to note that from the slope it follows that $32\beta^2\langle r^{-3}\rangle k'^2/\beta_{35}$ = 615 cm^{-1}, which is very close to the theoretical value of the slope which corresponds to localized free-ion d orbitals,[3] i.e., $32\beta^2\langle r^{-3}\rangle$ = 620 cm^{-1}.

The suggested correlation seems very promising. However, theoretical relations between parameters β_{35}, k', and $\langle r^{-3}\rangle$ should be carried out in order to elucidate the fundamental nature of such a correlation.

Correspondence

Magnetic Susceptibility of Porphyrins

Sir:

In view of the active interest in magnetic properties of metalloporphyrins it is important to know accurately the diamagnetism of the porphyrin moiety. Most researchers use either Pascal's constants[1] or one of four published porphyrin magnetic susceptibility values (Table I).[2-4] With use of Pascal's constants the calculated diamagnetism for protoporphyrin IX dimethyl ester is -346×10^{-6} (cgs emu/mol units are used throughout) which is considerably smaller than the experimental values,[2] but the calculated value for H_2TPP (-365×10^{-6}) is similar to one experimental value reported in the literature,[3] leaving considerable uncertainty concerning the "constitutive correction" for the porphyrin ring. Application of Pascal's constants to correct for the substituents in H_2T-piv-PP[4] yields -467×10^{-6} for H_2TPP which is substantially different from the earlier value.[2] The questions raised by these comparisons and diamagnetic susceptibility measurements in our laboratory led to an interlaboratory comparison, the results of which we report here.

Experimental Section. The porphyrins were prepared and purified as previously described.[5] In each case the final purification steps involved chromatography on Baker 0537 alumina by using chloroform as eluant followed by recrystallization. A commerical (Strem Chemicals) sample of H_2TPP was also used. Magnetic susceptibility measurements in Denver, CO, were made on a Bruker BM4 Faraday balance with a 1-μg sensitivity Sartorius balance. The product $H(\mathrm{d}H/\mathrm{d}s)$ ranged from 2×10^6 to 10×10^6 G^2 cm^{-1}. Magnetic susceptibility measurements by Professor I. A. Cohen were made with an Ainsworth Faraday balance with 1-μg sensitivity and a central magnetic field of about 7 kG. $HgCo(SCN)_4$ was used as the primary standard, with χ_g = 16.2×10^{-6} cm^3 g^{-1} at 20 °C,[6] and $Ni(en)_3S_2O_3$[7] was used as secondary standard to calibrate the technique.

Table I. Literature Values for the Magnetic Susceptibility of Porphyrins

compd	susceptibility (×10⁶)	ref
protoporphyrin IX dimethyl ester	−585	2
mesoporphyrin IX dimethyl ester	−595	2
tetraphenylporphyrin (H_2TPP)	−386	3
tetrakis(pivaloylphenyl)porphyrin	−690	4

Table II. Magnetic Susceptibility of Porphyrins

	susceptibility (×10⁶)		
compd[a]	av[b]	extrapd[c]	cor to H_2TPP[d]
H_2-*p*-MeTPP	−658	−765	−718
	−620	−711	−644
	−583	−718	−671
	−721[e]		
H_2-*o*-MeTPP	−638	−724	−677
	−602	−745	−698
H_2-*i*-PrTPP	−751	−846	−704
	−719	−861	−719
H_2TPP	−595	−720	
	−549	−731	
	−572[f]	−627	
	−524[f]	−633	
	−396[e,f]		

[a] Abbreviations used: H_2-*p*-MeTPP, tetrakis(*p*-methylphenyl)porphyrin; H_2TPP, tetraphenylporphyrin; H_2-*o*-MeTPP, tetrakis(*o*-methylphenyl)porphyrin; H_2-*i*-PrTPP, tetrakis(*p*-isopropylphenyl)porphyrin. [b] Values measured at four or five field strengths were averaged, ignoring the field dependence. [c] Value obtained by least-squares extrapolation to infinite field strength. [d] The correction involved use of Pascal's constants to account for differences in ring substituents. [e] Measurement by Professor I. A. Cohen at 7 kG. [f] Commercial sample.

Results and Discussion. The magnetic susceptibility measurements of free-base porphyrins were all found to be dependent on the magnetic field strength. The Faraday method measurements can validly be corrected for ferromagnetic impurities by extrapolating to infinite field.[8] The Faraday measurement data obtained in Denver, CO, have been corrected for field dependence in this way. Table II presents the magnetic susceptibilities for several porphyrins and the values for H_2TPP obtained from them by Pascal's constant calculations. The susceptibility values extrapolated to infinite field are strikingly different from the average values. Also the slope of the χ vs. reciprocal of field strength plot differed for different aliquants of the same bulk sample of porphyrin. The data implied an adventitious ferromagnetic impurity. Energy-dispersive X-ray fluorescence measurements demonstrated the presence of Fe in the H_2-*i*-PrTPP and H_2TPP samples (only these two were tested). The commercial H_2TPP sample contained more Fe than the purified H_2-*i*-PrTPP sample. It is possible that the Fe is in the ferromagnetic impurity. It should be noted that only a very small amount of ferromagnetic impurity is needed to cause the results observed, since the field dependence amounted to less than about 20-μg difference from the value that would have been expected for each measurement if there had been no ferromagnetic impurity. However such small differences have a large impact on the final values since the weight changes due to diamagnetism are so small (e.g. less than about 0.2 mg in the Faraday measurements).

