transfer from H_2O to R is not significantly advanced in the transition state.

The heterolytic reactions are accompnaied by substantial and negative activation entropies, as shown in Table II. This suggests a transition state with larger charge separation as compared to that of reactant. Hence, the interpretation we offer is that the rate-limiting step is intramolecular charge transfer to form an incipient carbanion, and the transition state might be represented as $[HOCr^{\delta+}(L)R^{\delta-}\cdots H–OH^+]^{\ddagger}$. We further note that heterolysis applies only to the complex in which the trans ligand is OH^-, not H_2O. The evident role for coordinated OH^- is to act as a strong electron donor, which improves the energetics of carbanion formation.

The aralkyl complexes are not subject to heterolytic solvolysis, even in the case of the trans hydroxy species. This contrasts with the very slow but easily observed decomposition of $(H_2O)_5CrCH_2Ph^{2+}$.[23]

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Solvent-Dependent Redox Thermodynamics of Metal Amine Complexes. Delineation of Specific Solvation Effects

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Solvent-dependent formal potentials, E_f, and reaction entropies, $\Delta S_{rc}°$, for four reversible Co(III/II) couples featuring macrobicyclic "cage" ligands have been obtained. These are utilized, together with corresponding data for other Co(III/II) and Ru(III/II) amine couples and for M(III/II) polypyridine couples, to unravel effects on the redox thermodynamics arising from specific ligand–solvent and other interactions. The solvent dependencies of E_f (vs ferrocenium–ferrocene) for each redox couple are fitted by using a multiparameter approach, incorporating various well-known empirical quantities describing solvent basicity, acidity, polarity, and internal ordering. For most amine couples, solvent basicity appears to play a prevailing role, associated with interactions involving the amine hydrogens, although solvent polarity also exerts a substantial, albeit less solvent-dependent, influence upon E_f. The presence of a deprotonated amide group in the Co(III/II) amine couple is signaled by the additional presence of a significant solvent acidity component in the multiparametric fit. The solvent basicity and other specific contributions to the E_f–solvent behavior for the polypyridine couples are markedly smaller than for the amines. While the inclusion of a "solvent internal ordering" term does not exert a statistically significant influence on the E_f–solvent dependence for any of the redox couples, the $\Delta S_{rc}°$–solvent dependencies are correlated most successfully with this parameter. Besides identifying the major specific solvation factors upon the redox thermodynamics for such inorganic redox couples, the present multiparametric solvent-dependent analysis also provides a novel, although approximate, means by which the extent of such obfuscating influences upon E_f can be assessed.

Introduction

The ways in which outer-sphere effects such as solvation and the nature of the counterion affect the kinetics and the thermodynamics of electron transfer are incompletely understood. In order to explore these issues, an examination of the solvent-dependent formal potentials, E_f, of redox couples provided by cobalt "cage" complexes[1-7] is likely to be useful. A key feature of the macrobicyclic ligands of such complexes is that they render the normally labile high-spin Co(II) oxidation state substitutionally inert.[3,7-9] These redox couples are therefore free of complications due to ligand loss in the Co(II) oxidation state and exhibit chemical and electrochemical reversibility.[3,7-13] Limited data are also available on the redox properties of cage complexes in nonaqueous solvents.[7,8,11] One aim of the work described here is to expand on these results.

In addition to the cage complexes, the solvent dependencies of the $[Ru(NH_3)_6]^{3+/2+}$ and $[Co(en)_3]^{3+/2+}$ formal potentials (en = 1,2-ethanediamine) have been reexamined in the present study; previous investigations have shown that E_f values for these couples correlate with solvent basicity.[11,14,15] A complication with the latter redox couple is that $[Co(en)_3]^{2+}$ is labile, so that it is often necessary to add 1,2-ethanediamine in order to prevent irreversible reduction.[11] By analogy with the significant observed effect of added 1,2-ethanediamine on E_f for the $[Ru(en)_3]^{3+/2+}$ couple,[13] the addition of 1,2-ethanediamine to the solvents of interest is likely to influence the thermodynamic parameters obtained from the solvent dependence of the $[Co(en)_3]^{3+/2+}$ couple. The cage complexes can therefore provide a less ambiguous indicator of the

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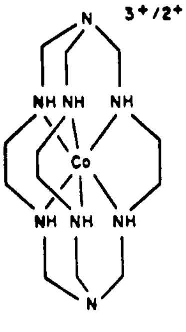
various solvent contributions to the redox potentials of Co(III/II) amine couples. The couples comprising cobalt cage complexes[16] that are used in this study are $[Co(sep)]^{3+/2+}$ (I), $[Co((NO_2)_2\text{-sar})]^{3+/2+}$ (II), $[Co(NHCOCH_3)_2\text{-sar})]^{3+/2+}$ (III), and $[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$ (IV) (see structures). Complexes I-III contain acidic protons[5,8] and will be used to probe the effects of solvent basicity on the thermodynamics of electron transfer. The dipolar complex, IV, is amphiprotic; it is used here to prove the effects of solvent basicity as well as acidity.



