complex to that for Ni(salen)Co(hfa)$_2$ should give us the measured moment for Cu(salen)Co(hfa)$_2$ in the absence of coupling. When this was done, the calculated susceptibility closely approximated the measured susceptibility above 45°K. Below this temperature, the measured susceptibility is smaller than the calculated one. The difference increases as the temperature approaches 4°K, indicative of a small amount of antiferromagnetic coupling. The coupling could be intermolecular or intramolecular involving copper and cobalt. Since the amount of coupling is small, a calculation of the coupling constant would not be accurate because of the nonnegligible orbital contributions from the cobalt.

The adduct Cu(salen)Co(hfa)$_2$ exists in solution as well as the solid state. The visible spectrum of the complex is not an addition of the spectra of Cu(salen) and Co(hfa)$_2$. The molecular weight in methylene chloride measured by vapor pressure osmometry gave a value of 725 (theoretical 803), indicating extensive association of the two metal species in solution. The solution magnetic moment of 5.1 BM at room temperature also is consistent with the cobalt atom being in an octahedral high-spin d^7 configuration.

Also, there is no detectable solution esr signal at room temperature. When the esr spectrum of Cu(salen) is observed on a series of solutions to which varying quantities of Co(hfa)$_2$ are added, it is found that the signal strength decreases with addition of the cobalt until stoichiometric quantities are added. At this point, the signal disappears completely. Apparently, the cobalt becomes coupled to the copper causing very rapid relaxation of the unpaired spin. One would expect that a nmr signal could be observed if this is the case. Unfortunately, this proposal cannot be tested because Cu(salen)Co(hfa)$_2$ is only sparingly soluble in noncoordinating solvents like methylene chloride.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6640.

Evaluation of the Thermodynamic Data Reported for the Reversible Oxygenation of the Amine Complexes of Cobalt(II) Protoporphyrin IX Dimethyl Ester

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Abstract: Recently, Stynes and Ibers, *et al.*, reported thermodynamic data, determined from visible spectroscopic measurements, for the reversible oxygenation of various amine complexes of cobalt(II) protoporphyrin IX dimethyl ester. In evaluating the equilibrium constants for their systems, they employed the Hill equation in a way that appeared questionable. This, coupled with the fact that Walker has challenged one of the essential conclusions of Ibers, *et al.*, caused us to report our reexamination of the data for this system. The method employed in the reexamination involved rigorously solving for both K^{-1} and $\epsilon_C - \epsilon_A$ with numerical techniques and representing the solution graphically as we have strongly advocated in the past. It was found that, on the whole, the systems investigated by Ibers, *et al.*, were poorly defined and in most instances no numerical data can be obtained.

Stynes and Ibers,[1] and others[2] reported thermodynamic data, determined from visible spectroscopic measurements, for the reversible oxygenation of various amine complexes of cobalt(II) protoporphyrin IX dimethyl ester.

$$\mathrm{LCoP} + \mathrm{O_2(g)} \xrightleftharpoons{K_{eq}} \mathrm{LCoP(O_2)} \qquad (1)$$

The equilibrium constant expression for a system such as described by eq 1 can be written as

$$K = \frac{[C_C]}{[C_B - C_C][C_A - C_C]} \qquad (2)$$

where C_A is the initial molar concentration of acid, C_B is the initial molar concentration of base, and C_C is the equilibrium molar concentration of complex. The Benesi–Hildebrand (B-H) analysis[3,4] is one of the most common procedures for manipulating eq 2 to arrive at a linear form of the equilibrium constant expression. Ibers, *et al.*, employed an approach referred to as the Hill equation.[1–3] The application of this equation in the calculation of thermodynamic parameters from spectroscopic observables can be shown to suffer from many of the pitfalls which have been described in the literature for B-H type analyses.[4–7] These procedures

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[1] H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 1559 (1972).

[2] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, **95**, 1142 (1973).

[3] A. V. Hill, *J. Physiol.* (*London*), 40, IVP (1910).

[4] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, 81, 6138 (1959).

