density at the tungsten atoms is small. However the α spin is substantially localized on the iron atom in each case.

The overall charge distributions for molecules $[Fe(MoS_4)_2]^{3-}$ and $[Fe(WS_4)_2]^{2-/3-}$ are quite similar. This paradox is seen in Table IVa to arise from the subtle but significant redistribution of electron density between the d^6 and d^7 molecules. Further, the calculated charge distribution for the hypothetical one-electron-oxidized species $[Fe(MoS_4)_2]^{2-}$ is also similar to that of the anion.[41] A detailed comparison between $[Fe(MoS_4)_2]^{2-}$ and $[Fe(MoS_4)_2]^{3-}$ indicates that the extra electron is distributed over the whole complex (Fe (0.143), Mo (0.07), S_B (0.065), S_T (0.113)) with about 85% of the added charge residing on the tetrathiomolybdate ligands.[42] A similar effect is also found for the $[Fe(WS_4)_2]^{2-/3-}$ anions (Table IV). This leads to a ready interpretation of the Mössbauer spectra of these complexes. The observed isomer shifts in the $[Fe(WS_4)_2]^{2-/3-}$ anions[39,39] of 0.44 and 0.45 mm/s indicate little change in charge on the iron nucleus[43] while the quadrupole splittings, 2.65 and 1.03 mm/s, indicate significant changes in the iron orbital populations.[40] In the case of the $[Fe(WS_4)_2]^{2-/3-}$ couple studied here there are indeed significant changes in the iron d orbital populations even though they lead to a similar overall charge on the iron atom (see Table IVa).

A puzzling feature of the bis(tetrathiomolybdate) and bis(tetrathiotungstate) complexes is that while both the dianionic and trianionic species may be isolated for tungsten,[23,44] only the trianion has been isolated for molybdenum. Electrochemical studies have shown the oxidation of $[Fe(MoS_4)_2]^{3-}$ to be irreversible in acetonitrile, and the stability of the $[Fe(WS_4)_2]^{2-}$ ion compared with the $[Fe(MoS_4)_2]^{2-}$ ion has been ascribed to greater thermal stability and stronger binding of the tetrathiotungstate ion.[5,6] The spin-polarized energy level scheme for $[Fe(MoS_4)_2]^{3-}$ suggests that oxidation should occur at the HOMO, the $7b_2^{\beta}$ orbital in Figure 6, leaving the complex in a quintet ($S = 2$) state similar to that found for $[Fe(WS_4)_2]^{2-}$. This leads to a similar d^6 configuration as is found in the iron(II) complex $[Fe(MoS_4)(SH)_2]^{2-}$.[19] The stable configuration for $[Fe(MoS_4)_2]^{2-}$ (tested by transition-state calculations) is the latter. The analogous $[Fe(WS_4)_2]^{2-}$ has four unpaired electrons[23] as would be expected for oxidation of an electron from the *xy* orbital.

Conclusions

Magnetization studies show unequivocally that $[Fe(MoS_4)_2]^{3-}$ has an $S = {}^3/_2$ ground state with a significant positive zero-field splitting. This is in accord with conclusions based on esr spectroscopy.

Scattered wave–SCF–Xα calculations are turning out to be useful indicators of the nature of the valence orbitals in thiomolybdate complexes. They reveal that formal oxidation states and d^n configurations retain a useful degree of meaning despite contradictory isomer shift data. For $[Fe(MoS_4)_2]^{3-}$, an iron(I) formulation is favored rather than the iron(III) formulation suggested by Mössbauer spectroscopy.

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Supplementary Material Available: Tables II and III containing magnetic susceptibility data and orbital energies and populations (6 pages). Ordering information is given on any current masthead page.

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[42] Calculation on $[Fe(MoS_4)_2]^{2-}$ with same geometry as for $[Fe(MoS_4)_2]^{3-}$ and Watson sphere of charge 2+. Charge distribution: Fe (s, 0.537; p, 0.682; d, 7.029), Mo (s, 0.468; p, 0.536; d, 4.409), S_B (s, 1.841; p, 4.409), S_T (s, 1.842; p, 4.641).

