

Redox Data of *Tris*(polypyridine)manganese(II) Complexes

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Abstract: Very little cyclic voltammetry data for *tris*(polypyridine)manganese(II) complexes, $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$, where $\text{N}^{\wedge}\text{N}$ is bipyridine (bpy), phenanthroline (phen) or substituted bpy or phen ligands, respectively; are available in the literature. Cyclic voltammograms were found for *tris*(4,7-diphenyl-1,10-phenanthroline)manganese(II) perchlorate only. In addition to our recently published related research article, the data presented here provides cyclic voltammograms and corresponding voltage-current data obtained during electrochemical oxidation and the reduction of four $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$ complexes, using different scan rates and analyte concentrations. The results show increased concentration and scan rates resulting in higher Mn(II/III) peak oxidation potentials and increased peak current-voltage separations of the irreversible Mn(II/III) redox event. The average peak oxidation and peak reduction potentials of the Mn(II/III) redox events stayed constant within 0.01 V. Similarly, the average of the peak oxidation and reduction potentials of the ligand-based reduction events of $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$ were constant within 0.01 V.

Dataset: Supplementary file

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Keywords: *tris*(polypyridine)manganese(II); Mn(II/III) oxidation; cyclic voltammetry

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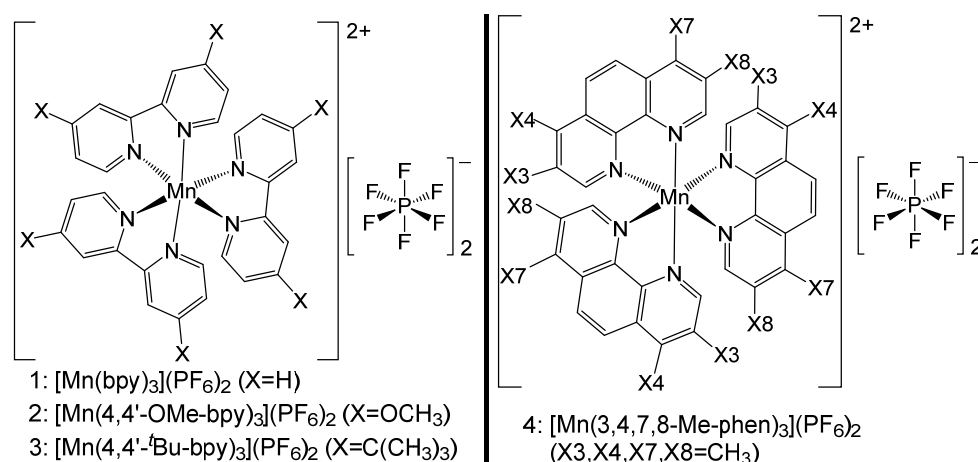
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1. Summary

A comprehensive set of voltage-current related data obtained during the electrochemical oxidation and reduction of four *tris*(polypyridine)manganese(II) complexes are provided in this article. The oxidized *tris*(polypyridine)manganese(III) complexes, $[\text{Mn}^{\text{III}}(\text{N}^{\wedge}\text{N})_3]^{3+}$ ($\text{N}^{\wedge}\text{N}$ = bipyridine (bpy), phenanthroline (phen) or substituted bpy or phen ligands), are unstable and have apparently never been isolated experimentally [1]. Only one related $[\text{Mn}^{\text{III}}(\text{terpyridine})_2]^{3+}$ complex has been isolated [2]. Experimental information on mononuclear $[\text{Mn}^{\text{III}}(\text{N}^{\wedge}\text{N})_3]^{3+}$ complexes was thus obtained through the electrochemical oxidation of $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$, using cyclic voltammetry experiments. Apart from our research article related to this dataset, “Electrochemical study of the Mn(II/III) oxidation of *tris*(polypyridine)manganese(II) complexes” [3], the literature on cyclic voltammetry experiments is limited, most probably due to the large peak current-voltage separation values of the Mn(II/III) oxidation process [4–6]. Only one cyclic voltammogram of the oxidation of a $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$ complex has been published [5], namely that of 0.001 M *tris*(4,7-diphenyl-1,10-phenanthroline)manganese(II) perchlorate in acetonitrile, at a scan rate of 0.10 V s⁻¹. Similarly, the literature on the reduction of $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$ complexes was also limited [4,7–9], i.e., only one cyclic voltammogram of the reduction of *tris*(4,7-diphenyl-1,10-phenanthroline)manganese(II) perchlorate complex in acetonitrile, at a scan rate of 0.00125 V s⁻¹ [9].