[5] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, 81, 6142 (1959).

have been shown to be capable of making worthless data look good. This tendency is enhanced in the application of the Hill equation by use of log functions in the analysis. These potential difficulties, coupled with the fact that Walker[8] challenged one of the essential conclusions of Ibers, *et al.*, that the enthalpy for O_2 uptake paralleled the pK_a of the conjugate acid of the amine, caused us to reexamine this most interesting system.

Calculations

Our procedure[4,5] for analyzing the data, incorporating some recent modifications,[9,10] has been described in detail in the literature. Briefly, the method graphically and numerically solves for the two essential unknowns K^{-1} and $\epsilon_C - \epsilon_A$ (where ϵ_C and ϵ_A represent molar absorptivities for the complex and free acid, respectively) in this type of system by employing several sets of measured absorbances corresponding to different concentrations of reagents. For a 1:1 adduct, the solutions of different concentration lead to a series of simultaneous K^{-1} equations of the form

$$K^{-1} = \frac{A_b - A_b^0}{\epsilon_C - \epsilon_A} - C_A - C_B + \frac{C_B C_A(\epsilon_C - \epsilon_A)}{A_b - A_b^0} \quad (3)$$

Here K is the equilibrium constant, A_b is the total absorbance which is related to the complex concentration and to the acid concentration at any given wavelength, A_b^0 is the absorbance of the initial concentration of acid, C_B is the initial concentration of base, and C_A is the initial concentration of acid. This series of simultaneous K^{-1} equations is solved for the best K^{-1} and $\epsilon_C - \epsilon_A$.

In solving eq 3, our computer program provides an error analysis as well as a graphical (K^{-1} *vs.* $\epsilon_C - \epsilon_A$) presentation of the mathematical solution. The error analysis involves the calculation of both the marginal standard deviation and conditional standard deviation for both unknowns K and $\epsilon_C - \epsilon_A$. If the fraction of complex formed in the series of experiments does not change drastically, all of the simultaneous equations corresponding to different concentrations will be identical and cannot be solved for the two unknowns.[9,10] In the error analysis good results may be obtained at a given value of $\epsilon_C - \epsilon_A$, but this is misleading for just as good results may be obtained at a drastically different value of $\epsilon_C - \epsilon_A$. However, the graphical plot demonstrates how parallel the slopes are for the K^{-1} *vs.* $\epsilon_C - \epsilon_A$ curves (each curve corresponds to a different set of concentrations). Meaningful results are obtained not only when the marginal and conditional standard deviations are small but also when the slopes of the K^{-1} *vs.* $\epsilon_C - \epsilon_A$ curves vary greatly.[9,10] We have found by empirically examining many plots that the ratio of the marginal standard deviation to the conditional standard deviation for either K or $\epsilon_C - \epsilon_A$ provides a good indication of whether or not the simultaneous K^{-1} equations are similar and thus whether or not the two unknowns are defined. If the conditional standard deviation is greater than 5%, the results can be rejected. However, if the conditional standard deviation is small, but the ratio is greater than 12, the values calculated for K and $\epsilon_C - \epsilon_A$ should also be immediately rejected, as the slopes of the curves in the K^{-1} *vs.* $\epsilon_C - \epsilon_A$ plot must be very similar. A value of the ratio of three or less and a small conditional standard deviation implies that the slopes of the curves are dissimilar and, therefore, a satisfactory value of K and $\epsilon_C - \epsilon_A$ can be obtained. Often a small ratio is obtained because the conditional deviation is large; however, these results are generally meaningless. If one finds a ratio between three and 12 and with a small (5% or less) conditional deviation, he should tread carefully, as it is quite likely that the slopes of the curves are such that considerably more error exists in the calculated results than the marginal deviation indicates.

