shown to undergo a two-step reduction to $Cr(terpy)_2^{2+}$ and $Cr(terpy)_2^{+}$, respectively.[2,3] In acetonitrile, however, $Cr(terpy)_3^{3+}$ exhibits four one-electron reductions to the +2, +1, 0 and –1 formal oxidation states.[4] Since the redox behavior of the corresponding bis(terpyridine)manganese(II) complex has not been studied in either aqueous or non-aqueous medium, the present work was undertaken to study, for the first time, the electroanalytical behavior of the tridentate imine ligands, 2,2′,2″-terpyridine and 4′-phenylterpyridine (terosine) complexed with manganese(II) and to extend the work on similar complexes of chromium(III).[5]

Experimental

2,2′,2″-terpyridine was purchased from the G. Frederick Smith Chemical Company and used as received. Terosine was synthesized by the method outlined by Frank and Reiner[6] and recrystallized six times from spectro nitromethane with the use of activated charcoal 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, 81.3; H, 5.05; 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. High purity nitrogen was washed with acetonitrile before use. All other chemicals were reagent grade and were used as received.

The compounds $Mn(tero)_2(ClO_4)_2$ and $Mn(terpy)_2(ClO_4)_2$ were prepared by mixing 1.2 millimol of the ligand dissolved in 25 ml of hot absolute ethanol with 0.5 millimol of $MnCl_2 \cdot 4H_2O$ dissolved in 10 ml of triply distilled water. The complexes were precipitated with $NaClO_4$, washed with 50% ethanol–water and purified with absolute ethanol. The crystalline products were dried at 80°C *in vacuo* over P_2O_5 for 6 hours. *Anal.* Calcd. for $Mn(tero)_2(ClO_4)_2$ (dark yellow): C, 57.8; H, 3.46; N, 9.63. Found: C, 57.4; H, 3.60; N, 9.65%. Calcd. for $Mn(terpy)_2(ClO_4)_2$ (light yellow): C, 50.0; H, 3.08; N, 11.7. Found: C, 50.0; H, 3.10; N, 11.7%.

$Cr(terpy)_2(ClO_4)_3$ and $Cr(tero)_2(ClO_4)_3$ were prepared in like manner as the chromium(II) compounds from anhydrous $CrCl_2$. This preparation was carried out under nitrogen atmosphere using nitrogen deaerated solvents. The Cr(III) compounds were formed by bubbling chlorine gas into the Cr(II) precipitate–solvent suspension. The oxidized solution was then filtered and recrystallized five times from 50% ethanol–water. The hydrated products were dried at 80°C *in vacuo* over P_2O_5 for 16 hours. The absence of water of hydration was confirmed by infrared spectroscopy. *Anal.* Calcd. for $Cr(terpy)_2(ClO_4)_3 \cdot 2H_2O$: C, 42.3; H, 3.05; N, 9.85. Found: C, 42.4; H, 2.97; N, 9.87%.

Electronic absorption spectra were taken on a Cary Model 14 spectrophotometer and first derivative spectra were taken on 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 and Galbraith Laboratories, Knoxville, Tennessee. Voltametric measurements were carried out in the same manner as described previously.[7]

Results and Discussion

Visible and UV Spectra

Visible spectral data for $Cr(terpy)_2(ClO_4)_3$, $Cr(tero)_2(ClO_4)_3$, $Mn(terpy)_2(ClO_4)_2$ and $Mn(tero)_2(ClO_4)_2$ are summarized in Table I. The individual molar extinction coefficients were determined at different concentrations ($<.5mM$) of the perchlorate salt of the respective compound in spectro acetonitrile solution. The shoulders in the spectra of the manganese(II) complexes were confirmed by the use of first derivative spectra. Values for the wavelength at the peak of the first derivative curves are also given in Table I. Ultraviolet spectral data for the ligand, terosine, and the complexes are summarized in Table II. These spectra are characterized by huge molar absorptivities resulting from charge-transfer and ligand bands. UV molar absorptivities for the complexes were determined at the concentration indicated; ε values for terosine were determined at different concentrations with the average value given in the table.

