Table IV. Rate Constant Expressions and Average Values for the H_2O_2–$S_2O_3^{2-}$–Cyanide Reaction

pH	nominal ratio $[S_2O_3^{2-}]/H_2O_2$	k_1,[a] L mol^{-1} s^{-1}	k_4/k_2[b]	k_4/k_3[c]
7	4.0	0.020	3	0.05
7	1.0	0.020	4	0.1
7	0.25	0.018	2	0.07
8	4.0	0.020	0.7	0.01
8	1.0	0.022	0.8	0.04
8	0.25	0.019	2	0.05
9	4.0	0.022	0.2	0.008
9	1.0	0.018	0.8	0.04
9	0.25	0.018	1	0.05

[a] $k_1 = (1/6TP)(H' - 4T' + (f-2)C') = -{}^{3}/_{7}TP(C' + T' + P'/3)$. [b] $k_4/k_2 = (3P/T)(4T' - 3C' - P')/(6P' - 3C' - 3T') = (3P/(2T))(7(fC' + H')/(6P' - 3C' - 3T') + 2/3)$. [c] $k_4/k_3 = (C/T)((T' - {}^{3}/_{7}(C' + T' + P'/3))/C') = (C/4T)((H' + {}^{6}/_{7}(C' + T' + P'/3) + (f-2)C')/C')$. T, P, T', P', H' are as defined in Table III. C = [cyanide]; C' = d[cyanide]/dt.

of H_2O_2 and $S_2O_3^{2-}$ are within 10–20% of k_1 values that are calculated on the basis of the mechanism proposed here. The ratio k_4/k_2 decreases as the pH increases, since higher pH favors SO_4^{2-} formation. Values of k_4/k_2 in Table IV (with cyanide present) are near those in Table III (with only H_2O_2 and $S_2O_3^{2-}$ reacted). Even though cyanide is more dilute than either H_2O_2 or $S_2O_3^{2-}$, it reacts almost as rapidly (see Table II). Thus, k_3 is much larger than k_2 or k_4 (see Table IV). Reactions 4 and 6 were assumed to be first order in H_2O_2 and $S_2O_3^{2-}$, respectively, but ratios of k_2/k_4 are consistent with an order near 0.5. The expected intermediate[9] in the peroxide–thiosulfate reaction is written as $HOS_2O_3^-$, but it was never identified explicitly. However, the unprotonated form of $HOS_2O_3^-$, $S_2O_4^{2-}$ (dithionite), did not produce $S_4O_6^{2-}$ when added to $S_2O_3^{2-}$ solution or SCN^- when added to cyanide solution.

Registry No. $S_2O_3^{2-}$, 14383-50-7; H_2O_2, 7722-84-1; $S_4O_6^{2-}$, 15536-54-6; cyanide, 57-12-5.

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Use of Internal Standards for the Measurement of Reaction Entropies

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Several years ago, Gagné et al. recommended the use of ferrocene as an internal standard for the measurement and reporting of formal reduction potentials, E^f, in nonaqueous solvents.[1] The procedure eliminates systematic errors associated with the use of nonaqueous reference electrodes and has been widely adopted. The subsequent availability of values of E^f vs. ferrocene has allowed meaningful comparisons of oxidizing and reducing strengths for numerous compounds.

A second useful property associated with redox couples is the temperature dependence of the formal reduction potential, dE^f/dT, measured in a nonisothermal cell. This quantity can be used to estimate entropy changes associated with a single redox couple, $\Delta S°_{rc}$.[2,3]

$$\mathrm{Ox} + ne^- \overset{E^f}{\rightleftharpoons} \mathrm{Red} \qquad (1)$$

$$\Delta S°_{rc} = S°_{Red} - S°_{Ox} = nF[dE^f/dT]_{\mathrm{nonisothermal}} \qquad (2)$$

Calculation of $\Delta S°_{rc}$, the reaction entropy for the redox couple, requires extrathermodynamic assumptions, which have been discussed in detail by Yee et al.[4] The most problematic of these assumptions from an experimental point of view is the requirement of a temperature-independent junction potential between the working and reference compartments of the nonisothermal cell. While it is possible to construct cells in which the temperature dependence of the junction potential is negligible,[4] these junctions can become temperature dependent or simply change with time. These experimental difficulties represent a potential source of systematic error in the reporting of values of $\Delta S°_{rc}$, and indeed, difficulties associated with construction of reliable nonisothermal cells may inhibit many from making these measurements.