The relevance of scan rate studies is to establish how redox behavior changes with scan rate, as well as to analyze the type of redox processes observed [10,11]. The present article provides, in addition to data provided in the related research article [3], redox data

of four $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$ complexes containing the bidentate ligands $\text{N}^{\wedge}\text{N}$ = bipyridine, 4,4'-di-methoxy-2,2'-dipyridyl, 4,4'-di-tetra-butyl-2,2'-dipyridyl and 3,4,7,8-tetramethyl-1,10-phenanthroline, each coordinated through two N atoms to Mn (see Scheme 1). Cyclic voltammograms were obtained at scan rates ranging over more than two orders of magnitude (0.05 to 5.12 V s^{-1}) and concentrations varying over one order of magnitude (0.001 to $0.010 \text{ mol dm}^{-3}$), using acetonitrile as a solvent. The redox data of the *tris*(polypyridine)manganese(II) complexes were added to the published redox data of related complexes of Fe [12], Ru [13], Os [14] and Co [15,16]. The information herein is helpful to researchers who design complexes with specific redox properties, for example, as may be required in studies of redox mediators in dye-sensitized solar cells [17,18], antimicrobial activity [19,20] or molecular catalysts for CO_2 and/or H_2O reduction [21].



Scheme 1. Complex numbering and structure of Mn(II) polypyridine complexes.

2. Data Description

Results obtained from voltage-current data of the cyclic voltammograms (Figures 1–4 for oxidation, Figure 5 for reduction) of four Mn(II) complexes are presented in Tables 1–8 of this article. These four complexes, 1–4, contain different polypyridine ligands, namely, bipyridine, substituted bipyridine and substituted phenanthroline ligands (see Scheme 1). The cyclic voltammograms presented herein provide more detailed electrochemical data for 1–4 (i.e., at different scan rates and concentrations) than presented in the related research article [3], wherein only data from one scan rate (0.10 V s^{-1}) and concentration ($0.005 \text{ mol dm}^{-3}$) were presented. A full electrochemical dataset of the related $[\text{Mn}(\text{phen})_3](\text{PF}_6)_2$ complex is available in the related research article [3].

2.1. Oxidation Data

Figures 1–4 show the CVs obtained during electrochemical oxidation of complexes 1–4, at different scan rates (0.05 – 5.12 V s^{-1}) and different analyte concentrations (0.001 – 0.01 mol dm^{-3} at a scan rate of 0.10 V s^{-1}). Tables 1–4 list the electrochemical data of the complexes corresponding to Figures 1–4. The metal-based oxidations [3] are representative of the Mn(II/III) redox process. The CV data illustrate increased concentrations and scan rates resulting in increased peak oxidation potentials of the irreversible Mn(II/III) redox transitions. The average of the peak oxidation (E_{pa}) and peak reduction potentials (E_{pc}), namely $\frac{1}{2}(E_{\text{pa}} + E_{\text{pc}})$ of the Mn(II/III) redox couple, however, stayed within 0.01 V of the average value, irrespective of the increase in the peak current voltage separations upon increases in the scan rate and analyte concentration (e.g., see Figure 1a). The large peak current voltage separations (ΔE_{p}) and small peak current ratios clearly indicate the Mn(II/III) oxidation process to be chemically and electrochemically irreversible [10,11].