Magnetic Susceptibilities

Room temperature magnetic moments of 6.08 and 6.02 B.M. were found for $Mn(terpy)_2(ClO_4)_2$ and $Mn(tero)_2(ClO_4)_2$ respectively. These values correspond to a high spin d^5 octahedral configuration.[8] Measured diamagnetic corrections ($\times 10^6$ cgs) of 223 and 298 were taken for terpyridine and terosine,

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

	First Derivative Peak (nm)	λ (nm)	ε
$Cr(terpy)_2^{3+}$	–	472	1470 ± 20
	–	442	2390 ± 20
	–	418	2220 ± 20
$Cr(tero)_2^{3+}$	–	563	260 ± 10
	–	467 (sh)	1540 ± 20
	–	438 (sh)	2860 ± 50
	–	397 (sh)	4750 ± 50
$Mn(terpy)_2^{2+}$	475	456 (sh)	53.6 ± .4
	436	427 (sh)	90.7 ± 3
	408	400 (sh)	191 ± 3
	384	377 (sh)	435 ± 5
$Mn(tero)_2^{2+}$	435	426 (sh)	130 ± 2
	407	399 (sh)	274 ± 2
	383	374 (sh)	691 ± 5

[a] Solvent = Spectro acetonitrile.

TABLE II. Ultra-violet Spectral Data for Terosine and the Manganese and Chromium Complexes.[a]

	λ (nm)	ε
Terosine	308 (sh)	8,090 ± 100
	274	32,100 ± 200
	251	35,500 ± 200
	247 (sh)	33,500 ± 200
	224 (sh)	21,100 ± 200
$Mn(terpy)_2(ClO_4)_2$ $6.68 \times 10^{-6} M$	331	16,800
	314 (sh)	23,100
	302	23,100
	280	37,100
	275 (sh)	36,500
	267 (sh)	29,500
	249 (sh)	28,900
	239 (sh)	41,300
	232	46,600
$Mn(tero)_2(ClO_4)_2$ $1.15 \times 10^{-5} M$	334 (sh)	15,900
	321 (sh)	21,800
	283	66,100
	278 (sh)	65,500
	271 (sh)	56,600
	251	52,300
	247 (sh)	49,800
$Cr(terpy)_2(ClO_4)_3$ $2.99 \times 10^{-5} M$	364	21,900
	349 (sh)	18,000
	347	18,200
	335 (sh)	13,500
	325	12,800
	315 (sh)	11,100
	285 (sh)	20,100
	277 (sh)	23,800
	266 (sh)	31,900
	264	32,400
	233 (sh)	47,200
	222	63,000
$Cr(tero)_2(ClO_4)_3$ $2.08 \times 10^{-5} M$	361 (sh)	36,300
	346	45,600
	341 (sh)	44,200
	288 (sh)	44,000
	285	44,100
	278 (sh)	41,700
	269 (sh)	34,800
	232 (sh)	51,600
	217 (sh)	69,000

[a] Solvent = Spectro acetonitrile.

respectively, and 32 was taken for the perchlorate anion correction.

Voltammetry

The voltammetric study of the free ligands has been reported in a previous communication.[7] The first reduction wave for terpyridine and terosine occurs at –2.07 and –1.98 volts *vs.* Ag/AgCl sat. NaCl, with limiting current to concentration ratio of 4.74 and 4.36 μA/m*M*, respectively. Both of these waves were found to be irreversible.

Table III summarizes the voltammetric data observed for the bis complexes. Both $Cr(terpy)_2^{3+}$ and $Cr(tero)_2^{3+}$ each exhibit four diffusion controlled reduction waves, *i.e.*, $i_dh^{1/2}$ is constant at various mercury column heights. For both complexes plots of $E_{d.c.}$ *vs.* $\log[i/(i_d-i)]$ gave straight lines with slopes close to 59.2 mV for all four waves. Figure 1 shows a typical cyclic voltammogram of the four reduction waves for the bis(terosine)chromium(III) complex. Cyclic voltammetric data for the Cr(III) terosine and Cr(III) terpyridine complexes show peak splittings and current heights expected for reversible one-electron charge

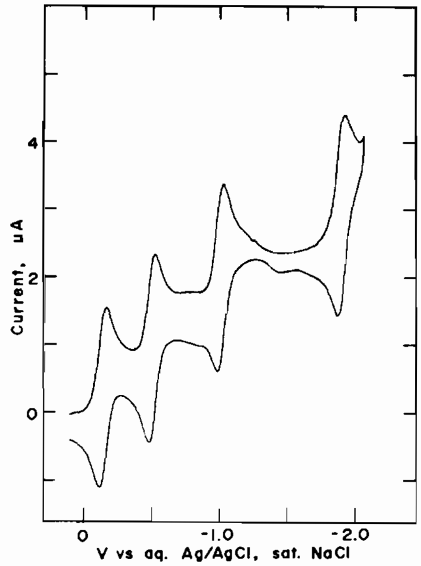

Figure 1. Cyclic voltammogram on Hg of 0.351 m*M* $Cr(tero)_2(ClO_4)_3$ in spectro acetonitrile and 0.1*M* $TEABF_4$. Scan rate = 110 mV/sec.

