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Metal–Bis[poly(pyrazolyl)borate] Complexes. Electrochemical, Magnetic, and Spectroscopic Properties and Coupled Electron-Transfer and Spin-Exchange Reactions

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Electrochemical, magnetic, and spectroscopic properties are reported for homoleptic divalent (M = Mn, Fe, Co, Ni, Ru) and trivalent (M = Cr, Mn, Fe, Co) metal–bis[poly(pyrazolyl)borate] complexes, $[M(pzb)_2]^{+/0}$, where pzb^- = hydrotris(pyrazolyl)borate (Tp), hydrotris(3,5-dimethylpyrazolyl)borate (Tp*), or tetrakis(pyrazolyl)borate (pzTp). Ligand field strengths in metal–pzb complexes increase as Tp* < Tp < pzTp, which reflects the importance of steric rather than electronic effects on spectroscopic properties. However, metal-centered redox potentials become more negative as pzTp < Tp < Tp*, which follows the electron-donating ability of the ligands. Co(III)/Co(II) and Mn(III)/Mn(II) electrode reactions are accompanied by a change in metal atom spin-state; i.e., ($S = 0$) $[Co(pzb)_2]^+ + e^- \leftrightarrows$ ($S = {}^3/_2$) $[Co(pzb)_2]$ and ($S = 1$) $[Mn(pzb)_2]^+ + e^- \leftrightarrows$ ($S = {}^5/_2$) $[Mn(pzb)_2]$. Apparent heterogeneous electron-transfer rate constants derived from sweep-rate dependent cyclic voltammetric peak potential separations in 1,2-dichloroethane are small and decrease as pzTp > Tp > Tp* for the Co(III)/Co(II) couples. Slow electron transfer is characteristic of coupled electron transfer and spin exchange. $[M(Tp)_2]^{+/0}$ redox potentials relative to values for other homoleptic $MN_6^{3+/2+}$ couples change as M varies from Cr to Ni. For early members of the series, $[M(Tp)_2]^{+/0}$ potentials nearly equal those of complexes with aliphatic N-donor ligands (e.g., triazacyclononane, sarcophagine). However, $[M(Tp)_2]^{+/0}$ potentials approach those of $[M(bpy)_3]^{3+/2+}$ for later members of the series. The variation suggests a change in the nature of the metal–pzb interaction upon crossing the first transition row.

Introduction

Poly(pyrazolyl)borate (pzb^-) ligands are utilized extensively in organometallic and coordination chemistry.[1-5] Their tunable electronic and steric properties have led to widespread applications in metalloenzyme model chemistry,[6] polymerization catalysis,[7] C–H bond activation,[8] and metal ion extraction.[9] There also is intrinsic interest in the electronic characteristics of pzb^- ligands relative to those of other facially coordinating, six-electron donors such as 1,4,7-triazacyclononane (tacn), tris(pyrazolyl)methane (tpm), and cyclopentadienyl (Cp^-).[10,11] Finally, poly(pyrazolyl)borates support spin-crossover behavior in Fe(II) complexes, for which the position of the $^1A_{1g} \leftrightarrows {}^5T_{2g}$ spin-equilibrium is shifted dramatically by small changes in pyrazolyl substituents.[2,12,13]

Our laboratory is interested in the energetics and mechanism of concerted electron-transfer and spin-exchange reactions.[14-17] These processes occur as closely coupled

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(1) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3148.
(2) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3158.
(3) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(4) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419.
(5) Trofimenko, S. *Scorpionates—The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
(6) Vahrenkamp, H. *Acc. Chem. Res.* **1999**, *32*, 589.
(7) Murtuza, S.; Casagrande, O. L., Jr.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882.
(8) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.
(9) Kitano, T.; Sohrin, Y.; Hata, Y.; Kawakami, H.; Hori, T.; Ueda, K. *J. Chem. Soc., Dalton Trans.* **2001**, 3564.
(10) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428.
(11) Brunker, T. J.; Cowley, A. R.; O'Hare, D. *Organometallics* **2002**, *21*, 3123.
(12) Beattie, J. K.; Binstead, R. A.; West, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3044.
(13) Buchen, Th.; Gütlich, P. *Inorg. Chim. Acta* **1995**, *231*, 221.

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events in many chemical and biological systems. Poly(pyrazolyl)borates are useful ligands for such inquiries, because they form robust complexes with transition metals in adjacent oxidation states that are capable of undergoing spin-state transitions. Although metal−poly(pyrazolyl)borates have been studied extensively over the past 30 years,[1−5] their properties have not been investigated systematically with an eye toward coupled electron transfer and spin exchange. Thus, we have surveyed the electrochemical, magnetic, and spectroscopic properties of the homoleptic divalent ($[M(pzb)_2]$, M = Mn, Fe, Co, Ni, Ru) and trivalent ($[M(pzb)_2]^+$, M = Cr, Mn, Fe, Co) metal−bis[poly(pyrazolyl)borate] complexes with pzb^- = hydrotris(pyrazolyl)borate (Tp), hydrotris(3,5-dimethylpyrazolyl)borate (Tp*), or tetrakis(pyrazolyl)borate (pzTp). The objectives of the investigation are to identify new examples of coupled electron-transfer and spin-exchange behavior and to better understand the factors that enable pzb^- ligands to modulate the redox, magnetic, and spectroscopic properties of transition metal compounds.

Experimental Section

Materials. The ligand salts K(Tp), K(pzTp), and K(Tp*) were prepared as described by Trofimenko[18] and characterized by infrared and ^{1}H NMR spectroscopy. Solvents for electrochemical, magnetic, and spectroscopic measurements were obtained as distilled-in-glass reagents from Burdick & Jackson and used as received. The supporting electrolyte in electrochemical experiments, tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$), was obtained from Sigma-Aldrich and used as received.