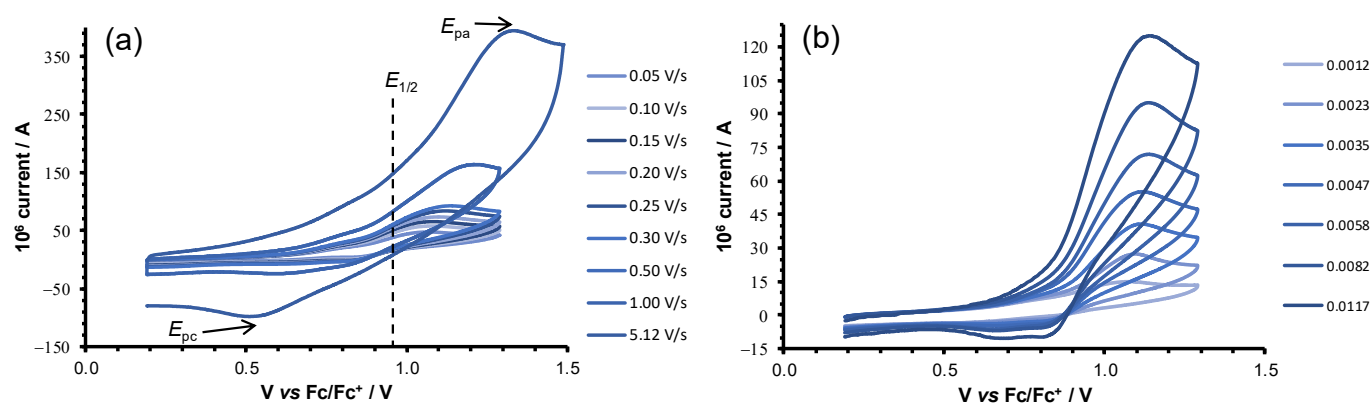


Figure 1. Cyclic voltammograms of *tris*(bipyridine)manganese(II) hexafluorophosphate (**1**), (a) at indicated scan rates in V/s and concentration 0.0042 mol dm⁻³ and (b) at a scan rate of 0.01 V/s and the indicated concentrations in moles per cubic decimeter, scanned in the positive direction. Data in Table 1. The E_{pa} and E_{pc} of the 5.12 V/s scan and the average $E_{1/2}$ value are indicated in (a).

Table 1. Electrochemical oxidation data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(bipyridine)manganese(II) hexafluorophosphate (**1**), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹) and concentrations C (mol dm⁻³).

ν (Vs ⁻¹)	C (mol dm ⁻³)	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.050	0.0042	1.069	0.848	0.221	0.959
0.100	0.0042	1.075	0.847	0.228	0.961
0.150	0.0042	1.087	0.830	0.257	0.959
0.200	0.0042	1.098	0.820	0.278	0.959
0.250	0.0042	1.110	0.815	0.295	0.963
0.300	0.0042	1.123	0.805	0.318	0.964
0.500	0.0042	1.134	0.790	0.344	0.962
1.003	0.0042	1.200	0.720	0.480	0.960
5.120	0.0042	1.356	0.547	0.809	0.952
0.100	0.0012	1.070	0.830	0.240	0.950
0.100	0.0023	1.100	0.820	0.280	0.960
0.100	0.0035	1.110	0.820	0.290	0.965
0.100	0.0047	1.110	0.819	0.291	0.965
0.100	0.0058	1.115	0.818	0.297	0.967
0.100	0.0082	1.120	0.816	0.304	0.968
0.100	0.0117	1.130	0.815	0.315	0.973
Average					0.961(4)

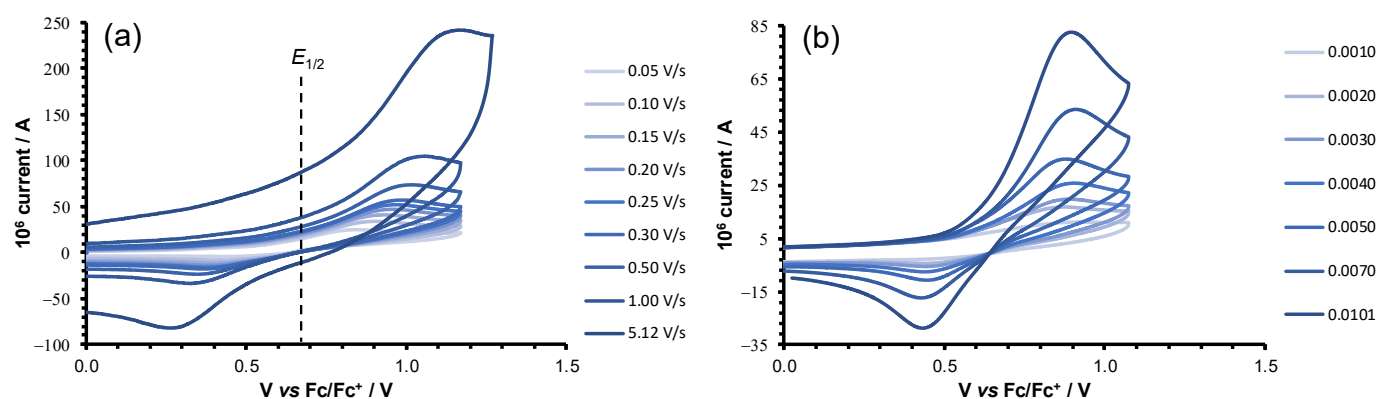


Figure 2. Cyclic voltammograms of *tris*(4,4'-di-methoxy-2,2'-dipyridyl)manganese(II) hexafluorophosphate (**2**), (a) at the indicated scan rates in V/s and concentration 0.0034 mol dm⁻³ and (b) at a scan rate of 0.01 V/s and the indicated concentrations in moles per cubic decimeter, scanned in the positive direction. Data in Table 2. Average $E_{1/2}$ value is indicated in (a).