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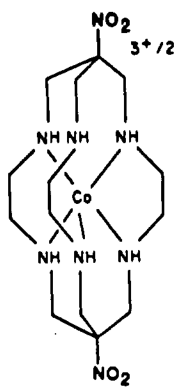

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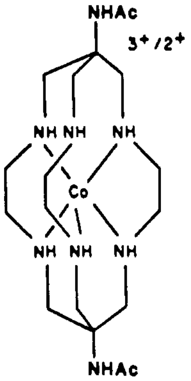

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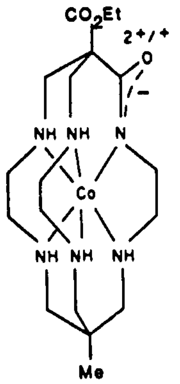

IV

Recently, a model was proposed to account for such effects of solvation on the kinetics and thermodynamics of electron transfer.[17] This model reflects the influence of specific solvation (hydrogen bonding, π-ring stacking, and internal solvent order) as well as more nonspecific effects[17-19] though an equation of the form

$$E_f = E_f^\circ + \Delta E_p + \Delta E_H + \Delta E_s \tag{1}$$

Here E_f° is the hypothetical formal potential in the absence of a specifically interacting solvent, ΔE_p accounts for the effects of solvent polarity and polarizability, ΔE_H accounts for the disruption of internal order of the solvent, and ΔE_s accounts for acidic/basic hydrogen bonding or π-ring solute–solvent interactions.[17-19] The hypothesis is that these terms are related to the empirical solvent parameters discussed by Taft et al.[20,21] represented in the following equation:[17-19]

$$E_f = E_f^\circ + a\alpha + b\beta + c\pi^* + h\delta_H \tag{2}$$

Here, α, β, π^*, and δ_H are respectively measures of the hydrogen-bonding acidity, hydrogen-bonding basicity, polarity, and the internal order of the solvent in question and a, b, c, and h are the coefficients derived from best fits to the experimental data. From this approach, the various terms in eq 2 can be paired with those in eq 1 to give[17-19]

$$\Delta E_p = c\pi^* \tag{3}$$

$$\Delta E_H = h\delta_H \tag{4}$$

$$\Delta E_s = a\alpha + b\beta \tag{5}$$

The values of a, b, c, and h for the forementioned redox couples resulting from statistical analyses of the solvent dependence of E_f are reported and discussed here.

Experimental Section

Most of the solvents were Aldrich "Gold Label" grade and used as received. Solutions were prepared in a drybox filled with N_2. Dioxane and THF (AR grade) were distilled, over sodium, in an N_2 atmosphere just prior to their use. The syntheses of the various amine and cage complexes have been or will be reported elsewhere.[1-7] KPF_6 (Merck) was twice recrystallized from aqueous solution and dried in a vacuum oven at 110 °C; tetrakis(1-butyl)ammonium tetrafluoroborate (Aldrich) was recrystallized twice from ethyl acetate.[22] Ferrocene (Fluka, purum) was used as received. The formal potentials, E_f, were obtained by bisecting the cathodic and anodic peak potentials observed in cyclic voltammograms or from the value of $E_{1/2}$ in the case of "steady-state" linear sweep voltammetry with microelectrodes. The temperature dependencies of E_f, so as to yield reaction entropies ΔS_{rc}°, were obtained over a temperature range of at least 50 °C, using a nonisothermal cell and instrumentation as outlined previously.[11,19,23-26] Unless otherwise stated, the uncertainties in E_f and ΔS_{rc}° are ± 2 mV and ± 4 J K^{-1} mol^{-1}, respectively. All potentials were measured against K(SCE), Na(SCE), or Ag/AgCl/KCl(saturated) reference electrodes. The ferrocenium/ferrocene (Fc^+/Fc) redox potentials (which were used as internal references) were measured by using either ferrocene or ferrocenium picrate.[27] All of the potentials reported here are vs Fc^+/Fc.

All correlations and statistical analyses were performed by using least-squares analyses of the solvent-dependent experimental data. The programs "STEPWISE" and "REGRESS" in the statistics package MINITAB[28] were used for the multiple linear regressions. The STEPWISE program considers all the solvent parameters and only retains those with an F statistic of 4 or greater (i.e. a t statistic of 2 or greater, where $t = F^{1/2}$).[28] The REGRESS program allows the number and type of solvent parameters to be chosen and obtains the best fit of all of the chosen parameters in a multiple linear regression. The values of t and R^2 obtained in these statistical analyses are included in the appropriate tables.

Results

The redox potentials, E_f, of the cage complexes were determined in 0.1 M KPF_6 or $[Bu)_4N]BF_4$ solutions of various protic and aprotic solvents, using the Fc^+/Fc couple as an internal standard.[29-31] The specific effects of counterions on the redox ther-

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(16) en = 1,2-ethanediamine; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane; sar = sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; $(NO_2)_2$-sar = 1,8-dinitrosarcophagine; $(NHCOCH_3)_2$-sar = 1,8-diacetamidosarcophagine; $CO_2CH_2CH_3,CH_3$-oxosar-H = 1-(ethylformato)-8-methyl-2-oxosarcophaginato; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline; Fc^+ = ferrocenium; Fc = ferrocene; py = pyridine.