Divalent $[M(pzb)_2]$ complexes with M = Mn, Fe, Co, and Ni[18] and with M = Ru[19] were prepared by published procedures. The trivalent complexes $[Cr(Tp)_2]Cl$,[20] $[Co(Tp)_2]Cl$,[21] and $[Fe(pzb)_2]PF_6$[22] also were prepared by reported methods. $[Co(pzTp)_2]Cl$ was prepared in a manner analogous to $[Co(Tp)_2]Cl$ by reaction of $[Co(NH_3)_5Cl]Cl_2$ with K(pzTp). The manganese(III) compounds, $[Mn(pzb)_2]PF_6$ (pzb^- = Tp, Tp*, pzTp), were prepared by oxidation of the corresponding $[Mn(pzb)_2]$ complexes with $NOPF_6$. A representative procedure follows this paragraph.

Synthesis of $[Mn(Tp)_2]PF_6$. A 0.040 g quantity of $NOPF_6$ was added to 0.125 g of $[Mn(Tp)_2]$ dissolved in 20 mL of CH_3CN. The solution, which turned yellow immediately, was stirred for 30 min and allowed to evaporate. Yellow crystals were obtained upon evaporation and were washed with hexane to remove unreacted $[Mn(Tp)_2]$. The product was recrystallized from 10:3 CH_3CN/hexane. Anal. Calcd for $C_{18}H_{20}N_{12}B_2MnPF_6$: C, 34.54; H, 3.22; N, 26.85. Found: C, 35.24; H, 3.72; N, 27.91.

Methods. Electrochemical experiments were conducted in a three-electrode cell consisting of a glassy carbon working electrode (Bioanalytical Systems, area = 0.0707 cm^2), a Pt auxiliary electrode, and a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, MF-2079, $E°' = 0.232$ V vs NHE[23]). Cyclic voltammetric data were recorded by use of an EG&G PAR 273A potentiostat. Electrochemical experiments were conducted under a blanket of dinitrogen gas in 1,2-dichloroethane containing 0.1 M $TBAPF_6$. The formal potential of each couple was estimated as the average of the anodic and cathodic peak potentials ($E°' = [E_{pa} + E_{pc}]/2$) with an uncertainty of 0.01−0.02 V. The $E°'$ of the ferrocene/ferricenium couple was used as an internal standard and was found to have a value of 0.50 ± 0.01 V versus Ag/AgCl under the described conditions.

Values of the apparent standard heterogeneous electron-transfer rate constant, $(k_{s,h})_{app}$, were obtained from the scan rate dependence of the voltammetric peak potential separation, $\Delta E_p = E_{pa} - E_{pc}$,[24] using methods described previously.[25] Measured values of ΔE_p were corrected for contributions from uncompensated solution resistance using published data for the specific resistance of the solvent and supporting electrolyte.[26] Data were collected at scan rates between 0.01 and 0.2 V s^{-1}, under which conditions resistive corrections to ΔE_p were ≤ 30 mV. The relationship between $(\Delta E_p)_{corr}$ and $(k_{s,h})_{app}$ was established by digital simulation (DigiSim 3.03, Bioanalytical Systems)[27] using values of $\alpha = 0.50$, $D = 5.0 \times 10^{-6}$ cm^2 s^{-1}, and $T = 298$ K.

Electronic spectra were recorded in 1,2-dichloroethane or acetonitrile solvent employing an HP 8453A spectrometer. Infrared spectra were recorded in KBr disks on a Nicolet 5PC spectrometer. Magnetic moment measurements were conducted by use of a Johnson Matthey magnetic susceptibility balance (MSB-1) employing solutions of the complexes in 1,2-dichloroethane or acetonitrile. Results were corrected for diamagnetic contributions of the ligands.

Results

Magnetism and Spectroscopy. Magnetic and spectroscopic properties are collected in Table 1. The magnetic moments of the divalent complexes containing M = Mn, Co, and Ni obtained in 1,2-dichloroethane solution are consistent with high-spin configurations having $S = {}^5/_2$, ${}^3/_2$, and 1, respectively. $[Ru(Tp)_2]$ and $[Fe(pzTp)_2]$ are low-spin, $[Fe(Tp^*)_2]$ is high-spin, and $[Fe(Tp)_2]$ exhibits a value of μ_{eff} that is indicative of spin-crossover behavior. Temperature-dependent studies of its $^1A_{1g} \leftrightarrows {}^5T_{2g}$ equilibrium[2,12,17] reveal that $[Fe(Tp)_2]$ is ~25% high-spin in solution at 298 K. The magnetic moments of the trivalent complexes with M = Cr(III), Mn(III), Fe(III), and Co(III) in acetonitrile solution are consistent with values of $S = {}^3/_2$, 1, ${}^1/_2$, and 0, respectively. The result for manganese(III) is notable, because a low-spin configuration is uncommon for this oxidation state.

The ligand field spectra of the complexes are consistent with their magnetic properties. Spectroscopic features and 10Dq values for $[Fe(pzTp)_2]$ and $[Fe(Tp)_2]$ are characteristic of low-spin, octahedral M(II) complexes; those for $[Fe(Tp^*)_2]$, $[Co(pzb)_2]$, and $[Ni(pzb)_2]$ are characteristic of high-spin, octahedral M(II) complexes. The spectra of $[Cr(Tp)_2]^+$, $[Co(pzTp)_2]^+$, and $[Co(Tp)_2]^+$ are representative of the indicated M(III) species. The $[Mn(pzb)_2]^+$ and $[Fe(pzb)_2]^+$

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(14) Turner, J. W.; Schultz, F. A. *Inorg. Chem.* **1999**, *38*, 358.
(15) Turner, J. W.; Schultz, F. A. *Inorg. Chem.* **2001**, *40*, 5296.
(16) Turner, J. W.; Schultz, F. A. *Coord. Chem. Rev.* **2001**, *219−221*, 81.
(17) Turner, J. W.; Schultz, F. A. *J. Phys. Chem. B* **2002**, *106*, 2009.
(18) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.
(19) Onishi, M.; Ikemoto, K.; Hiraki, K. *Inorg. Chim. Acta* **1991**, *190*, 157.
(20) Abrams, M. J.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1985**, *106*, 69.
(21) Hayashi, A.; Nakajima, K.; Nonoyama, M. *Polyhedron* **1997**, *16*, 4087.
(22) Mason, S. J.; Hill, C. M.; Murphy, V. J.; O'Hare, D.; Watkin, D. J. *J. Organomet. Chem.* **1995**, *485*, 165.
(23) Yu, Q.; Salhi, C. A.; Ambundo, E. A.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 5720.
(24) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.
(25) Olson, G. M.; Schultz, F. A. *Inorg. Chim. Acta* **1994**, *225*, 1.
(26) Kadish, K. M.; Ding, J. Q.; Malinski, T. *Anal. Chem.* **1984**, *56*, 1741.