[43] This is supported by very similar calculated charge densities at the iron nucleus (spin polarized) of 11 876.297 and 11 875.974 au, respectively.

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E and *C* Parameters from Hammett Substituent Constants and Use of *E* and *C* To Understand Cobalt–Carbon Bond Energies

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An updated list of *E* and *C* parameters was calculated from a larger data base than that used in an earlier fit. The new data base included 42 acids, 55 bases, and about 500 data points. We also report best-fit parameters for 13 enthalpy–frequency shift relations. From this updated list, we have discovered relationships which lead to equations that enable one to calculate *E* and *C* parameters from Hammett substituent constants for a series of substituted phenols and pyridines. This procedure provides a simple method for greatly increasing the number of acids and bases included in the correlation. An *E* and *C* analysis was used to study the dissociation energy of the cobalt–carbon bond in alkyl-substituted bis(dimethylglyoximato)cobalt(II) complexes. This analysis gave calculated dissociation energies that were within experimental error of the measured values and gave a value for cobalt–carbon bond dissociation for the unligated complex. The basic procedure allows for the incorporation of ligand influence on bond dissociation energies into the correlation.

Introduction

The correlation of enthalpies of adduct formation, ΔH, by eq 1 has proven to be a powerful tool in understanding and predicting the interaction between Lewis acids (acceptors) and bases (donors).[2] In eq 1, the *E* and *C* parameters are related to electrostatic

$$-\Delta H + W = E_A E_B + C_A C_B \qquad (1)$$

and covalent interactions, respectively, A and B are subscripts referring to an acceptor and a donor, respectively, and *W* is any constant enthalpy contribution to ΔH associated with a given acceptor reacting with a series of donors or a given donor reacting with a series of acceptors. In most systems studied to date, $W = 0$.

One current objective in this area of chemistry involves expanding the applicability[3,4] and number of donors and acceptors included in this model. One of the barriers to expanding the

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number of donors and acceptors is the difficult and time-consuming determination of experimental enthalpies needed to determine new parameters. In recent work,[5] the relationship between the more easily measured spectroscopic parameters that form the basis of the Kamlet–Taft[6] β–π^* scale and the E and C parameters has been shown. Other spectral relations[3] can also be used to expand the number of E and C parameters. This expansion has not only provided easier means to determine E and C parameters[3,6] but has also provided new insights into the interpretation of established spectral correlations.[4]

Correlations of quantities other than enthalpies obey a modified E and C equation of the general form shown by eq 2.[7] In eq 2

$$\Delta X + W = E_A{}^*E_B + C_A{}^*C_B \tag{2a}$$

$$\Delta X + W = E_AE_B{}^* + C_AC_B{}^* \tag{2b}$$

ΔX is a nonenthalpic change such as a spectral shift or free energy associated with adduct formation. E^* and C^* parameters differ from the unstarred E and C parameters and contain the conversion factor from kilocalories to the units associated with ΔX. Equation 2a is used when the acid is held constant and ΔX measured for a series of bases while eq 2b is the analogue when the base is held constant. It should be pointed out that eq 2a and 2b are independent and cannot be solved simultaneously. With use of eq 2 it was shown[4,5] that (i) the specific interactions involved in the β correlation are dominated by electrostatic interactions, (ii) hydrogen-bonding frequency shifts are more dependent upon the covalency in the interaction than hydrogen-bonding enthalpies accounting for deviation in the enthalpy–frequency shift correlations,[8] (iii) certain systems that do not give linear ΔH vs. ΔS plots and as a result give poor fits of ΔG or ΔH to one-term equations may be fit with the E and C equation,[4] and (iv) the stretching frequency of coordinated CO depends systematically upon the strength of the interaction of a Lewis base transmitted across a Rh–Rh bond.[9]