Table 2. Electrochemical oxidation data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(4,4'-di-methoxy-2,2'-dipyridyl)manganese(II) hexafluorophosphate (**2**), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹) and concentrations C (mol dm⁻³).

ν (Vs ⁻¹)	C (mol dm ⁻³)	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.050	0.0034	0.858	0.494	0.364	0.676
0.100	0.0034	0.900	0.450	0.450	0.675
0.150	0.0034	0.927	0.420	0.507	0.674
0.200	0.0034	0.963	0.390	0.573	0.677
0.250	0.0034	0.967	0.388	0.579	0.678
0.300	0.0034	0.973	0.376	0.597	0.675
0.500	0.0034	0.987	0.372	0.615	0.680
1.003	0.0034	1.042	0.370	0.672	0.706
5.120	0.0034	1.145	0.270	0.875	0.708
0.100	0.0010	0.885	0.455	0.430	0.670
0.100	0.0020	0.890	0.455	0.435	0.673
0.100	0.0030	0.895	0.455	0.440	0.675
0.100	0.0040	0.896	0.455	0.441	0.676
0.100	0.0050	0.898	0.450	0.448	0.674
0.100	0.0070	0.905	0.444	0.461	0.675
0.100	0.0101	0.905	0.441	0.464	0.673
Average ^a					0.675(4)

^a Data of 1.003 and 5.120 Vs⁻¹ scan not included in average.

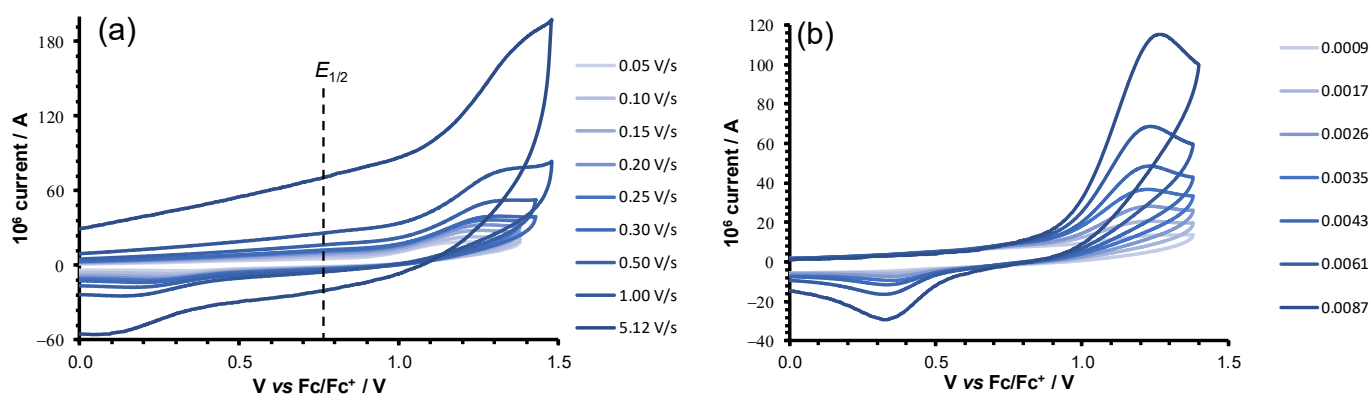


Figure 3. Cyclic voltammograms of *tris*(4,4'-di-tetra-butyl-2,2'-dipyridyl)manganese(II) hexafluorophosphate (**3**), (a) at the indicated scan rates in V/s and concentration 0.0027 mol dm⁻³ and (b) at a scan rate of 0.01 V/s and the indicated concentrations in moles per cubic decimeter, scanned in the positive direction. Data in Table 3. Average $E_{1/2}$ value is indicated in (a).

Table 3. Electrochemical oxidation data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(4,4'-di-tetra-butyl-2,2'-dipyridyl)manganese(II) hexafluorophosphate (**3**), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹) and concentrations C (mol dm⁻³).