Table 1. Magnetic and Spectroscopic Properties of Metal−Bis[poly(pyrazolyl)borate] Complexes

	μ_{eff}, μ_B[a]			10Dq, cm^{-1} (ϵ, M^{-1} cm^{-1})[a]				ν_{B-H}, cm^{-1}[b]	
	pzTp	Tp	Tp*	pzTp	Tp	Tp*	assignment	Tp	Tp*
					Divalent Complexes				
$[Mn(pzb)_2]$	5.8	5.8	5.7				*g*	2459	2524
$[Fe(pzb)_2]$	0.9[c]	2.2[c,d]	4.8[c]	19 100 (100)	19 200 (110)[e]	12 700 (5.6)[f]	$^1T_{1g} \leftarrow {}^1A_{1g}$	2485	2508
$[Co(pzb)_2]$	4.6	4.4	4.8	11 400 (4.6)	11 200 (2.5)	10 500 (5.3)	$^4T_{2g} \leftarrow {}^4T_{1g}$	2464	2506
$[Ni(pzb)_2]$	3.1	3.1	3.2	12 000 (4.9)	11 900 (3.6)	11 400 (4.6)	$^3T_{2g} \leftarrow {}^3A_{2g}$	2467	2508
$[Ru(pzb)_2]$		1.0					*g*	2486	
					Trivalent Complexes				
$[Cr(pzb)_2]Cl$		3.5			21 700 (32)		$^4T_{2g} \leftarrow {}^4A_{2g}$	2508	
$[Mn(pzb)_2]PF_6$	3.8	3.2	3.2	26 000 (5400)	25 800 (3200)	24 100 (5700)	$^3E_g \leftarrow {}^3T_{1g}$	2537	2558
$[Fe(pzb)_2]PF_6$	2.1	2.3	2.7	18 000 (1500)	18 000 (1500)	17 000 (1000)	$^2A_{2g}$, $^1T_{1g} \leftarrow {}^2T_{2g}$	2520	2559
$[Co(pzb)_2]Cl$	0.8	0.8		21 800 (160)	21 800 (90)		$^1T_{1g} \leftarrow {}^1A_{1g}$	2549	

[a] Data obtained in 1,2-dichloroethane for divalent complexes and in CH_3CN for trivalent complexes. [b] [K(Tp)], $\nu_{B-H} = 2436 \pm 1$ cm^{-1}; [K(Tp*)], $\nu_{B-H} = 2437 \pm 2$ cm^{-1}. [c] From ref 17. [d] Value varies with temperature. [e] ϵ uncorrected for spin-equilibrium. [f] $^5E_g \leftarrow {}^5T_{2g}$. [g] Ligand field transition not observed.

complexes exhibit intense absorptions at 27 600−29 200 cm^{-1} ($\epsilon = 0.7-1.7 \times 10^4$ M^{-1} cm^{-1}) and 36 100−37 600 cm^{-1} ($\epsilon = 0.6-1.2 \times 10^4$ M^{-1} cm^{-1}) for Mn and at 20 600−22 400 cm^{-1} ($\epsilon = 4.0-6.9 \times 10^3$ M^{-1} cm^{-1}) for Fe, values which are characteristic of charge-transfer transitions. For both metals, a shoulder is observed on the low-energy side of these features at an energy consistent with a low-spin d−d transition. These values are reported in Table 1. For the $[Mn(pzb)_2]^+$ complexes, a low-energy band arising from the split d−d transition that is characteristic of tetragonally distorted, high-spin Mn(III)[28] is not observed. This finding is consistent with assignment of S = 1 for $[Mn(pzb)_2]^+$.

Poly(pyrazolyl)borates exhibit ligand field strengths comparable to those of other N donor ligands. For example, values of 10Dq for $[M(Tp)_2]$ and $[M(Tp)_2]^+$ nearly equal those for the corresponding bis(tacn) complexes and bis(tpm) complexes.[29] A notable exception is low-spin Fe(II), where 10Dq = 19 200 cm^{-1} for $[Fe(Tp)_2]$ (Table 1) and 16 800 cm^{-1} for $[Fe(tacn)_2]^{2+}$.[15] Pyrazole substituents influence the spectoscopic properties of metal−pzb complexes. A decrease in 10Dq in the order pzTp ≈ Tp > Tp* is observed for all families of complexes. The sequence is the same as that predicted by steric effects but is the inverse of that based on inductive effects, where the electron density on the N donors inferred by ligand pK_a values[32] increases as pzTp < Tp < Tp*.

Infrared spectroscopy also is useful in characterizing the coordination environment of metal−poly(pyrazolyl)borates.[33] The data in Table 1 are consistent with κ^3 coordination and indicate that the B−H stretching frequency is sensitive to changes in pyrazole ring substitution, oxidation state, and spin state. There are three principal observations: (1) ν_{B-H} increases upon coordination; the magnitude of the shift is 20−60 cm^{-1} larger for Tp* than for Tp complexes and is slightly metal-dependent. (2) The coordination-induced increase in ν_{B-H} is 35−80 cm^{-1} larger for M(III) complexes than for M(II) complexes. (3) For cases in which low-spin M(II) forms are encountered [$Fe(Tp)_2$ and $Ru(Tp)_2$], ν_{B-H} is ~20 cm^{-1} larger than for analogous high-spin M(II) complexes.