Earlier work[10] has shown that the Hammett substituent correlation is a special case of the E and C model. The conditions that need to be imposed to convert the more general E and C equation into the one-term, two-parameter Hammett equation have been described. In this work, we propose a model to relate the one-term Hammett substituent constants to the E and C parameters. The equation suggested is an extension of an approach used to predict $E_A{}^{1:1}$ and $C_A{}^{1:1}$ for Lewis acids that are themselves 1:1 adducts between metal–metal-bonded Lewis acids and donors. In the metal–metal systems the E_A and C_A parameters for the free acid, e.g., $Rh_2(but)_4$(but = butyrate), forming 1:1 adducts are determined by standard methods.[2] In forming a 2:1 adduct, one needs to determine the $E_A{}^{1b1}$ and $C_A{}^{1:1}$ parameters for the 1:1 adduct, that is the parameters for $B:Rh_2(but)_4$, where B is the coordinated Lewis base. These parameters were calculated from the equations

$$E_A{}^{1:1} = E_A - kE_B \tag{3}$$

$$C_A{}^{1:1} = C_A - k'C_B \tag{4}$$

where E_A and C_A are the *free* acid values, E_B and C_B are the free base B parameters, and k and k' are empirical constants determined from experimental 2:1 enthalpies. These k/E_A and k'/C_A ratios reflect the ability of the metal–metal bond to transmit the electrostatic and covalent coordination properties of the coordinated base. In this article, we investigate the use of equations of the above general form to predict the modifications made to E and C numbers of phenol and pyridine when substituents are placed on the rings from knowledge of the Hammett constants of the substituents.

Results and Discussion

A. Update of *E* and *C* Parameters from an Increased Data Base. The perturbations made on Lewis acids and bases by replacing a hydrogen atom on an aromatic ring with another substituent are relatively minor. These changes have been successfully correlated with Hammett substituent constants, and we are interested in determining if the Hammett constants can lead to reliable predictions of small changes in E and C. In order to test this possibility, accurate E and C parameters are needed to account for the small changes. Accordingly, an updated list of E and C parameters was calculated from a larger data base than that used in the earlier fit. The parameters shown in Table I involve an increase from 31 to 45 acids and 43 to 48 bases and are calculated from about 500 data points compared to 300 used earlier. The new fit was done with use of frequency shift and enthalpy data. The earlier fit included enthalpies estimated from ΔH vs. $\Delta\nu$ correlations. These estimated enthalpy data have been replaced by the frequency shift data and the appropriate frequency shift correlation. The fit was accomplished by the simultaneous minimization of eq 1 and 2a. The iminimization routine used a pseudolinearization method[11a] since $-\Delta H$ and $\Delta\chi$ are not linear in E, C, and W. The method uses the partial derivatives of the E, C, and W equation. The partial derivatives yield a system of equations that can be solved by using traditional matrix techniques.

Since there is no independent solution for E and C parameters, the acid iodine is defined to have E and C numbers of 1 and the bases are defined to have an E number of 1.32 for dimethylacetamide and a C number of 7.40 for diethyl sulfide as in our earlier report.[2]

B. Prediction of *E* and *C* Numbers from Hammett Substituent Constants. In this study, E and C numbers for a series of substituted phenols and pyridines have been used to test the relevance of the following equations in predicting E and C parameters for the substituted derivatives from Hammett substituent constants:

$$E^X = E^H + k\sigma_X \tag{5}$$

$$C^X = C^H + k'\sigma_X \tag{6}$$

In these equations E^X and C^X are the E and C values for the substituted derivative, E^H and C^H are those of the parent compound, σ is the Hammett substituent constant,[11b] and k/E and k'/C are related to the ability of the intervening atoms to transmit the perturbation by X to the donor or acceptor atom. The terms are summed to accommodate the convention used to define σ. The values of k and k' would vary for each family of acids or bases.