We judge that the "best" value to use for the magnetic susceptibility of H_2TPP is the average of the extrapolated values from the Faraday measurements, corrected for substituents by using Pascal's constants (the commercial sample

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(1) E.g.: Boudreaux, E. A.; Mulay, L. N. "Theory and Applications of Molecular Paramagnetism"; Wiley: New York, 1976; p 491 ff.

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(3) Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* **1971**, *1*, 57.

(4) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Hayes, S. E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2761.

(5) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660.

(6) Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

(7) Curtis, N. F. *J. Chem. Soc.* **1961**, 3147.

(8) Earnshaw, A. "Introduction to Magnetochemistry"; Academic Press: New York, 1968; pp 87, 96.

was excluded from the average): -700×10^{-6}. The difference between the experimental value of -700×10^{-6} and the Pascal's constant value of -365×10^{-6} for H_2TPP equals -335×10^{-6} which could be used as a new "constitutive correction" for the porphyrin ring.

Acknowledgment. We thank Professor I. A. Cohen (Brooklyn College, CUNY) for his collaboration in this interlaboratory comparison. We thank Mr. B. Jablonski in Professor D. E. Leyden's laboratory for making the X-ray fluorescence measurement.

Registry No. H_2-*p*-MeTPP, 14527-51-6; H_2-*o*-MeTPP, 37083-40-2; H_2-*i*-PrTPP, 38350-65-1; H_2TPP, 917-23-7.

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Correlations between Outer-Sphere Self-Exchange Rates and Reaction Entropies for Some Simple Redox Couples

Sir:

The free-energy barrier ΔG_{λ}^{*} to outer-sphere electron exchange between metal complexes consists of inner-shell ΔG_{in}^{*} and outer-shell $\Delta G_{\text{out}}^{*}$ contributions arising from the structural reorganization of the reactants and the surrounding solvent, respectively, that are required prior to electron transfer.[1] However, the interpretation of the observed reactivities in terms of theoretical models is limited by the lack of independent information on the nature and magnitude of these inner- and outer-shell terms. It is therefore worthwhile to search for experimental methods of providing estimates of such terms. One parameter that should yield information relevant to this question is the entropy difference $\Delta S_{\text{rc}}^{\circ}$ ($=\bar{S}_{\text{red}}^{\circ} - \bar{S}_{\text{ox}}^{\circ}$) between the two ions forming the redox couple. ($\Delta S_{\text{rc}}^{\circ}$ should not be confused with $\Delta S_{\text{ex}}^{\circ}$, the standard entropy change for the electron exchange reaction. The latter quantity is equal to zero since the reactants and products of exchange reactions are identical ($\Delta S_{\text{ex}}^{\circ} = \Delta S_{\text{rc}}^{\circ} - \Delta S_{\text{rc}}^{\circ}$).) The absolute ionic entropies $\bar{S}^{\circ}$ of aquo ions are very sensitive to both the size and charge of the ions, probably due to the effect of the ions upon the structure of the surrounding water.[2-4] Therefore $\Delta S_{\text{rc}}^{\circ}$ should be sensitive to the changes in solvent polarization that are required in order for electron transfer to occur and should become significantly larger as the difference in the effective radii $\Delta\bar{a}$ of the reduced and oxidized species increases.[5] Since large values of $\Delta\bar{a}$ are also associated with large inner-shell contributions to ΔG_{λ}^{*}, some of the factors that tend to increase ΔG_{in}^{*} are also expected to increase $\Delta S_{\text{rc}}^{\circ}$. ($\Delta G_{\text{in}}^{*}$ is primarily determined by differences between the radii of the reactants while $\Delta G_{\text{out}}^{*}$ is mainly determined by the actual sizes of the reactants.) Estimates of $\bar{S}^{\circ}$ for a number of aquo cations and complex anions have been available for some time,[6] but values of $\Delta S_{\text{rc}}^{\circ}$ for transition-metal redox couples of kinetic significance have been largely unavailable.[7] In addition, the existing data have been obtained by using a variety of methods and conditions so that intercomparisons are difficult. However, determinations of $\Delta S_{\text{rc}}^{\circ}$ have recently been made for a number of transition-metal redox couples in aqueous media by using a nonisothermal electrochemical cell arrangement.[2,8] In this communication, these and some values of $\Delta S_{\text{rc}}^{\circ}$ for additional redox couples that were obtained[9] by using the same method[2] are used to explore possible correlations between ΔG_{λ}^{*} and $\Delta S_{\text{rc}}^{\circ}$.