ν (Vs ⁻¹)	C (mol dm ⁻³)	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.050	0.0027	1.203	0.331	0.872	0.767
0.100	0.0027	1.246	0.290	0.956	0.768
0.150	0.0027	1.251	0.279	0.972	0.765
0.200	0.0027	1.272	0.262	1.010	0.767
0.250	0.0027	1.296	0.237	1.059	0.767
0.300	0.0027	1.300	0.229	1.071	0.765
0.500	0.0027	1.310	0.220	1.090	0.765
1.003	0.0027	1.340	0.190	1.150	0.765
5.120	0.0027	1.450	0.080	1.370	0.765
0.100	0.0009	1.200	0.360	0.840	0.780
0.100	0.0017	1.200	0.355	0.845	0.778
0.100	0.0026	1.205	0.350	0.855	0.778
0.100	0.0035	1.210	0.340	0.870	0.775
0.100	0.0043	1.210	0.330	0.880	0.770
0.100	0.0061	1.220	0.320	0.900	0.770
0.100	0.0087	1.230	0.310	0.920	0.770
Average					0.770(4)

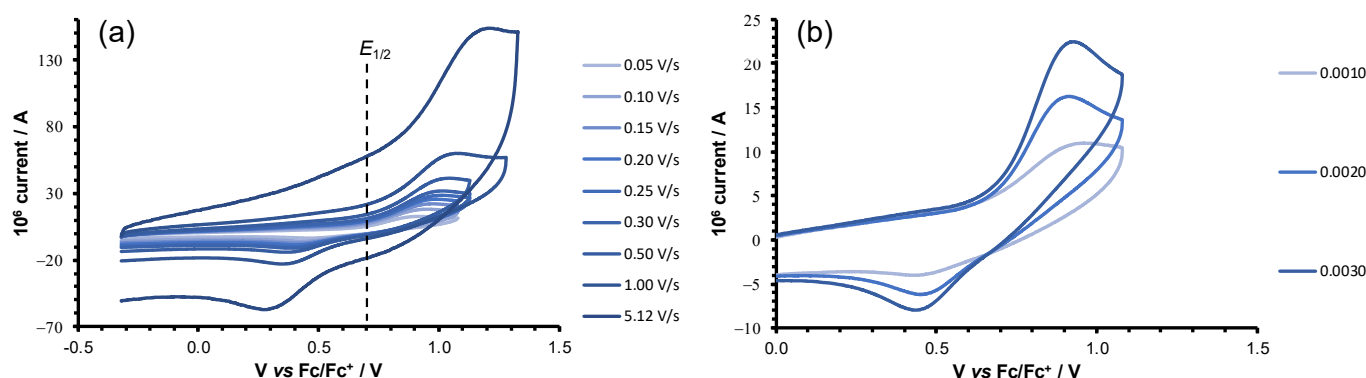


Figure 4. Cyclic voltammograms of *tris*(3,4,7,8-tetramethyl-1,10 phenanthroline)manganese(II) hexafluorophosphate (**4**), (a) at the indicated scan rates in V/s and concentration 0.0011 mol dm⁻³ and (b) at a scan rate of 0.01 V/s and the indicated concentrations in moles per cubic decimeter, scanned in the positive direction. The solution was saturated at 0.0030 mol dm⁻³. Data in Table 4. Average $E_{1/2}$ value is indicated in (a).

Table 4. Electrochemical oxidation data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(3,4,7,8-tetramethyl-1,10 phenanthroline)manganese(II) hexafluorophosphate (**4**), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹) and concentrations C (mol dm⁻³). The solution was saturated at 0.0030 mol dm⁻³.

ν (Vs ⁻¹)	C (mol dm ⁻³)	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.050	0.0011	0.920	0.479	0.441	0.700
0.100	0.0011	0.954	0.449	0.505	0.702
0.150	0.0011	0.970	0.430	0.540	0.700
0.200	0.0011	0.980	0.420	0.560	0.700
0.250	0.0011	1.000	0.400	0.600	0.700
0.300	0.0011	1.000	0.400	0.600	0.700
0.500	0.0011	1.000	0.400	0.600	0.700
1.003	0.0011	1.050	0.350	0.700	0.700
5.120	0.0011	1.162	0.296	0.866	0.729
0.100	0.0010	0.925	0.468	0.457	0.697
0.100	0.0020	0.925	0.484	0.441	0.705
0.100	0.0030	0.945	0.455	0.490	0.700
Average^a					0.700(3)

^a Data of 5.120 Vs⁻¹ scan not included in average.