Herein, we report a simple procedure for measuring $\Delta S°_{rc}$ that eliminates the need for nonisothermal cell measurements. This is achieved by recording the reduction potential for the sample redox couple, E^f_{sam}, vs. the reduction potential of an internal standard, E^f_{std}, at a variety of temperatures in a single-compartment thermostated cell. By choice of a value of $\Delta S°_{rc}$ for the internal standard, $\Delta S°_{rc}$ for the sample redox couple can be readily calculated. We suggest the use of ferrocene as an internal standard for measurements in nonaqueous solvents and the use of ruthenium hexaammine in aqueous solutions. The internal standard procedure for measuring $\Delta S°_{rc}$ is illustrated for $Co(phen)_3^{3+,2+}$ in water and for $Co(Cp)_2^{+,0}$ (cobaltocene) in acetonitrile.

Values of reaction entropies can be related to the electron-transfer reactivity associated with a redox couple in a variety of ways. Even though the reasons are unclear, there is an unmistakable correlation between the magnitude of $\Delta S°_{rc}$ for a couple and the reorganization energy associated with the self-exchange reaction associated with the couple.[5] Youngblood and Margerum used values of $\Delta S°_{rc}$ for Cu(III,II) and Ni(III,II) oligiopeptide complexes to demonstrate changes in the number of coordinated water molecules for the oxidized and reduced states of the complexes.[6] Similarly, measurement of $\Delta S°_{rc}$ has been used to examine the solvation of redox active sites in proteins.[7] In particular, we comment on the use of $\Delta S°_{rc}$ values obtained by the internal standard method to obtain thermodynamic parameters associated with electron-transfer cross-reactions.

Experimental Section

Water, acetonitrile, and supporting electrolytes were purified as described in previous publications.[8,9] Ferrocene (Strem), cobaltocenium tetrafluoroborate (Strem) and hexaammineruthenium(III) chloride (Matthey Bishop) were used as received. Solutions of tris(1,10-phenanthroline)cobalt(II) ion, $Co(phen)_3^{2+}$, were prepared from a stock solution of $Co^{II}(ClO_4)_2$ and 1,10-phenanthroline.[8]

Electrochemical measurements were made by utilizing a BAS-100 electrochemical analyzer. Working electrodes were either platinum or glassy carbon and were polished prior to use. The auxiliary electrode was platinum foil or gauze. Saturated sodium chloride calomel (SSCE) and silver/silver nitrate (0.01 M), $TBABF_4$ (0.5 M) reference electrodes were used in the aqueous and nonaqueous experiments, respectively. Cell temperatures were maintained with a Lauda constant-temperature bath.

Results and Discussion

Measurement of $\Delta S°_{rc}$ Utilizing an Internal Standard. The relationship between the temperature dependence of the difference

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Table I. Formal Reduction Potentials from Cyclic Voltammetry

aqueous[a]				nonaqueous[b]			
T, K	$E^f(Co(phen)_3^{3+,2+})$, V	$E^f(Ru(NH_3)_6^{3+,2+})$, V	ΔE^f, V	T, K	$E^f(Co(Cp)_2^{+,0})$, V	$E^f((FeCp)_2^{+,0})$, V	ΔE^f, V
283.6	0.120	−0.200	0.320	284.3	−1.236	0.099	−1.335
286.8	0.124	−0.196	0.320	295.6	−1.224	0.106	−1.330
292.2	0.127	−0.196	0.323	302.3	−1.214	0.113	−1.327
296.2	0.129	−0.196	0.325	306.1	−1.212	0.113	−1.325
301.4	0.132	−0.193	0.325	310.7	−1.206	0.116	−1.322
307.4	0.138	−0.189	0.327	316.2	−1.202	0.119	−1.321
313.0	0.143	−0.185	0.328	321.8	−1.198	0.211	−1.319
318.1	0.151	−0.183	0.334				
322.2	0.155	−0.180	0.335				
324.4	0.159	−0.178	0.337				

[a] Potentials vs. SSCE. [b] Potentials vs. Ag/Ag$^+$.