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Table I. Formal Potentials, E_f (mV), and Reaction Entropies, $\Delta S°$ (J K^{-1} mol^{-1}), for Co(III)/Co(II) Couples Containing Macrobicyclic Ligands and for the Ferrocenium–Ferrocene (Fc^+/Fc) Couple in 0.1 M KPF_6 or $[(Bu)_4N]BF_4$ Solutions

	$[Co(sep)]^{3+/2+}$		$[Co((NO_2)_2\text{-}sar)]^{3+/2+}$		$[Co(NHCOCH_3)_2\text{-}sar)]^{3+/2+}$		$[Co(CH_3,COOC_2H_5\text{-}oxosar\text{-}H)]^{2+/+}$		Fc^+/Fc	
solvent	E_f^a vs Fc^+/Fc	$\Delta S°^b$	E_f^a vs Fc^+/Fc	$\Delta S°^b$	E_f^a	$\Delta S°^b$	E_f^a	$\Delta S°^b$	E_f vs SCE	$\Delta S°^b$
acetone			-434	176			-1129	184	314	67
acetonitrile	-689	215	-334	190	-675	163	-1083	167	243	48^f
N,*N*-dimethylformamide			-742	189	-963	201	-1284	175	347	56^f
dimethyl sulfoxide	-1112	184^d	-840	187	-1059	*e*	-1345	159	359	52^f
1,4-dioxane^g			-536							106^g
formamide	-897	142^d	-659	120	-874	110	-1130	77	258	0^f
methanol^c			$\sim -592^e$	*e*			-1035	167	305	13^f
N-methylformamide	-996	167^d	-713	111 ± 10	-935	155	-1206	94	332	17^f
nitromethane			-164	169	*e*	*e*	-959	~140	132	59^f
propylene carbonate	-888	201^d					-1103	151	202	46^f
tetrahydrofuran^g			-533	206						71^g
water	-667	79^d	-390	102	-623	75	-957	30	142	-21^f

[a] Formal potential versus the Fc^+/Fc couple at 25 °C using the cell configuration K(SCE)(aq)/0.1 M KPF_6(solvent)‖0.1 M KPF_6(solvent)‖Hg. [b] Reaction entropy obtained from the nonisothermal cell arrangements. [c] 0.09 M KPF_6. [d] Reference 13; 0.1 M $LiClO_4$. [e] Solubility or adsorption problems precluded obtaining accurate E_f and/or $\Delta S°$ values. [f] $\Delta S°$ values from ref 22. Measured $\Delta S°$ values of the Fc^+/Fc couple are not sensitive to either supporting electrolyte or the cell configuration used (Sahami, S. Ph.D. Thesis, Michigan State University, 1981). [g] 0.1 M $[(Bu)_4N]BF_4$.

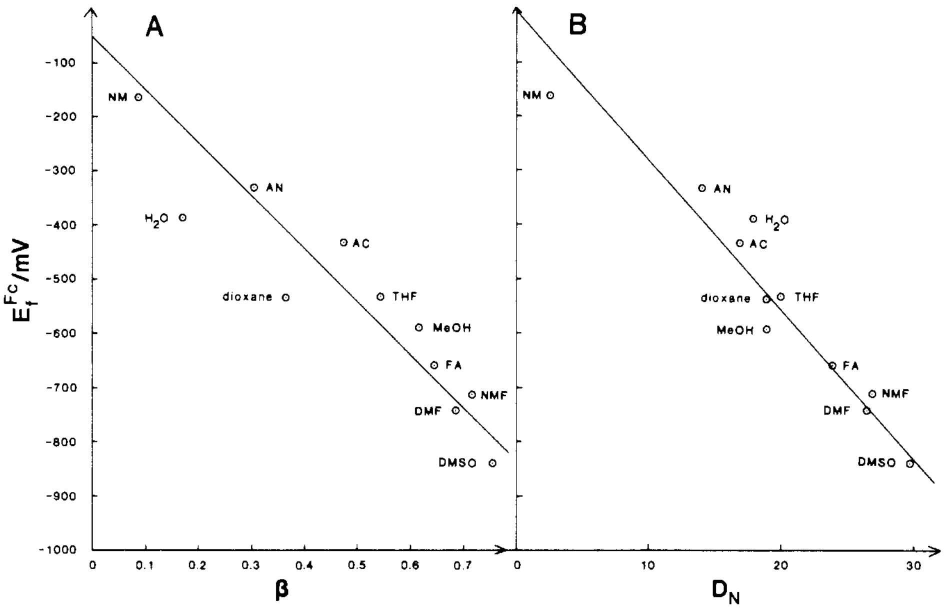

Figure 1. Plots of E_f for $[Co((NO_2)_2\text{-}sar)]^{3+/2+}$ versus measures of solvent basicity: (A) hydrogen-bonding basicity β; (B) donor number D_N.

modynamics, although significant in some cases, were deduced to have a small or negligible effect on the present analysis. (Possible exceptions are the least polar solvents, especially tetrahydrofuran and dioxane.) This matter will be addressed in detail elsewhere.[13] All of the couples exhibited either reversible or quasi-reversible voltammetric behavior under the experimental conditions. In addition, the temperature dependencies of the formal potentials were determined, enabling the reaction entropies, $\Delta S°$, to be obtained.[24] These data are summarized in Table I, along with the solvent-dependent values of E_f (vs SCE) and $\Delta S°$ for the Fc^+/Fc couple (some of which have not been determined previously).[27] Table II contains similar data for the $[Ru(NH_3)_6]^{3+/2+}$ and $[Co(en)_3]^{3+/2+}$ complexes, taken primarily from ref 11.