TABLE III. Voltammetric Data for the Complexes.

Complex Couple	D.C. Polarography				Cyclic Voltammetry		A.C. Polarography[e]		
	$E_{1/2}$ (V)	$i_d\left(\frac{\mu A}{mM}\right)$	Slope (mV)	$i_d/h^{1/2}$ [d]	Scan Rate $\left(\frac{mV}{sec}\right)$	ΔEp (mV)	Ep (V)	$Ip\left(\frac{\mu A}{mM}\right)$	Half-width (mV)
$Mn(terpy)_2$									
II→III[c]	+1.278	–	+60	–	30 Pt	70	+1.298 (Pt)	–	104
II→I	–1.115	2.85	–62	0.25±.01	40 Hg	80	–1.115	1.01	108
I→0	–1.455	2.79	–62	0.26±.01	50 Hg	72	–1.455	1.48	120
$Mn(tero)_2$									
II→III[c]	+1.223	–	+61	–	45 Pt	68	+1.230 (Pt)	–	104
II→I	–1.071	2.79	–62	0.19±.00	90 Hg	72	–1.069	1.80	100
I→0	–1.344	2.85	–58	0.19±.00	90 Hg	68	–1.349	1.93	100
$Cr(terpy)_2$									
III→II	–0.118	3.15[a]	–59	0.23±.00	100 Hg	60	–0.120	3.30[b]	95
II→I	–0.519	3.40[a]	–58	0.24±.00	100 Hg	60	–0.525	3.40[b]	95
I→0	–1.027	3.35[a]	–59	0.22±.00	100 Hg	60	–1.035	3.30[b]	92
0→–I	–1.950	3.10[a]	–58	0.21±.00	100 Hg	70	–1.95	2.20[b]	92
$Cr(tero)_2$									
III→II	–0.120	2.77	–59	0.12±.00	90 Hg	60	–0.121	2.49	95
II→I	–0.487	2.95	–60	0.12±.00	90 Hg	60	–0.484	2.55	93
I→0	–1.001	2.91	–57	0.11±.00	35 Hg	65	–0.990	2.24	96
0→–I	–1.912	2.86	–58	0.11±.00	110 Hg	70	–1.896	1.63	98

All voltages *vs.* aq. Ag/AgCl sat. NaCl
Solvent = spectro acetonitrile
Background electrolyte = 0.1*M* $TEABF_4$
All currents measured at the midpoint except $Cr(terpy)_2$.

[a] Time average currents. [b] Peak currents. [c] Done at the rotating platinum electrode D.C. and A.C. [d] Data taken at four different column heights. [e] Applied frequency = 23 Hz; applied potential = 5 mV; IR compensation = 225 ohms.

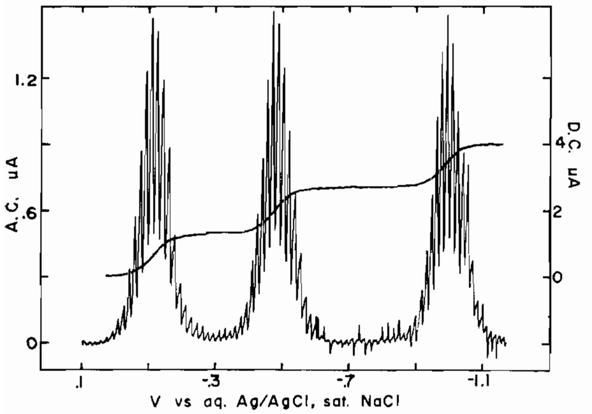

Figure 2. D.C. and A.C. polarograms of 0.369 m*M* $Cr(tero)_2(ClO_4)_3$ (III→II, II→I and I→0) in spectro acetonitrile and 0.1*M* $TEABF_4$.

transfers. In addition low frequency in-phase AC polarograms (Figure 2) for all waves show half peak potential widths very close to the theoretical value of 92 mV[9] characteristic of one-electron reversible processes.