The first family of acids analyzed in this fashion are the substituted phenols. Extensive literature exists on these acids, and the reported E_A parameters plotted vs. their substituent constants lead to a forced-intercept least-squares line with a slope of 0.515 and an intercept of 4.54. A similar plot of C_A vs. σ leads to a line with a slope of 0.145 and an intercept of 0.302. Thus, the E_A and C_A values for any substituted phenol can be calculated from

$$E_A{}^X = 4.54 + 0.515\sigma \tag{7}$$

$$C_A{}^X = 0.302 + 0.145\sigma \tag{8}$$

Parameters obtained from these least-squares lines give calculated results from eq 1 that fitted the experimental data for substituted phenols equally well. The forced-intercept fit was preferred over

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(7) The equation $\Delta X + W = E_A{}^*E_B + C_A{}^*E_B$ is used to correlate nonenthalpic changes for a given acid interacting with a series of bases whose E_B and C_B parameters are those used in eq 1. Similarly, for a given base interacting with a series of acids, eq 2 would have the form $\Delta X + W = E_AE_B{}^* + C_AC_B{}^*$, where the E_A and C_A parameters are those used in eq 1. The unstarred E and C parameters for both acids and bases are given in Table I.

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a standard least-squares fit because of the extensive data base available for phenol. More importantly, we are in a position to estimate new enthalpies for substituted phenols whose E_A and C_A parameters have not been determined. Table II shows a comparison of the reported E_A and C_A numbers for substituted phenols with those calculated from eq 7 and 8.

The substituted pyridines constitute an analogous family of commonly studied bases. In contrast to the phenols, in the pyridine family the substituent change is being made on a heterocyclic ring. Quantitative, solvation–minimized data are not as plentiful for these donors as for the phenols. Graphs of the C_B and E_B number as a function of substituent constant give the forced-intercept least-squares lines

$$E_B{}^X = 1.30 - 0.227\sigma \qquad (9)$$

$$C_B{}^X = 6.69 - 3.94\sigma \qquad (10)$$

The E_B and C_B values calculated from these equations are compared to the values obtained from a fit of the experimental data in Table II. Equations 9 and 10 report tentative values for k and k' because of the limited range of substituent constants. Attempts to obtain data that would enable us to extend the set to the 4-CN substituent were hampered by the poor solubility of this donor in noncoordinating solvents. The ratio of the proportionality constant k' to C (the intercept) indicates that the substituent effect is in the opposite direction for a donor ($k'/C_B = -0.589$ from eq 10) compared to that of the acceptor ($k'/C_A = 0.480$ from eq 8) and is more readily transmitted through the intervening atoms of pyridine than for phenol. The ratio for k to E suggests that this effect is also in the opposite direction and more important for pyridine than for phenol though the tentative nature of the pyridine parameters renders this latter conclusion tentative.

The available data needed to accurately define eq 9 and 10 are limited, but this work provides useful tentative values and indicates the procedure to be employed to utilize Hammett substituent constants to predict E and C numbers for compounds once k and k' values have been determined by study of four or more widely differing substituted derivatives in a family. We now will proceed to further test the phenol and pyridine predictions and show some additional insights concerning chemical reactivity that can be obtained by using the E and C models.

C. Frequency Shifts for a Series of Substituted-Phenol Hydrogen Bonding to *N*,*N*-Dimethylacetamide from Predicted *E* and *C* Numbers. The approach described in the part B can be used to calculate the E_A and C_A numbers for a series of substituted phenols. We are in a position to test the reliability of our predicted parameters by correlating reported frequency shifts for a large number of substituted-phenol hydrogen bonding to *N*,*N*-dimethylacetamide. Table III contains a list of the reported frequency shifts,[12] the E_A and C_A numbers for substituted phenols calculated from σ by using eq 8 and 9, and the calculated frequency shifts obtained by substituting these E_A and C_A numbers into eq 11. Equation 11 arose from a least-squares minimization

$$\Delta\nu_{OH} = 29.2E_A + 690C_A \qquad (11)$$

of $E_B{}^*$ and $C_B{}^*$ for *N*,*N*-dimethylacetamide from the experimental frequency shifts fit to eq 2b with use of our E_A and C_A values calculated from Hammett substituent constants (see Table IIA).[7] The excellence of this fit of the data can be shown by substituting our Hammett-equation-derived E_A and C_A values (eq 7 and 8) into eq 11 to calculate the shifts shown in Table III. The equation indicates that there is no intercept in this plot, and this is consistent with earlier reports that showed no intercept in a plot of $\Delta\nu_{OH}$ vs. ΔH when the base was held constant and a series of hydrogen-bonding acids were studied.[8,13]