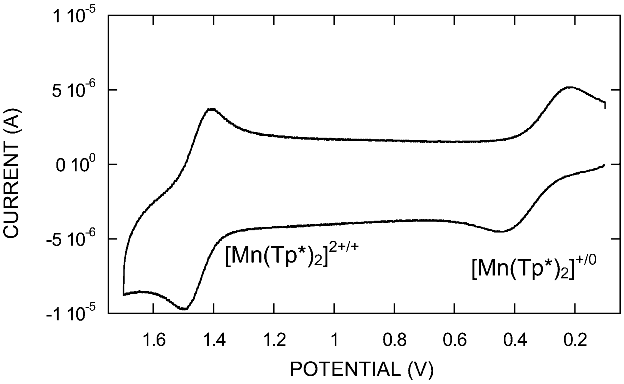

Figure 1. Cyclic voltammetric oxidation of 0.24 mM $[Mn(Tp^*)_2]$ in 0.1 M $TBAPF_6$/1,2-dichlorethane at $v = 0.1$ V s^{-1}.

Electrochemistry. Divalent $[M(pzb)_2]$ complexes with M = Cr, Mn, Fe, Co, Ni, and Ru exhibit a chemically reversible, diffusion-limited, electrode reaction corresponding to the following oxidation:

$$[M(pzb)_2] \leftrightarrows [M(pzb)_2]^+ + e^- \quad E_1^{\circ\prime} \tag{1}$$

In addition, Mn complexes with pzb^- = Tp and Tp* exhibit a second such reaction:

$$[Mn(pzb)_2]^+ \leftrightarrows [Mn(pzb)_2]^{2+} + e^- \quad E_2^{\circ\prime} \tag{2}$$

The cyclic voltammogram in Figure 1 illustrates the sequential one-electron oxidations of $[Mn(Tp^*)_2]$. In cases where compounds can be isolated as both M(II) and M(III) complexes, electrochemical response is independent of the initial oxidation state.

Electrochemical data are presented in Table 2. Ligand structure exerts a small influence on the thermodynamics of

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(27) Rudolph, M.; Reddy, D. R.; Feldberg, S. *Anal. Chem.* **1994**, *66*, 589A.

(28) Davis, T. S.; Fackler, J. P.; Weeks, M. J. *Inorg. Chem.* **1968**, *7*, 1994.

(29) For metal−bis(tacn) complexes, 10Dq = 11 700, 12 500, 22 800, and 21 800 cm^{-1} for M = Co(II), Ni(II), Cr(III), and Co(III), respectively.[30] Comparable values are observed for metal−bis(tpm) complexes.[31]

(30) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953.

(31) Astley, T.; Gulbis, J. M.; Hitchman, M. A.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1993**, 509.

(32) Sohrin, Y.; Matsui, M.; Hata, Y.; Hasegawa, H.; Kokusen, H. *Inorg. Chem.* **1994**, *33*, 4376.

(33) (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121. (b) Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 5148.

Table 2. Electrochemical Data for Metal−Bis[poly(pyrazolyl)borate] Redox Couples[a]

	$E°'$, V vs $Fc^{+/0}$			$i_p/v^{1/2}AC$, $\mu A\ s^{1/2}\ V^{-1/2}\ cm^{-1}\ mM^{-1}$			$(k_{s,h})_{app}$, cm s^{-1}		
redox couple	pzTp	Tp	Tp*	pzTp	Tp	Tp*	pzTp	Tp	Tp*
$[Cr(pzb)_2]^{+/0}$		−1.73			510(30)				
$[Mn(pzb)_2]^{+/0}$	0.07	0.06	−0.13	500(20)	400(10)	470(10)	$4.3(4) \times 10^{-4}$	$5.3(1) \times 10^{-5}$	$5.9(9) \times 10^{-4}$
$[Mn(pzb)_2]^{2+/+}$	*b*	1.31	0.99	*b*	560(20)	680(20)	*b*	$5(1) \times 10^{-3}$	$1.1(2) \times 10^{-2}$
$[Fe(pzb)_2]^{+/0}$	−0.17	−0.27	−0.44	570(10)	470(30)	600(30)	$1.7(3) \times 10^{-2}$		
$[Co(pzb)_2]^{+/0}$	−0.50	−0.53	−0.58	560(30)	530(50)	430(40)[c]	$4.4(2) \times 10^{-3}$	$1.9(1) \times 10^{-4}$	$2.2(4) \times 10^{-5}$
$[Ni(pzb)_2]^{+/0}$	0.89	0.81	0.59	590(30)	590(30)	480(30)			
$[Ru(pzb)_2]^{+/0}$		−0.21			490(20)				

[a] Data obtained at a glassy carbon electrode in 1,2-dichloroethane containing 0.1 M $TBAPF_6$. [b] Redox couple not observed. [c] Value determined from cathodic peak current.

eqs 1 and 2. Electrode potentials become more negative (i.e., oxidation is facilitated) in the sequence pzTp < Tp < Tp*. The range of $E°'$ values is ~0.1−0.3 V. The one-electron character of these reactions is established on the basis of the voltammetric peak current parameter, $i_p/v^{1/2}AC$, which equals 430−680 $\mu A\ s^{1/2}\ V^{-1/2}\ cm^{-2}\ mM^{-1}$. This range of values is consistent with previously determined quantities for one-electron transfers in 1,2-dichloroethane.[34]