Table II. Formal Potentials and Reaction Entropies for $[Ru(NH_3)_6]^{3+/2+}$ and $[Co(en)_3]^{3+/2+\,a}$

		$[Co(en)_3]^{3+/2+}$		$[Ru(NH_3)_6]^{3+/2+}$	
solvent	$(\Delta S_{rc}°)_{Born}{}^b$	E_f^c	$\Delta S_{rc}°^d$	E_f^c	$\Delta S_{rc}°^d$
acetone				-434	197^e
acetonitrile	110	-589	197	-298	185^e
N,*N*-dimethylformamide	130	-970	213	-739	192
dimethyl sulfoxide	74	-1039	218	-781	167
formamide	30	-813	176	-553	121
N-methylformamide	56	-945	192	-707	138
nitromethane	113	-488	188		
propylene carbonate	59	-633	209	-373	172
water	59	-587	155	-305	79

[a] Taken from ref 11, unless otherwise stated. Supporting electrolyte was mostly 0.1 M $LiClO_4$. [b] Reaction entropies (J K^{-1} mol^{-1}) for amine couples, calculated from Born model (from Table I of ref 11). [c] Formal potentials (mV) versus the Fc^+/Fc couple. [d] Reaction entropies (J K^{-1} mol^{-1}) obtained from the temperature dependence of E_f. [e] This work.

A summary of the various empirical solvent parameters utilized here is given in Table III. When the formal potentials (vs Fc^+/Fc) for each of the cage complexes I–III are plotted against the Lewis basicities (Gutmann "donor number", D_N)[32] or the hydrogen-bonding basicities (β)[20] of the solvents, roughly linear plots are obtained (e.g. Figure 1). Similar correlations are obtained for $[Co(en)_3]^{3+/2+}$ and $[Ru(NH_3)_6]^{3+/2+}$ (cf. refs 11, 14, 15). The redox potentials for the bipyridyl couples, however, are much less sensitive to the basicity of the solvent than are those of the amine couples.[11] For the amphiprotic cage complex, IV, such correlations were found to be relatively poor and were even worse when the redox potentials were correlated with any other of the single solvent parameters. Not surprisingly, however, more satisfactory correlations were obtained when the acidic as well as basic solvent

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Table III. Empirical Solvent Parameters at 25 °C

solvent	$\pi^{*\,a,b}$	$\beta^{a,c}$	$\alpha^{a,d}$	$\delta_H{}^{a,e}$	$D_N{}^{f,g}$	$A_N{}^{f,h}$
acetone	0.71	0.48	0.08	9.8	17.0	12.5
acetonitrile	0.75	0.31	0.19	12.0	14.1	18.9
N,*N*-dimethylformamide	0.88	0.69	0.00	12.1	26.6	16.0
dimethyl sulfoxide	1.00	0.76	0.00	13.0	29.8	19.3
1,4-dioxane	0.55	0.37	0.00	10.0	~19	10.8
formamide	0.97	(0.65)[j]	0.71	17.9	24	39.8
methanol	0.60	(0.62)	0.93	14.5	19.0	~37
N-methylformamide	(0.92)[i]	(0.72)[j]	(0.50)[k]	(~20)[l]	~27	32.1
nitromethane	0.85	(0.09)[j]	0.22	12.3	2.7	20.5
propylene carbonate	(0.83)	0.40	0.00	13.3	15.1	18.3
tetrahydrofuran	0.58	0.55	0.00	9.5	20.0	8.0
water	1.09	(0.18)	1.17	23.4	18.0	54.8

[a] From refs 20 and 21. Values in parentheses are of greater uncertainty. [b] Polarity parameter. [c] Hydrogen-bonding basicity parameter. [d] Hydrogen-bonding acidity parameter. [e] "Internal solvent order" parameter (Hildebrand constant), from ref 33. [f] From ref 32. [g] Donor number, Lewis basicity parameter. [h] Acceptor number, Lewis basicity parameter. [i] Calculated from $\pi^* = -0.573 + [14.65(\epsilon - 1)(n^2 - 1)]/[2\epsilon + 1)(2n^2 + 1)]$; see refs 20 and 21. [j] Calculated from $D_N = -0.78 + 38.4\beta$; see refs 20 and 21. [k] Calculated from $A_N = 0.16 + 16.7\pi^* + 32.9\alpha$; see refs 20 and 21. [l] Estimated from value observed for formamide.