There are many advantages to be gained by graphically representing the simultaneous solution of these K^{-1} equations (*i.e.*, the series of eq 3). By examining the intersections of the individual curves, one can observe the existence of a trend in the intersections with solution concentration. If this trend does exist, it implies complications from solution nonideality. Secondly, one can quickly see if one spectral curve represents a poor set of experimental data relative to the other spectral curves. Armed with a technique for determining if a spectral curve is "bad," one can then investigate possible experimental reasons for the bad result or use a statistical analysis to satisfactorily disregard the particular curve. Finally, from a quick visual inspection of the graphical display one can determine if the range of slopes in the experiments is sufficient to accurately define both K and $\epsilon_C - \epsilon_A$. If the slopes of the plotted curves vary over a wide range, both K and $\epsilon_C - \epsilon_A$ can be accurately obtained. However, if the slopes of the plotted curves are very similar, the solution is undefined. This provides a visual check on the conditions leading to the number obtained for the ratio of the marginal to conditional standard deviation discussed above.

Results and Discussion

The use of the graphical display to determine the significance of results[4,5] first called attention to the problems of estimating the validity of data calculated from a spectrophotometric experiment. Deranleau[7] and Person[6] have subsequently provided additional quantitative criteria referred to as the saturation factors and the range of the experiments to describe these potential shortcomings in a set of experimental data. The saturation factor for any one experiment is the ratio of the concentration of complex formed in the experiment to the initial concentration of the most dilute component. If in a series of incremental base additions (acid most dilute) the saturation factor does not change appreciably, the K and $\epsilon_C - \epsilon_A$ are not defined. The range of the experiments as stated by Person defines the minimum and maximum donor concentrations required to determine meaningful values of K and $\epsilon_C - \epsilon_A$. This range in effect describes the variation in base concentration needed to cause the saturation factor to change appreciably.

It is relatively easy to show the relationship between the slopes of curves on the graphical display originally[4,5]

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(7) D. A. Deranleau, *J. Amer. Chem. Soc.*, **91**, 4044 (1969).

(8) F. A. Walker, *J. Amer. Chem. Soc.*, **95**, 1154 (1973).

(9) F. L. Slejko, R. S. Drago, and D. G. Brown, *J. Amer. Chem. Soc.*, **94**, 9210 (1972).

(10) R. M. Guidry and R. S. Drago, *J. Chem. Educ.*, submitted for publication.

Table I. Thermodynamic Data for Reversible O_2 Binding to Cobalt(II) Protoporphyrin IX Dimethyl Ester Base

Compound	Temp, °C	K_{eq},[a] (l. mol^{-1})	Marg stand dev of K_{eq},[b] l. mol^{-1}	Cond stand dev of K_{eq}, l. mol^{-1}	Marg stand dev/ cond stand dev	K_{eq},[d,e] l. mol^{-1}	ΔH,[d] kcal mol^{-1}
PyCoP	−45.0	Not defined (12)	5.7	0.52	11	20.6 ± 1.4	
	−57.5	Not defined (28)	9.6	2.3	4.2	75.6 ± 10.5	−9.2 ± 0.6
	−63.5	Not defined (53)	11	4.2	2.6	106.3 ± 12.3	
(*t*-Bu(py))CoP	−37.4	Not defined	*c*	*c*	*c*	11.1 ± 0.8	
	−45.0	Not defined (28)	3.9	0.73	5.3	24.2 ± 1.1	−10.0 ± 0.5
	−63.5	Not defined (87)	23	10	2.3	140.1 ± 9.7	
(MeIm)CoP	−30.8	Not defined (58)	14	4.6	3.0	66.0 ± 4.6	
	−37.4	Not defined (118)	23	10	2.3	134.1 ± 9.3	−11.5 ± 0.5
	−45.0	236.1	34	17	2.0	283.9 ± 13.1	
ImCoP	−30.8	Not defined (23)	4.2	0.83	5.1	47.8 ± 3.3	
	−45.0	Not defined (201)	33	22	1.5	205.6 ± 14.2	−11.2 ± 0.5
	−57.5	Not defined (834)	112	78	1.4	756.3 ± 52.3	
	−63.5	Not defined (1.6×10^4)	1.1×10^4	9.5×10^3	1.2	*f*	
(BzIm)CoP	−45.0	Not defined (6)	4.4	0.27	16	10.3 ± 0.7	
	−63.5	Not defined (57)	14	4.8	2.9	65.5 ± 4.5	−9.6 ± 0.6