D. Frequency Shifts for a Series of Substituted-Pyridine Adducts with Methanol from Predicted *E* and *C* Numbers. The linear dependence of $E_B{}^X$ and $C_B{}^X$ upon σ for substituted pyridines enables us to calculate the E_B and C_B numbers for a series of pyridines. Frequency shifts have been reported for a large number of substituted pyridines hydrogen bonding to methanol.[14] These frequency shifts will be utilized to test the reliability of eq 9 and 10 through correlation with the resultant E_B and C_B parameters. The calculated E_B and C_B parameters and reported frequency shifts for methanol are given in Table IV. The $E_A{}^*$ and $C_A{}^*$ correlation for methanol from the updated list of E and C parameters (Table I) is given by eq 12. Using the reported σ values, we calculate

$$\Delta\nu_{OH} = 254E_B + 23.7C_B - 207 \qquad (12)$$

E_B and C_B values for a series of substituted pyridines using eq 9 and 10, which when substituted back into eq 12 delivers the $\Delta\nu_{OH}$(calcd) values in Table IV. The close agreement with $\Delta\nu_{OH}$(measd) demonstrates the viability of eq 9 and 10 for obtaining new E and C numbers from Hammett substituent constants.

E. Utilization of *E* and *C* Numbers for Substituted Pyridines Derived from the Hammett Substituent Constant Relation. In recent articles,[15] a series of studies are reported that lead to a measurement of the dissociation energy for a cobalt–carbon bond in alkyl-substituted bis(dimethylglyoximato)cobalt(II) complexes. The bond energies have been reported to be a function of the axial base coordinated to cobalt in this system (see eq 13). The thermodynamic cycle enables us to represent this data as an E, C, and W case is indicated by the series of equations

$$\begin{aligned}
&(\mathrm{DH})_2\mathrm{Co^{II}} + {}^{\bullet}\mathrm{R} \rightarrow (\mathrm{DH})_2\mathrm{Co^{III}R} \quad -W \\
&\mathrm{B(DH)_2Co^{II}} \rightarrow \mathrm{B} + (\mathrm{DH})_2\mathrm{Co^{II}} \quad \Delta H^{\mathrm{II}} \\
&\mathrm{B} + (\mathrm{DH})_2\mathrm{Co^{III}R} \rightarrow \mathrm{B(DH)_2Co^{III}} \quad -\Delta H^{\mathrm{III}} \\
\text{net: }\; &\mathrm{B(DH)_2Co^{II}} + {}^{\bullet}\mathrm{R} \rightarrow \mathrm{B(DH)_2Co^{III}R} \quad -\Delta H^{\mathrm{A}} \qquad (13)
\end{aligned}$$

In these equations, B represents a series of substituted pyridines, DH is dimethylglyoximato, and $^{\bullet}$R is the $C_6H_5\dot{C}(H)CH_3$ radical. The second and third equations involve dissociation and coordination of Lewis bases from and to Lewis acids, respectively, and this is the type of reaction that eq 1 has consistently predicted correctly. The sum of the second and third equations should fit to

$$-\Delta\Delta H = \Delta E_A\, E_B + \Delta C_A\, C_B$$

where

$$-\Delta\Delta H = -\Delta H^{\mathrm{III}} + \Delta H^{\mathrm{II}}$$

$$\Delta E_A = E_A[(\mathrm{DH})_2\mathrm{Co^{III}R}] - E_A[(\mathrm{DH})_2\mathrm{Co^{II}}]$$

$$\Delta C_A = C_A[(\mathrm{DH})_2\mathrm{Co^{III}R}] - C_A[(\mathrm{DH})_2\mathrm{Co^{II}}]$$