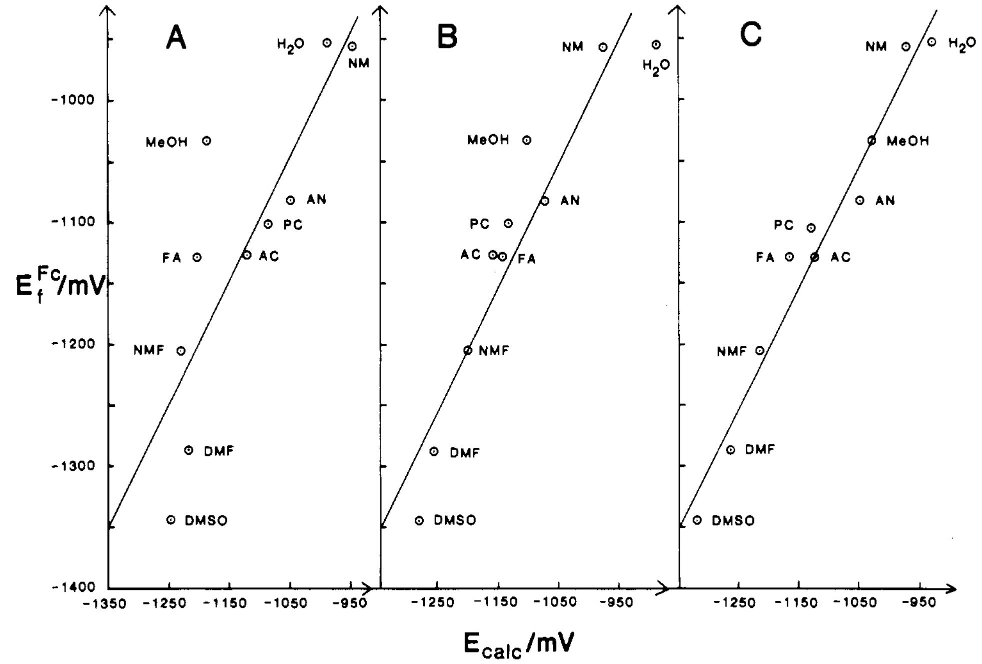

Figure 2. Plots of E_f for $[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$ versus (A) $E_{calcd} = -903 - 450\beta$, (B) $E_{calcd} = -970 - 415\beta - 131\alpha$, and (C) $E_{calcd} = -772 - 413\beta + 146\alpha - 238\pi^*$.

properties were included in the analysis, i.e. when equations of the form (cf. eq 2)

$$E_f = E_f{}^\circ + a\alpha + b\beta \qquad (6)$$

or the related expression

$$E_f = E_f{}^\circ + a'A_N + b'D_N \qquad (7)$$

are utilized, where A_N is the so-called solvent "acceptor number".[32]

For the amine complexes II and IV, for which the most data are available, the correlations are improved significantly when the solvent polarities (π^*) are considered, although the addition of the internal solvent order parameter (δ_H)[33] did not improve significantly any of the fits. Thus, the solvent dependencies of E_f for the amine couple II were fitted to an equation of the form[17-21]

$$E_f = E_f{}^\circ + b\beta + c\pi^* \qquad (8)$$

and those for the amphoteric cage system IV to

$$E_f = E_f{}^\circ + a\alpha + b\beta + c\pi^* \qquad (9)$$

by the use of the multiple linear regression program. Figure 2 is an illustration of the improvement in the correlation for the latter system brought about by including the additional terms in eq 9. Parts A–C of Figure 2 consist of plots of the observed solvent-dependent E_f values against the corresponding calculated values, E_{calc}, obtained from the least-squares best fit to eq 9 by including the first two, first three, and all four terms on the right-hand side of eq 9, respectively, in the numerical analysis. The progressively better fits obtained under these circumstances are clearly evident. Comparable results could be obtained by employing A_N and D_N in place of α and β (see eq 7); however, use of the latter solvent parameters is preferred here, in part since A_N appears to be a composite of α and π^*.[20,21]

A summary of the best-fit values of the coefficients b and c associated with β (or D_N) and π^*, respectively, along with $E_f{}^\circ$ for each redox couple is provided in Table IV. Parameters are given for fits obtained in the absence as well as presence of the solvent polarity (π^*) term. The quality of the fit obtained in each case is denoted by the t values given; larger $|t|$ values correspond to better fits. Values of a obtained by including α (or A_N) in the analysis are also included in some fits for complex IV, although this factor was found to be statistically insignificant for the other redox couples. A more detailed summary of the results of this statistical treatment for the cage systems II and IV is given in Table V. This takes the form of comparisons between the experimental E_f values in each solvent with the corresponding calculated best-fit values obtained by including various empirical

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Table IV. Correlations of Solvent-Dependent Formal Potentials with Empirical Solvent Parameters, Resulting from Multiparametric Fits Using Eqs 6–9[a]

		$E_f°$,	β or D_N		π^*		α or A_N		
redox couple	n[b]	mV vs Fc^+/Fc	b	t[c]	c	t[c]	a	t[c]	R^2
I	6	−538	−670	−4.99					86.2
		−476	−666	−4.31	−69	−0.23			86.4
II	10[d]	−113	−846	−8.61					90.3
		+156	−859	−14.29	−314	−3.80			96.82
	11	−31	−25.8[e]	−10.86[e]					92.91
III	6	−479	−682	−8.19					94.37
		−362	−684	−7.60	−123	−0.65			95.07
IV	10	−903	−450	−4.35					70.31
		−970	−415	−6.14			131	3.49	89.18
		−772	−413	−9.83	−238	−3.48	146	6.15	96.41
		−872	−13.0[e]	−3.92[e]					65.75
		−994	−14.1[e]	−12.50[e]			5.29[f]	7.95[f]	96.59
$[Co(en)_3]^{3+/2+}$	8	−393	−767	−8.74					92.72
		−169	−748	−8.74	−257	−1.22			94.39
$[Ru(NH_3)_6]^{3+/2+}$	7	−84	−851	−6.22					88.56
		+186	−871	−6.71	−284	−1.28			91.88
$[Cr(bpy)_3]^{3+/2+}$	8	−595	−115	−3.61					68.50
		−679	−121	−3.95	+95	1.27			
$[Fe(bpy)_3]^{3+/2+}$	5	739	−179	−6.40					93.18
		672	−171	−8.24	+73	1.94			95.73
$[Co(bpy)_3]^{3+/2+}$	6	−26	−126	−4.15					81.14
		−41	−127	−3.63	+16	0.27			81.43
$[Co(phen)_3]^{3+/2+}$	8	+54	−185	−7.70					90.81
		+33	−186	−7.07	+23	0.36			91.05

[a] For each fit (each row below), parameters included are those for which corresponding coefficients a–c are given. (Generally, fits are included for which a and/or c is set equal to zero, so to enable the effect of including these parameters on the fit to be assessed.) [b] Number of solvents used in regression analysis. [c] The t function is a measure of the significance of each added value to the fit. (The higher the t value, the better the fit.) [d] Formal potentials in dioxane have been omitted from the analyses involving β and π^*. [e] Correlations involving D_N. [f] Correlation involving A_N.