The most interesting electrochemical result is the influence of ligand structure and of metal and oxidation-state change on the apparent heterogeneous electron-transfer rate constant. Values of $(k_{s,h})_{app}$ are collected in Table 2. Data for the determination of $(k_{s,h})_{app}$ from the sweep-rate dependence of $(\Delta E_p)_{corr}$ are presented in Tables S1−S4. The $[Fe(pzTp)_2]^{+/0}$ couple is chosen as an example of rapid electron transfer in 1,2-dichloroethane/0.1 M $TBAPF_6$. It exhibits values of $(\Delta E_p)_{corr}$ equal to 62−72 mV at $v = 0.01-0.2\ V\ s^{-1}$, which yield $(k_{s,h})_{app} = 1.7 \pm 0.3 \times 10^{-2}\ cm\ s^{-1}$.[35] Electron transfer is much slower for $[Co(pzb)_2]^{+/0}$ and $[Mn(pzb)_2]^{+/0}$ under the experimental conditions. For these systems, $(\Delta E_p)_{corr}$ ranges from 115 to 660 mV at $v = 0.2\ V\ s^{-1}$, and $(k_{s,h})_{app}$ is 4−1000 times smaller than the apparent rate constant of $[Fe(pzTp)_2]^{+/0}$. Figure 2 illustrates the sluggish behavior of $[Co(pzb)_2]^{+/0}$ couples and the influence of ligand structure on apparent electron-transfer rate. In this case, $(k_{s,h})_{app}$ varies by a factor of 100 and decreases as pzTp > Tp > Tp*. A final observation is the difference in apparent electron-transfer rate constant between the $[Mn(pzb)_2]^{+/0}$ and $[Mn(pzb)_2]^{2+/+}$ couples. The behavior is qualitatively evident from the voltammogram in Figure 1. In Table 2, $(k_{s,h})_{app}$ values for $[Mn(pzb)_2]^{2+/+}$ nearly equal those of $[Fe(pzTp)_2]^{+/0}$ but are 20−100 times larger than $(k_{s,h})_{app}$ for the corresponding $[Mn(pzb)_2]^{+/0}$ couple.

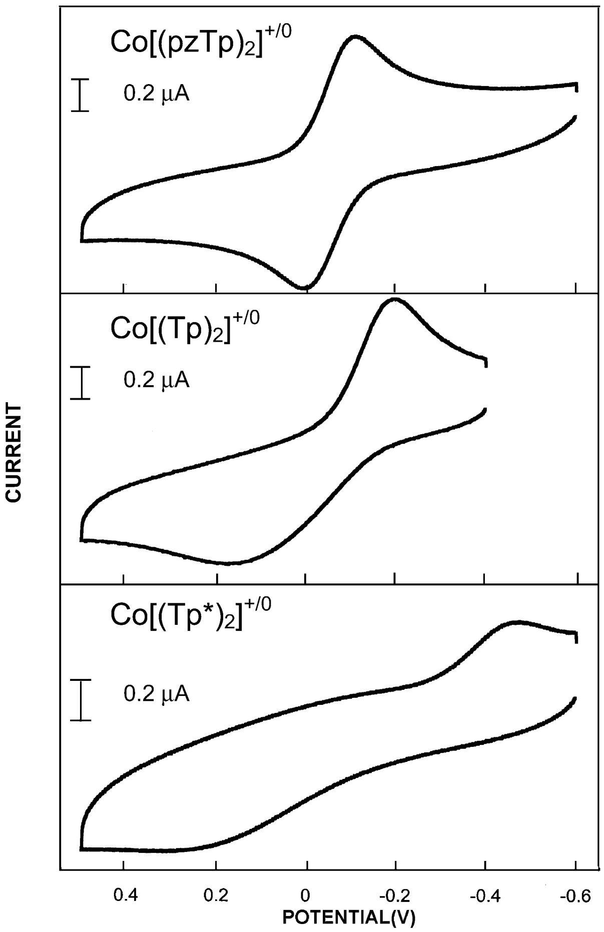

Figure 2. Cyclic voltammetric oxidation of (a) 0.35 mM $[Co(pzTp)_2]$, (b) 0.30 mM $[Co(Tp)_2]$, and (c) 0.53 mM $[Co(Tp^*)_2]$ in 0.1 M $TBAPF_6$/1,2-dichlorethane at $v = 0.1\ V\ s^{-1}$.

Discussion

Steric versus Electronic Effects. The issue of steric versus electronic control in metal−pyrazolylborate chemistry has been discussed in a number of contexts.[36,37] Placement of a bulky substituent at the 3-position of the pyrazole ring often is used to alter the properties of metal−pzb units for the purposes of catalysis and metalloenzyme modeling. Although sterically less demanding, the presence of a methyl group produces discernible changes in spectrochemical and electrochemical behavior.

Table 3 lists average metal−nitrogen bond distances for a number of metal−pzb and tacn complexes. For pzb^- complexes in the same spin-state, there is a systematic increase in M−N distance (pzTp < Tp < Tp*) that parallels the decrease in ligand field strength (Table 1). The sequence

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(34) (a) Mondal, J. U.; Zamora, J. G.; Kinon, M. D.; Schultz, F. A. *Inorg. Chim. Acta* **2000**, *309*, 147. (b) Mondal, J. U.; Zamora, J. G.; Siew, S.-C.; Garcia, G. T.; George, E. R.; Kinon, M. D.; Schultz, F. A. *Inorg. Chim. Acta* **2001**, *321*, 83.

(35) This result is smaller than the value of $k_{s,h}$ determined for $[Fe(pzTp)_2]^{+/0}$ by microelectrode voltammetry in 1:1 acetone/tetrahydrofuran (ref 17). The change of solvent may account for some of the difference. However, the inability to correct accurately for the effects of uncompensated solution resistance at a macroscopic working electrode in cyclic voltammetry experiments also is a contributing factor.

(36) Sohrin, Y.; Kokusen, H.; Matsui, M. *Inorg. Chem.* **1995**, *34*, 3928.

(37) Reference 4, pp 438−459.