[a] The number in parentheses is the value of K our computer program happens to settle on. The error limits are meaningless for the system is clearly not defined in view of the K^{-1} *vs.* ϵ plots. [b] The marginal standard deviation of K_{eq} represents 66% confidence limits. For 95% confidence, this deviation should be doubled. [c] In both runs at this temperature for this system, the ratio of deviations was greater than 50 and, therefore, they were immediately rejected. [d] These values and error limits at 95% confidence reported by Ibers and coworkers in ref 2. [e] Converted using the equation $K_{eq}^{1/m} = 760RTK_{eq}^{mm^{-1}}$ which is an ideal gas relationship. At these low pressures, O_2 should approach ideal gas behavior. [f] No value reported in ref 2.

advocated as the criteria for defining the solution by us and the range or saturation factors subsequently proposed.[6,7] Obviously the slopes of the curves from eq 3 are obtained by taking the partial derivative of K^{-1} with respect to $\epsilon_C - \epsilon_A$. The result is shown in eq 4.

$$\frac{\partial(K^{-1})}{\partial(\epsilon_C - \epsilon_A)} = -\frac{A_b - A_b^0}{(\epsilon_C - \epsilon_A)^2} + \frac{C_BC_A}{A_b - A_b^0} \qquad (4)$$

The term $(A_b - A_b^0)/(\epsilon_C - \epsilon_A)^2$ in eq 4 is small since in most determinations one works in dilute solution where the absorbance change is smaller than $\epsilon_C - \epsilon_A$ (which must be large in order to get a good absorbance change on complexation). When the equilibrium constant is small, if one doubles the concentration of base added in a series of experiments in which the total acid concentration is small and held constant, then the concentration of complex formed will likewise double. Therefore, in the graphical display one would observe a series of parallel curves, for as C_BC_A is doubled so is $A_b - A_b^0$. In order to obtain curves with varying slopes, one must design his experiment so that the ratio $C_BC_A/(A_b - A_b^0)$ changes appreciably for the series of solutions. For a low K this can only happen when the concentrations have been varied over a large range so as to convert both a little and most of the free acid to complex; that is, the change in saturation factor must be large. Our visual display automatically provides information at a glance about the change in the slope or ratio $C_BC_A/(A_b - A_b^0)$ in the series of solutions studied. Accordingly the slope of our lines are directly proportional to the reciprocals of the change in saturation factors in the series of solutions studied.

Using the same raw data[11] as Ibers and coworkers for the five systems studied, we have attempted to redetermine the equilibrium constants (for eq 1) with the various bases employed using our calculational procedure. By using our error analysis, we hoped to be able to ascertain whether a direct relationship does exist between the pK_a of the conjugate acid of the amine and the ΔH of formation of the Co–O bond in these systems as claimed by Ibers and coworkers[1,2] or whether it does not as claimed by Walker[6] based on her results from esr studies on the similar cobalt porphyrin $\alpha,\beta,\gamma,\delta$-tetra(*p*-methoxyphenyl)porphinatocobalt(II).

Our results are reported in Table I along with the marginal and conditional standard deviations and the ratio of marginal standard deviation to conditional standard deviation. When the value of an equilibrium constant appears as "not defined," it implies that not only was the above ratio greater than three,

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(11) At the time of the initial communication of these results,[1] Professor Ibers kindly provided us with copies of the portion of the Ph.D. thesis by H. C. Stynes, Northwestern University, 1972, containing the raw data on this system. Within 2 weeks, we informed him of our results. The subsequent appearance of ref 2 and 8 has encouraged this paper.