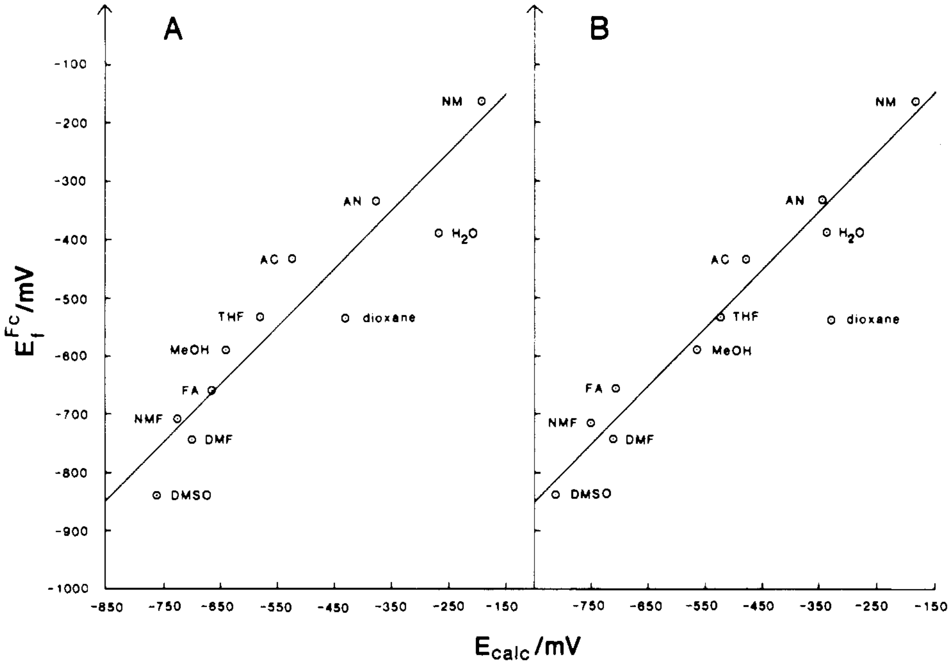

Figure 3. Plots of E_f for $[CO((NO_2)_2\text{-sar})]^{3+/2+}$ versus (A) $E_{calcd} = -113 - 846\beta$ and (B) $E_{calcd} = +156 - 859\beta - 314\pi^*$.

solvent parameters in the analysis (see footnotes to Table V).

All the amine couples exhibit large positive reaction entropies (Table I). This quantity does not correlate well with the measures of solvent basicity but exhibits a noticeable dependence upon the internal solvent order parameter, δ_H.

Discussion

The most clear-cut correlations for all of the complexes are found to be those involving the solvent basicity parameter, β (and both α and β for complex IV), which corresponds to the ΔE_s term in eqs 1 and 5. However, the presence of such statistically correlations does not, in itself, mean that the correlations are chemically meaningful. It is clearly necessary to examine if the correlation coefficients extracted from the multiparameter approach can be rationalized on chemical grounds as well as whether the addition of further adjustable parameters is instructive.

First, consider the values of b obtained in the multiparameter approach. It is to be expected that b should be larger for the cobalt cage and other metal amine (or amine) couples than for systems where ligand hydrogen bonding to basic solvent moieties is less important.[11] This trend is evident when the coefficients, b, for the amine systems are compared with those obtained for the $[M(bpy)_3]^{3+/2+}$ couples (Table IV). The M(III) oxidation state will induce greater Lewis acidity (i.e. electron deficiency) in the amine protons than will the M(II) state, thereby yielding stronger hydrogen bonding with the solvent molecules in the former versus the latter case.[11] The M(III) oxidation state is thereby stabilized more than is M(II), resulting in negative shifts in the redox

Table V. Observed Formal Potentials (E_f in mV vs Fc^+/Fc) for $Co((NO_2)_2\text{-sar})^{3+/2+}$ and $Co(CH_3,COOC_2H_5\text{-oxosar-H})^{2+/+}$ in Comparison with Corresponding Values (E_{calcd}) Extracted from Various Multiparametric Fits

	$[Co((NO_2)_2\text{-sar})]^{3+/2+}$				$[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$					
		E_{calcd}				E_{calcd}				
solvent	E_f	*a*	*b*	*c*	E_f	*d*	*e*	*f*	*g*	*h*
acetone	-434	-519	-479	-470	-1129	-1119	-1159	-1128	-1093	-1168
acetonitrile	-334	-375	-346	-395	-1083	-1043	-1074	-1051	-1055	-1093
N,*N*-dimethylformamide	-742	-697	-713	-717	-1284	-1214	-1256	-1266	-1218	-1284
dimethyl sulfoxide	-840	-756	-811	-800	-1345	-1245	-1285	-1324	-1259	-1312
1,4-dioxane	-536	-426	-335	-521		-1070	-1124	-1056	-1119	-1205
formamide	-659	-663	-707	-650	-1130	-1196	-1147	-1168	-1184	-1122
methanol	-592	-638	-565	-521	-1035	-1182	-1105	-1035	-1119	-1066
N-methylformamide	-713	-722	-751	-728	-1206	-1227	-1203	-1215	-1223	-1205
nitromethane	-164	-189	-188	-101	-959	-944	-979	-979	-907	-924
propylene carbonate		-451	-448	-421	-1103	-1083	-1136	-1135	-1068	-1110
tetrahydrofuran	-533	-578	-499	-547		-1151	-1198	-1137	-1132	-1234
water	-390	-265	-341	-495	-957	-984	-891	-935	-1106	-958