Table 3. Metal−Nitrogen Bond Distances (Å) in Metal-Bis[poly(pyrazolyl)borate] and Bis(triazacyclononane) Complexes

	ligand			
metal	pzTp	Tp	Tp*	tacn
Mn(II)	2.24(3)^a	2.25(3)^a	2.275^b	
Fe(II)	1.97(2)^c	1.97(1)^d	2.17(2)^{d,e}	2.03(1)^f
Fe(III)		1.96(1)^g	1.97(1)^h	1.99(3)^f
Co(II)	2.12(3)^a	2.13(1)^i		2.16(3)^j
Ni(II)	2.08(3)^a	2.09(1)^k	2.11(2)^{l,m}	2.11(1)^n

[a] Reference 9. [b] Value cited in ref 38. [c] Reference 36. [d] Reference 39. [e] High-spin. [f] Reference 40. [g] Reference 41. [h] Reference 22. [i] Reference 42. [j] Reference 43. [k] Reference 44. [l] Reference 45. [m] Tris(3-methylpyrazolyl) derivative. [n] Reference 46.

is the inverse of that predicted by ligand inductive effects and indicates that steric rather than electronic effects have a more important influence on the structural and spectroscopic properties of metal−pzb complexes. For [Fe(Tp)$_2$], these factors combine to produce 10Dq $= 19\,200$ cm^{-1}, $B = 800$ cm^{-1},[2] and 10Dq/$B = 24.0$, which places the complex at the spin-transition point.

[Fe(tacn)$_2$]$^{2+}$ also exhibits a $^1A_{1g} \rightarrow {}^5T_{2g}$ transition. Its thermodynamic parameters are similar to those of [Fe(Tp)$_2$] spin-crossover.[15] However, 10Dq $= 16\,800$ cm^{-1} for low-spin [Fe(tacn)$_2$]$^{2+}$, a value that is much smaller than the 10Dq of low-spin [Fe(Tp)$_2$]. The difference is surprising, because [M(tacn)$_2$]$^{2+}$ and [M(Tp)$_2$] exhibit almost identical 10Dq values for other metal ions. The energies of the first and second ligand field transitions of low-spin [Fe(tacn)$_2$]$^{2+}$ (16 800 and 25 600 cm^{-1})[15] yield an estimate of $B = 650$ cm^{-1}, from which 10Dq/$B = 25.8$.[47] Thus, the ratio 10Dq/B is similar for [Fe(tacn)$_2$]$^{2+}$ and [Fe(Tp)$_2$]. Table 3 shows that M−N bond distances are systematically 0.02−0.03 Å longer in tacn than Tp complexes for M = Fe(III), Ni(II), and Co(II). In the case of low-spin Fe(II), the Fe−N bond distance is 0.06 Å longer for the tacn complex. The larger difference in Fe−N distance is consistent with the observation of smaller 10Dq and B values for [Fe(tacn)$_2$]$^{2+}$.

The electrode potentials of the [M(pzb)$_2$]$^{+/0}$ and [Mn(pzb)$_2$]$^{2+/+}$ couples also are influenced by ligand substituents (Table 2). The positive shift in $E_1{}^{\circ\prime}$ for [M(pzTp)$_2$]$^{+/0}$ versus [M(Tp)$_2$]$^{+/0}$ is indicative of the electron-withdrawing character of the uncoordinated pyrazolyl group, consistent with the findings of Onishi et al. for [Ru(pzb)$_2$]$^{+/0}$ complexes.[48] The shift in $E_1{}^{\circ\prime}$ and $E_2{}^{\circ\prime}$ parallels the electron-releasing ability of the ligands (pzTp < Tp < Tp*) and is operative despite a small increase in M−N distance bond distance (Table 3). The trend in redox potentials is consistent with a sequence based on ligand inductive effects,[49,50] which is the inverse of that inferred from ligand field strengths. Correlation between 10Dq and $E^{\circ\prime}$ is not necessarily anticipated.[51]

Coupled Electron Transfer and Spin Exchange. Electrode reactions that are accompanied by a change in spin-state exhibit several characteristics that distinguish them from simple electron-transfer events.[16] One consequence is that the apparent heterogeneous electron-transfer rate constant, $(k_{s,h})_{app}$, can be small, because spin-equilibrium depletes the population of electroactive forms. Recently, we reported rate constants for [Fe(pzb)$_2$]$^{+/0}$ couples in 1:1 acetone/tetrahydrofuran employing fast scan-rate microelectrode voltammetry.[17] Values of $(k_{s,h})_{app}$ for reduction of low-spin [Fe(pzTp)$_2$]$^+$ to low-spin [Fe(pzTp)$_2$] and of low-spin [Fe(Tp)$_2$]$^+$ to a mixture of low- and high-spin [Fe(Tp)$_2$] are large and approximately equal. Spin exchange has a small impact on electrochemical behavior in the latter case, because only ~0.2 mole fraction of high-spin [Fe(Tp)$_2$] is present under the experimental conditions. However, the [Fe(Tp*)$_2$]$^{+/0}$ couple, which is characterized by complete conversion of low-spin [Fe(Tp*)$_2$]$^+$ to high-spin [Fe(Tp*)$_2$], exhibits a 10-fold smaller rate constant.

Additional examples of coupled electron transfer and spin exchange are encountered in this work. These include oxidation of high-spin [Mn(pzb)$_2$] to low-spin [Mn(pzb)$_2$]$^+$ (eq 1, M = Mn) and oxidation of high-spin [Co(pzb)$_2$] to low-spin [Co(pzb)$_2$]$^+$ (eq 1, M = Co). Although observation of low-spin Mn(III) is uncommon, the μ_{eff} values in Table 1 are comparable to the 2.8−3.7 μ_B range reported for other low-spin Mn(III) complexes.[52−55] Thus, we conclude that $S = {}^5/_2$ Mn(II) compounds are oxidized to $S = 1$ Mn(III) forms in eq 1. Further characterization of the [Mn(pzb)$_2$]$^+$ species formed in this reaction is in progress.