The interpretation of ΔG_{λ}^{*} is simplest for redox couples undergoing adiabatic electron transfer, for which the change in metal–ligand bond distances is not large. For such systems the inner-shell contribution ΔG_{in}^{*} is small and calculable, and the outer-sphere contribution $\Delta G_{\text{out}}^{*}$ can be obtained from ΔG_{λ}^{*}.[10] Although suitable systems are not abundant, Ru(III)/(II) couples containing ammine and/or polypyridine ligands provide such a class.[10] Estimates of $\Delta G_{\text{out}}^{*}$ for various $Ru(NH_3)_{2x}(bpy)_{3-x}^{3+/2+}$ couples where $x = 0$–3 have recently been made.[10] These are listed in Table I along with the corresponding values of $\Delta G_{\text{out}}^{*}$(calcd) calculated by using the Marcus model which treats the surrounding solvent as a dielectric continuum.[10] The values of $\Delta S_{\text{rc}}^{\circ}$ for these ruthenium couples have also been determined[2,9] and are given in Table I[12] along with the corresponding values of $\Delta S_{\text{rc}}^{\circ}$(calcd) calculated by using the dielectric-continuum Born model.[13,14]

It is seen that the increasing values of $\Delta G_{\text{out}}^{*}$ that are observed as the smaller ammonia ligands replace bipyridine in the ruthenium coordination sphere are also associated with markedly increasing values of $\Delta S_{\text{rc}}^{\circ}$. This is not surprising since greater changes in solvent polarization are required for electron transfer as the effective radii of the reactants decrease.[1,10] The dielectric-continuum estimates of $\Delta G_{\text{out}}^{*}$(calcd) and $\Delta S_{\text{rc}}^{\circ}$(calcd) are seen to be in broad agreement with the corresponding experimental parameters. However, it is interesting to note that there is substantially better agreement between $\Delta G_{\text{out}}^{*}$ and $\Delta G_{\text{out}}^{*}$(calcd) than between $\Delta S_{\text{rc}}^{\circ}$ and $\Delta S_{\text{rc}}^{\circ}$(calcd). This behavior may be related to the fact that $\Delta G_{\text{out}}^{*}$(calcd) is mainly determined by the optical dielectric constant ϵ_{op}[1] rather than by the static dielectric constant ϵ_{s}. The latter determines the value of $\Delta S_{\text{rc}}^{\circ}$(calcd).[13] It is known that ϵ_{op} is much less sensitive to solvent structure than is ϵ_{s}, so that any breakdown in the validity of the dielectric continuum model of ion–solvent interactions caused by alteration in solvent structure in the vicinity of the solute is likely to affect $\Delta G_{\text{out}}^{*}$ to a much smaller extent than $\Delta S_{\text{rc}}^{\circ}$.

Most other outer-sphere exchange reactions involve significant changes in metal–ligand bond distances so that the

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(1) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

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

(3) See for example: Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507.

(4) See for example: Criss, C. M.; Salomon, M. In "Physical Chemistry of Organic Solvent Systems"; Covington, A. K., Dickinson, T., Eds.; Plenum: New York, 1973; Chapter 2.

(5) Böttcher, W.; Brown, G. M.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1447.

(6) (a) Powell, R. E.; Latimer, W. M. *J. Chem. Phys.* **1951**, *19*, 1139. (b) Cobble, J. W. *Ibid.* **1953**, *21*, 1446.

(7) It should be noted that neither $\bar{S}^{\circ}$ nor $\Delta S_{\text{rc}}^{\circ}$ can be obtained without resort to at least one extrathermodynamic assumption.[2,4]

(8) With this approach, values of $\Delta S_{\text{rc}}^{\circ}$ can be obtained that are probably trustworthy to 1–2 cal deg^{-1} mol^{-1}.

(9) Yee, E. L.; Weaver, M. J., to be submitted for publication.

(10) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(11) The effective or equivalent radius, *a*, of a reactant is taken as equal to half of the cube root of the product of the diameters along the three L–M–L axes.[10]

(12) Although the values of $\Delta S_{\text{rc}}^{\circ}$ quoted in Tables I and II were obtained at ionic strength $\mu = 0.1$ M, they were found to be essentially independent of μ over the range $0 < \mu < 0.2$ M. For $\mu > 0.2$ M, gradual decreases of $\Delta S_{\text{rc}}^{\circ}$ with increasing μ are observed,[2] presumably arising from an increasing extent of ion pairing.

(13) Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513.

(14) Calculated from the formula[13] $\Delta S_{\text{rc}}^{\circ} = 9.65(Z_{\text{ox}}^2/\bar{a}_{\text{ox}} - Z_{\text{red}}^2/\bar{a}_{\text{red}})$ cal deg^{-1} mol^{-1}, where Z_{ox} and Z_{red} are the charges on and $\bar{a}_{\text{ox}}$ and $\bar{a}_{\text{red}}$ are the equivalent radii of the oxidized and reduced species, respectively.

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