[a] $E_{calcd} = -113 - 846\beta$. [b] $E_{calcd} = +156 - 859\beta - 314\pi^*$. [c] $E_{calcd} = -13 - 25.8D_N$. [d] $E_{calcd} = -903 - 450\beta$. [e] $E_{calcd} = -970 - 415\beta + 131\alpha$. [f] $E_{calcd} = -772 - 413\beta + 146\alpha - 238\pi^*$. [g] $E_{calcd} = -872 - 130D_N$. [h] $E_{calcd} = -994 - 14.1D_N + 5.29A_N$.

potential with increasing β and hence yielding negative values of *b*. Further, the value of *b* for $[Co((NO_2)_2\text{-sar})]^{3+/2+}$ is significantly (20%) higher than those obtained for $[Co(sep)]^{3+/2+}$ (I) and $[Co(NHCOCH_3)_2\text{-sar})]^{3+/2+}$ (III) (Table IV). This finding is consistent with the known acidity sequence of the N-H protons in the Co(III) complexes.[5,8,12]

For $[Co(CH_3COOC_2H_5\text{-oxosar-H})]^{2+/+}$, the deprotonated amide group in the Co(II) state is considerably more basic than that of the Co(III) ion.[6] Therefore, the Co(III) ion will be stabilized more than Co(III) by interactions with acidic solvent groups, so that the coefficient *a* (eqs 2 and 6) is predicted to be positive. Indeed, the signs of *a* and *b* are found to be positive and negative, respectively, for the oxosar system (Table IV). The resulting contributions of the $a\alpha$ and $b\beta$ terms to the solvent-dependent redox potentials are of comparable importance in some of the more acidic solvents, but the magnitude of *b* is smaller for the oxosar couple in comparison to the other cage systems. This might be expected in view of the lower charge type (2+/+) of the $[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$ couple relative to that (3+/2+) of the other systems, along with the fewer N-H protons present in $[Co(CH_3,COOC_2H5\text{-oxosar-H})]^{2+/+}$. The latter is probably the more important factor, as suggested by the observed close similarity in the solvent dependencies of E_f for $[Ru(NH_3)_5(SCN)]^{2+/1+}$ and $[Ru(NH_3)_5(py)]^{3+/2+}$.[34,35]

Both the signs and magnitudes of the coefficients *a* and *b* (the H-bonding terms), then, are consistent with chemical intuition, hence supporting the notion that the correlations are physically meaningful. The addition of the π^* parameter to the multiparameter equation is statistically significant in a clear-cut manner only for the $[Co((NO_2)_2\text{-sar})]^{3+/2+}$ and $[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$ redox couples, for which the most solvents have been examined. The *c* values obtained from the multiparametric fits in both these cases are negative (Table IV). This is intuitively reasonable since the oxidized [Co(III)] form of each of the amine couples should interact more strongly with the solvent dipoles than will the corresponding reduced [Co(II)] state.

Given the availability of apparently reliable estimates of the contribution to E_f of solvent polarity, $c\pi^*$ ($=\Delta E_p$; eq 3), as well as acidic/basic solute-solvent interactions, $a\alpha + b\beta$ ($=\Delta E_s$; eq 5), for II and IV, it is of interest to compare specifically the importance of these components to the measured solvent-dependent formal potential. To this end, Table VI consists of ΔE_s and ΔE_p values for both II and IV in a variety of solvents, with ΔE_s for the latter couple being subdivided into solvent basicity (β) and acidity (α) components. Significantly, except in the most basic solvents the values of $-\Delta E_p$ are roughly comparable to $-\Delta E_s$. Although the weaker solvent dependence of the former term tends to obfuscate its extraction by means of the present analysis, its importance to the overall redox thermodynamics is nonetheless apparent. The importance of E_p relative to E_s is particularly evident in water and nitromethane (Table VI). Unfortunately, the lack of clearly meaningful statistical fits involving the "solvent ordering" term $h\delta_H$ ($=\Delta E_H$; eq 4) vitiates consideration of this additional possible contribution to E_f, although this component is unlikely to be as important as ΔE_p and ΔE_s for the present systems (but see below).

Table VI. Values of the ΔE_s and ΔE_p Components (Eqs 1 and 2) of the Solvent-Dependent Formal Potentials for $[Co((NO_2)_2\text{-sar})]^{3+/2+}$ and $[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$, Extracted from Multiparametric Fits

	$[Co((NO_2)_2\text{-sar})]^{3+/2+}$ [a]		$[Co(CH_3,COOC_2H_5\text{-oxosar-H})]^{2+/+}$ [b]		
solvent	$\Delta E_s(\beta)$	ΔE_p	$\Delta E_s(\beta)$	$\Delta E_s(\alpha)$	ΔE_p
acetone	-412	-223	-198	+12	-169
acetonitrile	-266	-236	-128	+28	-179
N,*N*-dimethylformamide	-593	-276	-285	0	-209
dimethyl sulfoxide	-653	-314	-314	0	-238
1,4-dioxane	-318	-173	-153	0	-131
formamide	-558	-305	-268	+104	-231
methanol	-533	-188	-256	+136	-143
N-methylformamide	-618	-289	-297	+73	-219
nitromethane	-77	-267	-37	+32	-202
propylene carbonate	-344	-261	-165	0	-198
tetrahydrofuran	-472	-182	-227	0	-138
water	-155	-342	-74	+171	-259

[a] Calculated from the equation $E_{calcd} = 156 - 859\beta - 314\pi^*$. [b] Calculated from the equation $E_{calcd} = -772 - 413\beta + 146\alpha - 238\pi^*$.