The complexes $Mn(terpy)_2^{2+}$ and $Mn(tero)_2^{2+}$ each show two one-electron diffusion controlled reduction waves. DC polarograms of the I→0 wave for both manganese complexes gave evidence of intense adsorption occurring just negative of the half-wave potential, while the II→I wave for both complexes showed much less adsorption in the same section of the wave. Large spikes which apparently are due to adsorption also occurred with single sweep cyclic voltammetry using both mercury and platinum electrodes. However, when steady state cyclic voltammograms were taken, one of which is presented in Figure 3, these spikes diminished, indicating that the surface of the electrode had been altered due to the adsorption of some solution component. Cyclic voltammetric peak splittings and AC polarographic half-widths indicate that on these time scales the reduction processes of $Mn(terpy)_2^{2+}$ and $Mn(tero)_2^{2+}$ are quasi-reversible in nature.

At the rotating platinum electrode (RPE) both manganese complexes exhibited a one-electron oxidation process to $Mn(L)_2^{3+}$ (Figure 4). Voltammetric data in Table III indicate that the oxidation waves are also somewhat quasi-reversible.

Comparison of the half-wave potentials for each complex couple of a given metal shows a shift toward zero volts for all terosine complex couples with the exception of the chromium(III–II) terosine reduction. We have observed this same pattern in the corresponding cobalt and iron complexes of these ligands.[7] We feel that the observed shifts in potentials are probably due to the phenyl substituent acting as a weak electron donor in the high oxidation states and as a weak electron acceptor in the case of the lower oxidation states. The only structural difference between the terosine and terpyridine complexes is the two phenyl groups located para to the axial metal–ligand bonds, thus the total symmetry is D_{2d} for both ligand complexes. Ac-

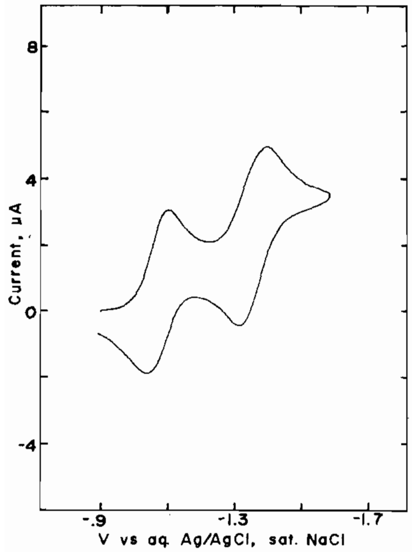

Figure 3. Cyclic voltammogram on Hg of 0.455 m*M* $Mn(tero)_2(ClO_4)_2$ (II→I and I→0) in spectro acetonitrile and 0.1*M* $TEABF_4$. Scan rate = 65 mV/sec.

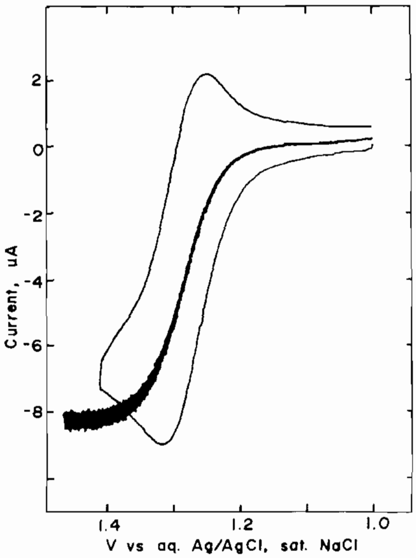

Figure 4. D.C. polarogram at the rotating platinum electrode and cyclic voltammogram on Pt of 0.682 m*M* $Mn(terpy)_2(ClO_4)_2$ (II→III) in acetonitrile and 0.1*M* $TEABF_4$. C.V. scan rate = 27 mV/sec.

cording to Swain and Lupton[10] a *para* phenyl group should act as a very weak electron donor (σ_p = −0.010). Our results indicate this to be true; however, comparison of the II–I, I–0 and 0–(–I) couples shows that this substituent can also, when forced to, act as a weak electron acceptor which is not unreasonable considering the closeness of the sigma parameter to zero. In making this conclusion on the basis of our electrochemical data we assume that the free energy of formation of $M(tero)_2^{2+}$ is equal to or more negative than the corresponding value for $M(terpy)_2^{2+}$. The validity of this assumption is supported by reported values for $\log\beta_3$ of 21.3 and 21.8 for Fe(phenanthroline)$_3^{2+}$ and Fe(4,7-diphenylphenanthroline)$_3^{2+}$, respectively.[11] The four and seven positions of 1,10-phenanthroline are symmetrically *para* to the central metal atom just as in the terosine complexes. This data indicates that the *para* phenyl groups stabilize the +2 formal oxidation states and, from the electrochemical data presented here, also the +3, +1, zero and in the case of the chromium complexes the −1 formal oxidation states. At this time we are continuing our investigation with other *para* substituted imine ligand complexes.

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