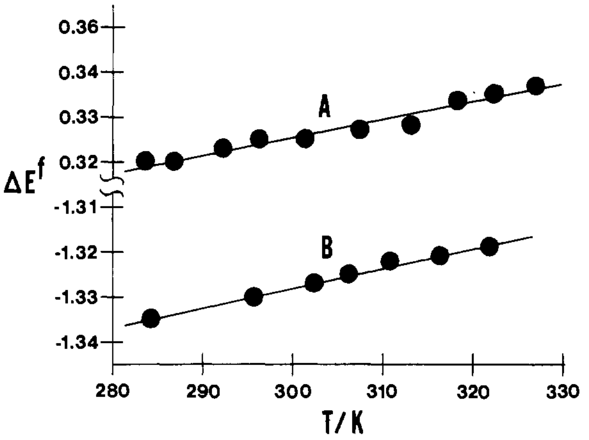

Figure 1. Plots of the difference in formal reduction potential vs. temperature: (A) $E^f(Co(phen)_3^{3+,2+}) - E^f(Ru(NH_3)_6^{3+,2+})$; (B) $E^f(Co(Cp)_2^{+,0}) - E^f(Fe(Cp)_2^{+,0})$.

in reduction potentials for a sample couple and an internal standard is derived from eq 2:

$$\Delta E^f/dT = d(E^f_{sam} - E^f_{std})/dT = (\Delta S^\circ_{rc,sam} - \Delta S^\circ_{rc,std})/nF \quad (3)$$

Assuming that $\Delta S^\circ_{rc,std}$ is known from accurate nonisothermal cell measurements, $\Delta S^\circ_{rc,sam}$ is obtained by measuring ΔE^f. This measurement can be accomplished by utilizing any of a variety of electrochemical techniques[10] in a single-compartment cell that is either jacketed or placed in a controlled-temperature bath. Both the sample and the standard are added to the electrolyte solution in roughly equal concentrations, and voltammograms that include waves due to both compounds are acquired over as wide a temperature range as possible. Assuming that both oxidation states of the couples are stable, as indicated by the usual criteria,[10] slow scan rates should be used so that the waves are electrochemically reversible. Since values of E^f for the sample and the standard are subtracted to obtain ΔE^f, systematic errors associated with measuring E^f tend to cancel, leading to accurate and reproducible values of ΔE^f. The slope of a plot of ΔE^f vs. T yields the quantity $(\Delta S^\circ_{rc,sam} - \Delta S^\circ_{rc,std})/nF$. From our experience, recording several voltammograms at each temperature is necessary in order to obtain low standard deviations for the determined reaction entropies.

This procedure is illustrated by utilizing the data in Table I. The sample redox couples are $Co(phen)_3^{3+,2+}$ in aqueous 0.5 M NaCl and $Co(Cp)_2^{+,0}$ in acetonitrile containing 0.5 M $(TBA)BF_4$. The internal standard redox couples used are $Ru(NH_3)_6^{3+,2+}$ and $Fe(Cp)_2^{+,0}$, respectively. Figure 1 contains plots of ΔE^f vs. T and the slopes of the least-squares lines through the data.