Since the 2,2'-bipyridyl and 1,10-phenanthroline couples feature only weakly acidic ring protons, the observation that the solvent-dependent E_f values for these systems correlate more noticeably with solvent basicity (β) than with polarity (π^*) (Table IV) is somewhat surprising. This may arise simply because β is more sensitive than π^* to the nature of the solvent. Nevertheless, the hydrogens in the ring 3,3'-position of coordinated 2,2'-bipyridine are significantly acidic,[36-38] and weak bases are known to associate with such bipyridine and phenanthroline metal complexes.[39]

While the solvent-dependent reaction entropies are not of central concern in the present work, it is interesting to note the marked behavioral differences in comparison with the corresponding redox free energies, i.e. E_f (cf. refs 11 and 23). The observed correlation of $\Delta S_{rc}°$ with the solvent ordering parameter δ_H for the present

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systems is not inconsistent with a correlation between $\Delta S_{rc}°$ and A_N noted previously for a number of low-spin metal complex redox couples,[34] given that the solvent dependencies of δ_H and A_N are similar (Table III). The present correlation implies that a major influence on the redox-induced entropy change $\Delta S_{rc}°$ is the degree to which the internal order ("structuring") of the solvent is diminished by decreasing the metal oxidation state. The large positive values of $\Delta S_{rc}°$ (Tables I and II) presumably reflect in part this smaller degree of solvent order surrounding the M(II) solute versus that for M(III).[11,23,34,40-42] This explanation is also consistent with the observed progressive decrease in $\Delta S_{rc}°$, in the sequence $[Co(en)_3]^{3+/2+}$ > $[Co(sep)]^{3+/2+}$ > $[Co((NO_2)_2\text{-sar})]^{3+/2+}$ $\simeq$ $[Co(NHCOCH_3)_2\text{-sar}]^{3+/2+}$ > $[Co(phen)_3]^{3+/2+}$ $\simeq$ $[Co(bpy)_3]^{3+/2+}$, as the effective solute radius increases. This topic will be dealt with in greater detail elsewhere.[40]

In comparing and contrasting the solvent-dependent behavior of $\Delta S_{rc}°$ with that of E_f, it is important to bear in mind that whereas the former are "true" absolute values (given the extrathermodynamic assumptions embodied in the nonisothermal cell[24]), the latter (free-energy) quantities are referenced here to the Fc^+/Fc couple. This difference takes on significance upon noting that the solvent dependencies of $\Delta S_{rc}°$ for the present amine (and ammine) redox couples are roughly similar to that for Fc^+/Fc (Tables I and II; cf. ref 34). Given that the solvent-dependent $\Delta S_{rc}°$ values correlate with δ_H, the essential absence of a corresponding E_f–δ_H correlation (vide supra) may be ascribed in part to its cancellation by referencing the solvent-dependent E_f values to that for Fc^+/Fc.

At least in principle, the formal potentials $E_f°$ (eqs 2 and 6–9) obtained after extracting the various solvent-dependent effects should provide a measure of E_f in the absence of such "specific solvation" factors. A complication, however, is that the $E_f°$ values so obtained depend significantly and, in some cases, substantially on the particular multiparametric fit employed (Table IV). Nevertheless, the $E_f°$ values listed in Table IV are of at least semiquantitative utility. An interesting feature of these results is that the elimination of such specific solvation effects yields less negative $E_f°$ values for the cobalt(III/II) amine couples. These "solvent corrected" values tend to lie closer to those for $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$. While the effect of π-bonding stabilization of the Co(II) state is undoubtedly responsible in part for the more positive E_f values observed for the latter couples, specific solvation of the amine ligands therefore appear to play an important role here.

It should be noted that the magnitude of the specific solvation effects considered here is often large, so as to yield alterations in E_f of ca. 0.5 V or greater. On the basis of the present (and earlier[11]) results for metal amine couples, one could anticipate comparable or even larger effects for other solutes featuring ligands engaging in specific solvent interactions. This should be especially true for metal aqua couples in view of the high acidity of the aqua ligand hydrogens, although solvent-dependent analyses are thwarted for these systems in view of proton and metal–oxygen lability.

Overall, such large specific solvent effects on the redox thermodynamics provide a clear signal of the limitations in the conventional continuum and related nonspecific approaches of ionic solvation. These factors will necessarily influence the kinetics of nonsymmetrical electron-transfer processes involving such redox couples inasmuch as thermodynamic driving-force effects are unassailably important.[17] Less obvious, however, is the degree to which specific solvation effects will influence the kinetics of self-exchange and other energetically symmetrical redox processes (i.e. how such factors will influence additionally the *intrinsic* electron-transfer barrier). A detailed analysis of this point suggests that the energetic effects, although perhaps significant, could be relatively small[35] and may well be obscured by other factors, at least when such information is sought by means of kinetic data alone. Recent discussions on this topic by one of us are to be found elsewhere.[17-19,40]

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