2.2. Reduction Data

Figure 5 shows the CVs obtained during the electrochemical reduction of complexes **1–4**, using different scan rates. Tables 5–8 list the electrochemical data of the reduction of the complexes corresponding to Figure 5a–d, respectively. The reduction is ligand-based [3]. Complexes **1–3** each show three reduction peaks, corresponding to consecutive reductions in the three coordinated N[^]N ligands. Data of only the first 2 reduction peaks of **4** are shown, since the reduction of **4** is irreversible. The data illustrate that with the increased scan rate, the peak current voltage separations increase for **1–3**, but the average of the peak oxidation (E_{pa}) and peak reduction potentials (E_{pc}) of each reduction peak, namely $\frac{1}{2}(E_{pa} + E_{pc})$, stayed within 0.01 V of the average value.

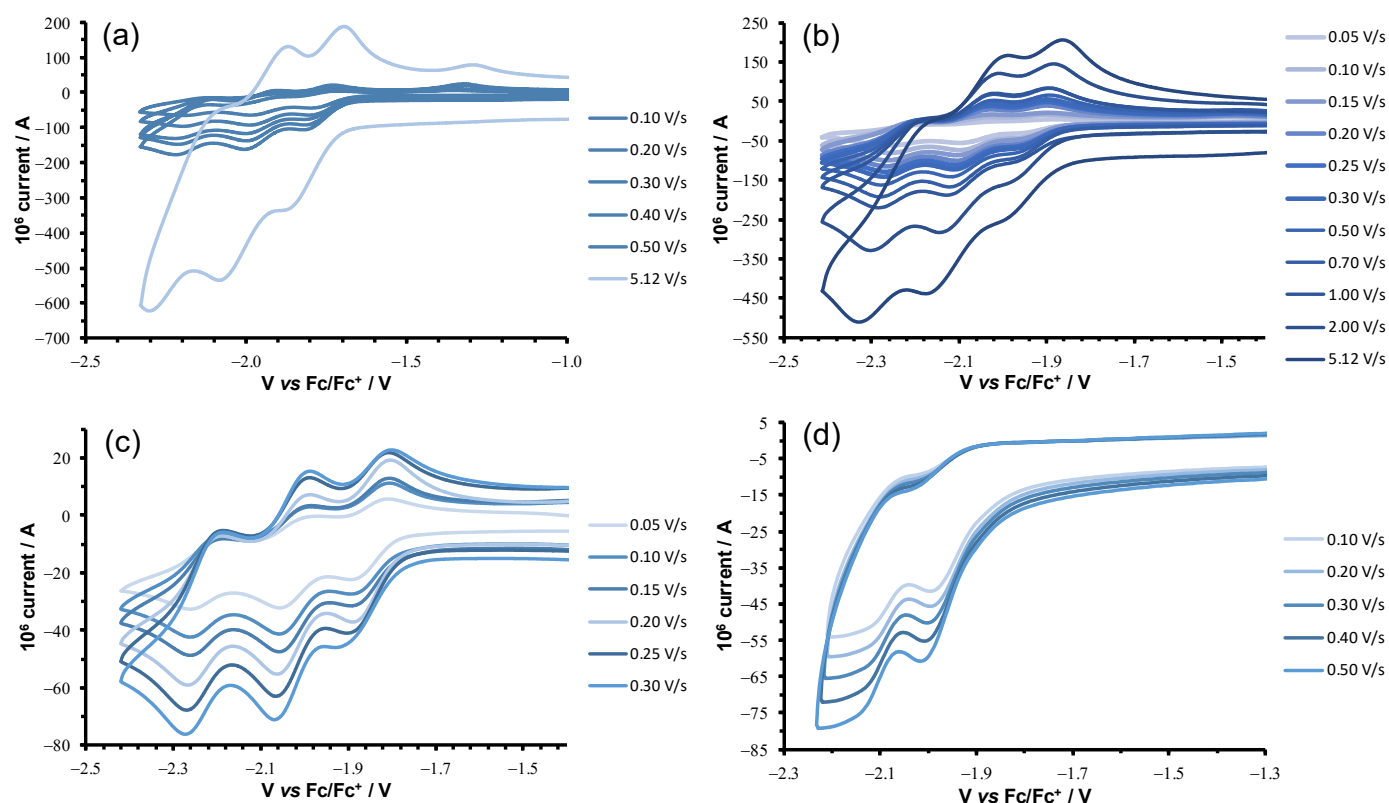


Figure 5. Cyclic voltammograms of (1)–(4) at the indicated scan rates in V/s, scanned in the negative direction. (a) *tris*(bipyridine)manganese(II) hexafluorophosphate (1) (b) *tris*(4,4'-di-methoxy-2,2'-dipyridyl)manganese(II) hexafluorophosphate (2), (c) *tris*(4,4'-di-tetra-butyl-2,2'-dipyridyl)manganese(II) hexafluorophosphate (3) (d) *tris*(3,4,7,8-tetramethyl-1,10 phenanthroline)manganese(II) hexafluorophosphate (4). Data Tables 5–8, respectively.