A value of ΔS°_{rc} for $Fe(Cp)_2^{+,0}$ in acetonitrile equal to 48 J mol^{-1} K^{-1} has been reported.[8] Use of the slope of line B in Figure 1 (4.39×10^{-4} V K^{-1}) and eq 3 yields 90 ± 2 J mol^{-1} K^{-1} as ΔS°_{rc} for $Co(Cp)_2^{+,0}$.[11] For $Ru(NH_3)_6^{3+,2+}$, a value of 54 ± 2 J mol^{-1} K^{-1} was determined in 0.5 M NaCl for a nonisothermal cell. This value is in good agreement with values in the literature for other electrolytes.[4] From the slope of line A in Figure 1 (4.02×10^{-4} V K^{-1}), a value of ΔS°_{rc} = 93 ± 2 can be calculated for $Co(phen)_3^{3+,2+}$, which is also in good agreement with values reported from direct nonisothermal cell measurements.[4]

There are several requirements for choosing an internal standard for ΔS°_{rc} measurements. The most important requirement is that a reliable value of ΔS°_{rc} is known for the couple. One criteria for reliability is that the value has been reproduced by nonisothermal cell measurements in several laboratories. Nevertheless, values of $\Delta S^\circ_{rc,sam}$ measured with an internal standard can be corrected if a more reliable value of $\Delta S^\circ_{rc,std}$ becomes available. Other requirements for an internal standard include chemical and electrochemical reversibility for the redox couple, lack of chemical reaction between the internal standard and the sample, and that the wave for the standard is well separated from the wave for the sample. For nonaqueous solvents, $Fe(Cp)_2^{+,0}$ is an excellent choice because values for ΔS°_{rc} in a variety of solvents have already been reported.[12,13] Should the wave for $Fe(Cp)_2^{+,0}$ not be separated from the wave of interest, $Co(Cp)_2^{+,0}$ could be used for the measurement of ΔE^f. Values of $\Delta S^\circ_{rc,sam}$ could still be related to ΔS°_{rc} for $Fe(Cp)_2^{+,0}$ by measuring ΔE^f in a solution containing ferrocene and cobaltocene. For aqueous solutions, $Ru(NH_3)_6^{3+,2+}$, $Co(phen)_3^{3+,2+}$, or, possibly, $Fe(phen)_3^{3+,2+}$ can be used as an internal standard. The authors note, however, that accurate nonisothermal cell measurements are relatively easy to do in water.

Use of ΔS°_{rc} for Calculating Thermodynamics of Cross-Reactions. Accurate values of E^f are required to calculate free energy changes ΔG°_{rxn} (or K_{12}) for electron-transfer cross-reactions. This knowledge is essential for interpreting the rate constant of the cross-reaction, k_{12}, utilizing the Marcus correlation equation.[14] Measurement of E^f as a function of temperature can be used to calculate ΔH°_{rxn} and ΔS°_{rxn}. These calculations are outlined in eq 4–8 for two one-electron couples. Marcus and Sutin have shown

$$Ox_1 + e^- \rightleftharpoons Red_1 \quad \{E^f_1, \Delta S^\circ_{rc,1}\} \quad (4)$$

$$Ox_2 + e^- \rightleftharpoons Red_2 \quad \{E^f_2, \Delta S^\circ_{rc,2}\} \quad (5)$$

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2 \quad \{\Delta G^\circ_{rxn} = -F(E^f_1 - E^f_2)\} \quad (6)$$

$$\Delta S^\circ_{rxn} = \Delta S^\circ_{rc,1} - \Delta S^\circ_{rc,2} \quad (7)$$

$$\Delta H^\circ_{rxn} = \Delta G^\circ_{rxn} + T\Delta S^\circ_{rxn} \quad (8)$$

that activation parameters are related to reaction thermodynamics for cross-reactions;[15] therefore, values of ΔH°_{rxn} and ΔS°_{rxn} are necessary for interpretation of activation parameters. It should be noted that reaction thermodynamics obtained in this matter

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are not affected by absolute errors in the value of $\Delta S^\circ_{\mathrm{rc,std}}$ used to calculate $\Delta S^\circ_{\mathrm{rc,1}}$ and $\Delta S^\circ_{\mathrm{rc,2}}$ because the former cancels in eq 7.