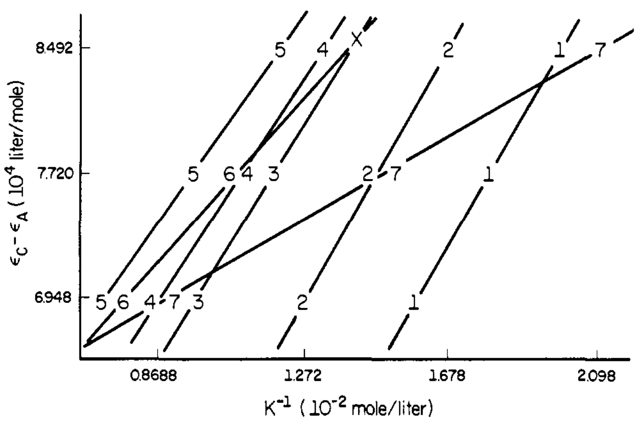

Figure 1. Plot of K^{-1} *vs.* $\epsilon_C - \epsilon_A$ for 1-methylimidazole, cobalt(II) protoporphyrin IX dimethyl ester, and oxygen in toluene solution. Regardless of the procedure used to calculate K and $\epsilon_C - \epsilon_A$, this graph shows the relationship between the simultaneous equations that have to be solved for the two unknowns.

but the slopes of K^{-1} *vs.* $\epsilon_C - \epsilon_A$ curves were very similar or else that the ratio was small mainly because the conditional deviation was so large (5% or greater). (The conditional deviation relates to the reproducibility of the experiment.) In these cases, the two unknowns K^{-1} and $\epsilon_C - \epsilon_A$ are not determined from the measured data. If accurate equilibrium constants at three temperatures could not be determined for a particular system, then there is no way in which accurate enthalpy data (van't Hoff plots were used) and other thermodynamic properties of the system could be obtained. Therefore, we conclude that in all cases the enthalpy is *NOT DEFINED.* The values of the equilibrium constants, enthalpy, and errors reported by Ibers, *et al.*,[1,2] are also shown in Table I for comparison with our analysis.[12]

When the conditional deviation is large, a small ratio is meaningless as shown in Figure 1, where the L = 1-methylimidazole system is shown. The mathematical solution of this data is determined by curve 7. Since curves 1 and 5 have the same slope, they should lie on top of one another in this region. If as much error as indicated in the difference of curves 1 and 5 exists in curve 7, the results from these data are meaningless. Yet, our statistical analysis (*i.e.*, the deviations and their ratio) indicates this is one of their better systems. This example has been shown to indicate the necessity of looking at the graphical plots.

In the best system reported,[1,2] we calculate a K of 236 for 1-methylimidazole with error limits of ±34 at 66% confidence. Clearly, with this error in the best K any enthalpy calculated from the reported equilibrium constants over a 20° temperature range is meaningless. Consequently, we must conclude that all of the arguments based on differences in bond strength or knowledge of the equilibrium concentrations of species are worthless. The system is further complicated by the equilibrium involving amine base and CoP.

The system L = pyridine at $-63.5°$ is an interesting one. Our analysis indicates K is poorly defined and has a value of 53, but Ibers, *et al.*, report a value of 106 ± 12. This points up the extent to which analysis of raw data can be an interpretation. We should insist that the raw data from any study of this sort be made available in the microfilm edition. It is impossible to judge the meaning of the results reported by Walker. With great pains, one can determine the area of a curve in esr to 10%. This and the method used to resolve the overlapping curves makes one very suspicious of the assigned errors.

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[12] The units of the equilibrium constants have been converted from mm^{-1} as reported by Ibers and coworkers to l. mol^{-1} for comparison purposes. In this system, the former units are preferable for most purposes, but our analysis is based on l. mol^{-1} units. It should be noted that the raw data[2] contain several spectrophotometric runs at each temperature for a given system. The factors varying in each run are the concentrations of oxygen and amine cobalt complex. In this paper any run that was extremely bad (ratio of deviations greater than 50) was immediately eliminated from the analysis. From the remaining trials, average values of the deviations, the ratio of the deviations, and the equilibrium constant were calculated at each temperature for a given system and are reported in Table I.