Table 5. Electrochemical reduction data (potential in V vs. Fc/Fc⁺) obtained from the CV *tris*(bipyridine)manganese(II) hexafluorophosphate (1), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹). Analyte concentration = 0.0044 mol dm⁻³.

ν (Vs ⁻¹)	Peak 1			Peak 2				Peak 3				
	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.100	-1.729	-1.794	0.065	-1.762	-1.903	-1.983	0.080	-1.943	-2.127	-2.192	0.065	-2.160
0.200	-1.727	-1.793	0.066	-1.760	-1.900	-1.985	0.085	-1.943	-2.120	-2.190	0.070	-2.155
0.300	-1.733	-1.806	0.073	-1.770	-1.887	-1.990	0.103	-1.939	-2.105	-2.214	0.109	-2.160
0.400	-1.712	-1.804	0.092	-1.758	-1.889	-1.996	0.107	-1.943	-2.100	-2.212	0.112	-2.156
0.500	-1.703	-1.814	0.111	-1.759	-1.893	-2.001	0.108	-1.947	-2.098	-2.211	0.113	-2.155
5.120	-1.681	-1.863	0.182	-1.772	-1.855	-2.075	0.220	-1.965	-2.047	-2.288	0.241	-2.168
Average^a				-1.763(5)				-1.943(4)				-2.159(2)

^a Data of 5.120 Vs⁻¹ scan not included in average for peak 2.

Table 6. Electrochemical reduction data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(4,4'-di-methoxy-2,2'-dipyridyl)manganese(II) hexafluorophosphate (2), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹). Analyte concentration = 0.0033 mol dm⁻³.

ν (Vs ⁻¹)	Peak 1			Peak 2				Peak 3				
	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.050	-1.880	-1.956	0.076	-1.918	-2.032	-2.089	0.057	-2.061	-2.195	-2.257	0.062	-2.226
0.100	-1.881	-1.958	0.077	-1.920	-2.036	-2.093	0.057	-2.065	-2.193	-2.251	0.058	-2.222

0.150	-1.882	-1.960	0.078	-1.921	-2.032	-2.092	0.060	-2.062	-2.194	-2.257	0.063	-2.226
0.200	-1.884	-1.962	0.078	-1.923	-2.014	-2.097	0.083	-2.056	-2.195	-2.262	0.067	-2.229
0.250	-1.888	-1.967	0.079	-1.928	-2.032	-2.105	0.073	-2.069	-2.182	-2.263	0.081	-2.223
0.300	-1.890	-1.969	0.079	-1.930	-2.027	-2.103	0.076	-2.065	-2.181	-2.267	0.086	-2.224
0.500	-1.873	-1.976	0.103	-1.925	-2.026	-2.112	0.086	-2.069	-2.174	-2.270	0.096	-2.222
0.700	-1.873	-1.977	0.104	-1.925	-2.025	-2.111	0.086	-2.068	-2.174	-2.274	0.100	-2.224
1.003	-1.870	-1.976	0.106	-1.923	-2.000	-2.121	0.121	-2.061	-2.174	-2.284	0.110	-2.229
2.007	-1.866	-1.975	0.109	-1.921	-1.998	-2.130	0.132	-2.064	-2.168	-2.295	0.127	-2.232
5.120	-1.851	-1.989	0.138	-1.920	-1.985	-2.164	0.179	-2.075	-2.161	-2.314	0.153	-2.238
Average				-1.923(3)				-2.065(4)				-2.227(4)

Table 7. Electrochemical reduction data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(4,4'-di-tetra-butyl-2,2'-dipyridyl)manganese(II) hexafluorophosphate (**3**), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹). Analyte concentration = 0.0028 mol dm⁻³.