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Bridging and Twist Angle Dependence of Magnetic Coupling in Doubly Bridged Copper(II) Dimers. X-ray Structure of Bis[chloro(*N*-phenyl(2-hydroxybenzylidene)aminato-*N*,*μ*-*O*)copper(II)][1]

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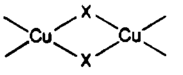
The elucidation of the structural and electronic factors that govern spin–spin coupling in magnetically condensed systems is of continuing interest.[2] Doubly bridged copper(II) dimers have proved to be well suited for such a study since, besides being conceptually simple (spin $^1/_2$ systems), they display a great variety of coordination geometries and superexchange pathways with consequent wide variations in the magnetic properties.[2]

The bridging CuXCu angle, ϕ, has been found to be of prominent importance in determining $2J$, the singlet–triplet splitting resulting from exchange coupling, in compounds with largely planar (I)[2a,b,3,4] or parallel-planar (II)[1,2a,b,5–7] geometries.



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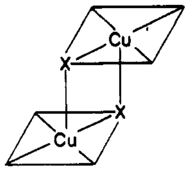


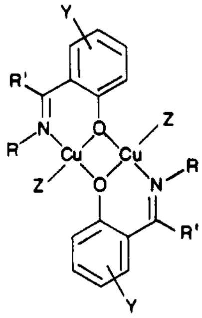
II

In particular, the remarkable linear relationship eq 1 has been established[3] for a series of type I compounds with X = OH^-.

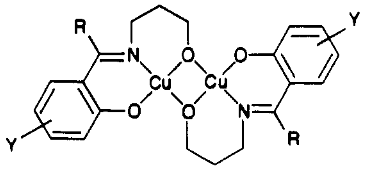
$$2J\ (\mathrm{cm}^{-1}) = -74.53\phi + 7270 \tag{1}$$

It has also been demonstrated, through results on nonplanar compounds of type III[8–13] or IV,[14,15] that distortions from planar toward tetrahedral ligand environment at copper markedly affect the magnitude of $2J$. The dihedral angle, τ, between the plane of the Cu_2O_2 bridging unit and the plane of the remaining ligands (V) has been used to parametrize this tetrahedral distortion, and a direct correlation between $2J$ and τ has been proposed for these systems.[8–15]

A seeming inconsistency between these two magnetostructural correlations is that τ differs significantly from 0° in several hydroxide-bridged dimers obeying eq 1 and that variations in ϕ in the series of nonplanar compounds do not seem to have any effect on $2J$. From an experimental viewpoint, it is not at all apparent why a single structural parameter can adequately explain the variation in $2J$ with geometry when both τ and ϕ vary.



III



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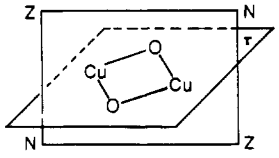

V

With an aim toward obtaining some further information on the relative merit of the τ and ϕ parameters in determining the magnetic properties of dimeric complexes having nonplanar metal environments, the crystal and molecular structure of bis[chloro(*N*-phenyl(2-hydroxybenzylidene)aminato-*N*,*μ*-*O*)copper(II)], denoted $Cu_2L_2Cl_2$, is now reported and discussed in terms of the magnetic properties of the compound.

Experimental Section

Synthesis. $Cu_2L_2Cl_2$ has been isolated previously by Harris and Sinn.[9b] We have obtained crystals of the compound suitable for X-ray analysis by a slightly varied method. $CuCl_2{\cdot}2H_2O$ (0.17 g, 1.0 mmol) was added to a mixed-solvent solution of bis(*N*-phenyl(2-hydroxybenzylidene)aminato)copper(II)[16,17] (0.46 g, 1.0 mmol) in absolute ethanol (15 mL) and chloroform (15 mL). The addition was made over a period of 0.5 h, at 50 °C, with constant stirring. The warm solution was filtered. The filtrate was allowed to stand at room temperature for 24 h. The nonhomogeneous microcrystalline solid that formed was filtered off. After the filtrate was allowed to stand at room temperature for an additional 48 h, dark brown crystals of the compound were collected by filtration and dried under vacuum (mp 205–207 °C). Anal. Calcd for $C_{26}H_{20}N_2O_2Cl_2Cu_2$: C, 52.89; H, 3.41; N, 4.74. Found: C, 52.86; H, 3.59; N, 4.74.

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