A distinguishing feature of coupled electron transfer and spin exchange is slow electrochemical kinetics. This behavior is exhibited by the [Mn(pzb)$_2$]$^{+/0}$ redox couples. Sluggish Mn(III/II) electron transfer also has been reported in electrochemical studies of [Mn(Tp*)$_2$]$^{+/0}$[56] and [Mn(tripod)$_2$]$^{+/0}$ (tripod$^-$ = [CpCoP(OC$_2$H$_5$)$_3$]$^-$).[57] The results in Figure 1 and Table 2 demonstrate that $(k_{s,h})_{app}$ is smaller for

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(38) Eichhorn, D. M.; Armstrong, W. H. *Inorg. Chem.* **1990**, *29*, 3607.
(39) Oliver, J. D.; Mullica, D. F.; Hutchinson, B. B.; Milligan, W. O. *Inorg. Chem.* **1980**, *19*, 165.
(40) Boeyens, J. C. A.; Forbes, A. G. S.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 2926.
(41) Calogero, S.; Gioia Lobbia, G.; Cecchi, P.; Valle, G.; Friedl, J. *Polyhedron*, **1994**, *13*, 87.
(42) Churchill, M. R.; Gold, K.; Maw, C. E., Jr. *Inorg. Chem.* **1970**, *9*, 1597.
(43) Küppers, H.-J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400.
(44) Bandoli, G.; Clemente, D. A.; Paolucci, G.; Doretti, L. *Cryst. Struct. Commun.* **1979**, *8*, 965.
(45) Cecchi, P.; Gioia Lobbia, G.; Marchetti, F.; Valle, G.; Calogero, S. *Polyhedron* **1994**, *13*, 2174.
(46) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157.
(47) Figgis, B. N.; Hitchman, M. A. *Ligand Field Theory and Its Applications.* Wiley-VCH: New York, 2000.
(48) Onishi, M.; Kumagae, S.; Asai, K.; Kawano, H.; Shigemitsu, Y. *Chem. Lett.* **2001**, 96.
(49) It has been noted in gas phase studies[50] that alkyl substituents are not intrinsically electron-donating and do not always result in lower ionization potentials. Thus, the contributions of both polarization and inductive effects need to be considered, although the two operate in the same direction for the monopositive/neutral redox couples studied in this work.
(50) Richardson, D. E.; Ryan, M. F.; Khan, Md. N. I.; Maxwell, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 10482.
(51) Lintvedt, R. L.; Fenton, D. E. *Inorg. Chem.* **1980**, *19*, 569.
(52) Griffith, W. P. *Coord. Chem. Rev.* **1975**, *17*, 177.
(53) Hansen, A. P.; Goff, H. M. *Inorg. Chem.* **1984**, *23*, 4519.
(54) Daugherty, P. A.; Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K. *Acta Chem. Scand.* **1991**, *45*, 244.
(55) Ganguly, S.; Karmakar, S.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 116.
(56) Chan, M. K.; Armstrong, W. H. *Inorg. Chem.* **1989**, *28*, 3777.
(57) Kölle, U.; Englert, U. *Eur. J. Inorg. Chem.* **2002**, 165.

$[Mn(pzb)_2]^{+/0}$ than for $[Mn(pzb)_2]^{2+/+}$. If sequential oxidation of $[Mn(pzb)_2]$ were to occur from $S = {}^5/_2$ Mn(II) to $S = 2$ Mn(III) to $S = {}^3/_2$ Mn(IV), the number of antibonding e_g* electrons would change by one in each step. This would produce approximately equal inner-shell reorganization energies with each electron transfer, from which Marcus theory[58] predicts approximately equal rates for the two reactions. However, it is evident that Mn(II/III) is slower than Mn(III/IV) electron transfer, which is consistent with oxidation of $S = {}^5/_2$ $[Mn(pzb)_2]$ to $S = 1$ $[Mn(pzb)_2]^+$.

The $[Co(pzb)_2]^{+/0}$ half-reactions represent a second example of coupled electron transfer and spin exchange. Slow electron transfer is anticipated for these systems, because there is a two-electron change in e_g* orbital occupancy upon conversion of $S = 0$ Co(III) to $S = {}^3/_2$ Co(II).[59,60] The $[Co(pzb)_2]^{+/0}$ couples exhibit small $(k_{s,h})_{app}$ values, which decrease as pzTp > Tp > Tp* (Table 2). The origin of the ligand structural influence on apparent electron-transfer rate is unclear. One explanation is that the reactions occur by simultaneous electron transfer and spin exchange with ligand-dependent reorganization energies. However, a second explanation is that the electrode reactions occur by coupled (stepwise) electron transfer and spin exchange involving high-spin Co(III) or low-spin Co(II) species as intermediates in the reaction pathway. If the mole fractions of these minor forms are sensitive to changes in pyrazole substituents, as found for $[Fe(pzb)_2]$,[2,13,17] small changes in their populations may have a dramatic influence on the apparent electron-transfer rate. Further studies are planned to explore the role of these factors in $[Co(pzb)_2]^{+/0}$ electrode kinetics.

Periodic Trends in Redox Potentials. Preparation of a series of homoleptic complexes affords an opportunity to explore trends in properties and obtain insight into relationships between structure and reactivity. Periodic trends in transition metal redox potentials have been investigated on several occasions.[61−63] Quantitative interpretation has been difficult to achieve because of the complexities of configuration interaction and metal−ligand covalency. Nevertheless, qualitative comparisons are insightful, especially for families of compositionally similar compounds. In this section, $[M(Tp)_2]^{+/0}$ potentials are compared with values for M(III/II) couples of other homoleptic MN_6 complexes in which the nitrogen donor ligands are 1,4,7-triazacyclononane (tacn), sarcophagine (sar), and 2,2′-bipyridine (bpy).