ν (Vs ⁻¹)	Peak 1				Peak 2				Peak 3			
	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.050	-1.797	-1.885	0.088	-1.841	-1.989	-2.048	0.059	-2.019	-2.174	-2.255	0.081	-2.215
0.100	-1.798	-1.884	0.086	-1.841	-1.984	-2.051	0.067	-2.018	-2.174	-2.257	0.083	-2.216
0.150	-1.793	-1.885	0.092	-1.839	-1.978	-2.058	0.080	-2.018	-2.170	-2.265	0.095	-2.218
0.200	-1.788	-1.885	0.097	-1.837	-1.978	-2.058	0.080	-2.018	-2.170	-2.267	0.097	-2.219
0.250	-1.788	-1.884	0.096	-1.836	-1.978	-2.058	0.080	-2.018	-2.169	-2.269	0.100	-2.219
0.300	-1.777	-1.903	0.126	-1.840	-1.968	-2.064	0.096	-2.016	-2.164	-2.271	0.107	-2.218
Average				-1.839(2)				-2.018(1)				-2.217(1)

Table 8. Electrochemical reduction data (potential in V vs. Fc/Fc⁺) obtained from the CV of *tris*(3,4,7,8-tetramethyl-1,10 phenanthroline)manganese(II) hexafluorophosphate (**4**), in acetonitrile (CH₃CN) as solvent at the indicated scan rates ν (Vs⁻¹). Concentration of analyte = 0.0011 mol dm⁻³.

ν (Vs ⁻¹)	Peak 1				Peak 2			
	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$\frac{1}{2}(E_{pa} + E_{pc})/V$
0.100	-1.911	-1.991	0.080	-1.951	-2.040	-2.120	0.080	-2.080
0.200	-1.911	-1.993	0.082	-1.952	-2.040	-2.120	0.080	-2.080
0.300	-1.911	-1.997	0.086	-1.954	-2.040	-2.126	0.086	-2.083
0.400	-1.911	-2.003	0.092	-1.957	-2.040	-2.133	0.093	-2.086
0.500	-1.911	-2.011	0.100	-1.961	-2.040	-2.141	0.101	-2.091
Average				-1.955(3)				-2.084(4)

3. Methods

Complexes **1–4** were synthesized, purified and characterized as described in the related research article [3]. The cyclic voltammetry (CV) scans were obtained under similar conditions as described therein, as well as in our previous work [22,23]. The CV experiments were performed on a BAS100B Electrochemical Analyzer connected to a desktop computer containing the BAS100W version 2.3 software. The software provides current-voltage and peak current--voltage data. The obtained current-voltage data were exported to Excel for further evaluation and visualization.

The temperature was kept constant at 298 K. The electrochemical cell contained three electrodes; a glassy carbon (surface area 1.257×10^{-5} m²) working electrode, a Pt wire auxiliary electrode and an Ag/Ag⁺ (0.010 mol dm⁻³ AgNO₃ in acetonitrile) reference electrode, mounted on a Luggin capillary. Ferrocene was used as the internal standard. Electrochemical measurements were carried out in anhydrous acetonitrile (anhydrous, $\geq 99.8\%$) containing the analyte and 0.1 mol dm⁻³ tetrabutylammonium hexafluorophosphate as the

supporting electrolyte. Care was taken to exclude water from the cell, since the presence of trace amounts of water may lead to the formation of mixed-valent *di*- μ -oxo bridged binuclear complexes, $[\text{Mn}^{\text{III,IV}}(\text{O})_2(\text{L})_4]^{3+}$ ($\text{N}^{\wedge}\text{N}$ = bpy, phen, 4,4'-Me-bpy, 4,4'-Ph-bpy, 4,7-Ph-phen), upon oxidation of $[\text{Mn}^{\text{II}}(\text{N}^{\wedge}\text{N})_3]^{2+}$ [5].

The analyte solution in a three-electrode cell was purged with argon gas before and throughout the CV experiment. Care was taken to keep the volume of the analyte solution constant, since the obtained current-voltage data depends on the analyte concentration as well as scan rate.

For the purpose of obtaining reproducible results, firm polishing of the working electrode before each CV scan was necessary, since electrode poisoning occurs during CV scans. Polishing of the working electrode was done on a Bühler polishing mat, moving the flat tip of the electrode in a figure-eight motion, at first using 1-micron diamond paste. The electrode was then rinsed with ethanol, water and acetonitrile, and dried. The polishing procedure was then repeated using 1/4-micron diamond paste.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/article/10.3390/data7090130/s1, Excel files with current-voltage data.

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