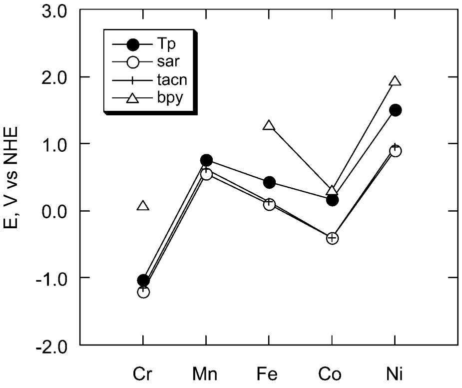

Figure 3. $MN_6^{3+/2+}$ redox potentials for first-row transition metal complexes. Data for $[M(Tp)_2]^{+/0}$ couples from Table 2; for $[M(tacn)_2]^{3+/2+}$ couples, from ref 30; for $[M(sar)]^{3+/2+}$ couples, from ref 64; for $[M(bpy)_3]^{3+/2+}$ couples, from refs 65 (M = Cr, Fe), 66 (M = Co), and 67 (M = Ni).

Figure 3 contains plots of $E°'$ as a function of metal for $[M(Tp)_2]^{+/0}$, $[M(tacn)_2]^{3+/2+}$, $[M(sar)]^{3+/2+}$, and $[M(bpy)_3]^{3+/2+}$ redox couples. As observed previously, $M^{3+/2+}$ potentials for first-row complexes increase generally from left to right across the periodic table in a manner congruent with the third ionization energies of gas phase metal atoms. The discontinuity at Fe that arises from the spin-pairing requirement of free Fe^{2+} is attenuated by ligand field stabilization. The $[M(bpy)_3]^{3+/2+}$ couples exhibit much more positive potentials than complexes with aliphatic N donor ligands, because the M(II) state is stabilized by metal t_{2g}-to-ligand π* back-bonding in the bpy complexes.

An interesting aspect of Figure 3 is the extent to which the difference between the $E°'$ values for $[M(Tp)_2]^{+/0}$ and the other $MN_6^{3+/2+}$ couples changes as M varies from Cr to Ni. For early members of the series, the $[M(Tp)_2]^{+/0}$ potential is almost identical to that of $[M(tacn)_2]^{3+/2+}$ and $[M(sar)]^{3+/2+}$. However, $E°'$ for $[M(Tp)_2]^{+/0}$ is more nearly equal that of $[M(bpy)_3]^{3+/2+}$ for later first-row metals. Poly(pyrazolyl)borates are considered to be ligands with moderate σ-donor and weak π-donor properties.[68] Apparently, these factors combine to stabilize M(III) relative to M(II) to nearly the same extent as σ-donating tacn and sar for early first-row metals. However, for later first-row metals, in which the t_{2g} set is filled or nearly so, either the π-donor properties of Tp are diminished or the ligand exhibits increased π-acceptor characteristics. In either event, $[M(Tp)_2]^{+/0}$ potentials assume relatively more positive values. This outcome is consistent with previous observations[10,11] that the electronic properties of Tp can exhibit a significant metal dependence.

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(58) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(59) Hendry, P.; Ludi, A. *Adv. Inorg. Chem.* **1990**, *35*, 117.

(60) The mechanism of low-spin Co(III) to high-spin Co(II) reduction and the large range of $CoN_6^{3+/2+}$ electron self-exchange rates are topics that have been discussed for many years. For a selection of experimental and theoretical treatments of the problem see: (a) Buhks, E.; Dixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014. (b) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754. (c) Hammershøi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *32*, 979. (d) Larsson, S.; Ståhl, K.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 3033. (e) Newton, M. D. *J. Phys. Chem.* **1991**, *95*, 30. (f) Shalders, R. D.; Swaddle, T. W. *Inorg. Chem.* **1995**, *34*, 4815. (g) Bernhardt, P. V.; Jones, L. A.; Sharpe, P. C. *Inorg. Chem.* **1997**, *36*, 2420. (h) Endres, R. G.; LaBute, M. X.; Cox, D. L. *Los Alamos National Laboratory, Preprint Archive, Physics* **2002**, 1−10. arXiv:physics/0212010. http://xxx.lanl.gov/pdf/physics/0212010.

(61) Van Gaal, H. L. M.; Van der Linden, J. G. M. *Coord. Chem. Rev.* **1982**, *47*, 41.

(62) Sharpe, P.; Eyler, J. R.; Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 2779.

(63) Johnson, D. A.; Nelson, P. G. *Inorg. Chem.* **1999**, *38*, 4949.

(64) Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Harrowfield, J. M.; Krausz, E. R.; Moran, G. M.; Sargeson, A. M.; White, A. H. *Aust. J. Chem.* **1993**, *46*, 111.

(65) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(66) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

(67) Henne, B. J.; Bartak, D. E. *Inorg. Chem.* **1984**, *23*, 369.

(68) Janiak, C.; Scharmann, T. G.; Green, J. C.; Parkin, R. P. G.; Kolm, M. J.; Riedel, E.; Mickler, W.; Elguero, J.; Claramunt, R. M.; Sanz, D. *Chem.−Eur. J.* **1996**, *2*, 996.

Concluding Remarks

Metal(II)−bis[poly(pyrazolyl)borate] complexes, $[M(pzb)_2]$, can be oxidized in a chemically reversible manner to $[M(pzb)_2]^+$ species. For M = Co and Mn, $[M(pzb)_2]^{+/0}$ electron transfer is accompanied by a change in metal atom spin-state. The kinetics of these reactions are slow and are influenced dramatically by the structure of the pzb^- ligand, with the apparent electrochemical rate constant decreasing as pzTp > Tp > Tp* for $[Co(pzb)_2]^{+/0}$. $[Co(pzb)_2]^{+/0}$ and $[Mn(pzb)_2]^{+/0}$ are promising systems for mechanistic investigations of coupled electron-transfer and spin-exchange reactions.

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Supporting Information Available: Tables S1−S4 containing values of $(\Delta E_p)_{corr}$ and $(k_{s,h})_{app}$ as a function of sweep rate for $[M(pzb)_2]^{+/0}$ and $[Mn(pzb)_2]^{2+/+}$ redox couples. This material is available free of charge via the Internet at http://pubs.acs.org.

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