The negative heat of association $-\Delta H^A$ should equal $-W - \Delta\Delta$H and leads to the relationship

$$-\Delta H^A = -W - \Delta\Delta H = \Delta E_A E_B + \Delta C_A C_B - W$$

An attempt to fit the enthalpies (ΔH^A) to the E, C, and W equation gave an excellent fit of the measured and calculated ΔH^A values as shown in Table V. The resulting parameters are $\Delta E_A = 4.27$, $\Delta C_A = 0.54$, and $W = -11$. These parameters indicate an increase in both the electrostatic bonding properties and covalent bonding properties of the acid $(\mathrm{DH})_2\mathrm{Co^{III}R}$ compared to those of $(\mathrm{DH})_2\mathrm{Co^{II}}$, which corresponds to the cobalt center in the cobalt(III) complex being more electronegative than cobalt(II).

Although recent experimental[15] and theoretical[16] studies suggest that steric effects are much more important than trans electronic

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Table I[a]

Enthalpy Acid Parameters

no.	acid[b]	no. of enthalpies	E_A	C_A	W	no.	acid[b]	no. of enthalpies	E_A	C_A	W
1	I_2	42	1.00[c]	1.00[c]		23	$SbCl_5$	4	7.28	5.09	
2	IBr	3	2.39	1.60		24	$HCCl_3$	6	2.98	0.07	
3	ICl	6	5.84	0.54		25	$CF_3(CF_2)_6H$	4	1.60	0.24	
4	C_6H_5SH	3	1.16	0.13		26	HNCO	4	3.19	0.18	
5	4-*t*-$C_4H_9C_6H_4OH$	5	4.32	0.25		27	HNCS	8	5.70	0.04	
6	4-$CH_3C_6H_4OH$	6	4.47	0.26		28	$Ga(CH_3)_3$	3	13.83	0.40	
7	C_6H_5OH	32	4.54	0.30		29	$In(CH_3)_3$	2	13.19	0.37	
8	4-FC_6H_4OH	10	4.54	0.30		30	$BF_3(g)$	4	12.19	0.81	
9	4-ClC_6H_4OH	5	4.60	0.33		31	$[Ni(TFACCAM)_2)]_2$	8	3.26	0.51	−0.16
10	3-FC_6H_4OH	13	4.69	0.35		32	$[Rh(COD)Cl]_2$	7	4.85	1.07	5.78
11	3-$CF_3C_6H_4OH$	18	4.80	0.36		33	$[Pd(\pi\text{-Ally})Cl]_2$	4	3.2	1.0	4.1
12	$(CH_3)_3COH$	3	2.09	0.26		34	$Zn[N(SiMe_3)_2]_2$	5	5.49	0.91	
13	CF_3CH_2OH	16	4.13	0.32		35	$Cd[N(SiMe_3)_2]_2$	5	4.99	0.68	
14	$(CF_3)_2CHOH$	17	5.77	0.37	0.16	36	MoPFB	5	6.29	0.19	
15	C_4H_4NH	5	2.75	0.20		37	MeCoDMG	6	9.58	1.19	6.15
16	$B(CH_3)_3$	6	5.79	1.57		38	CoPPIXDME	4	4.63	0.44	
17	$Al(CH_3)_3$	18	17.32	0.94		39	$Rh_2(CO)_4Cl_2$	6	9.23	1.71	11.19
18	$Al(C_2H_5)_3$	4	13.88	1.41		40	ZnTPP	4	5.43	0.45	
19	$Ga(C_2H_5)_3$	5	12.53	0.19		41	H_2O	9	2.61	0.26	
20	$(CH_3)_3SnCl$	9	5.74	0.04		42	$C_8H_{17}OH$	5	1.70	0.36	
21	SO_2	5	1.11	0.74		43	$(CF_3)_3COH$	8	6.12	0.64	0.87
22	$Cu(HFAcAc)_2$	9	3.64	1.30							

Frequency Shift Acid Parameters

no.	acid	no. of shifts	E_A*	C_A*	W	no.	acid	no. of shifts	E_A*	C_A*	W
6	4-$CH_3C_6H_4OH$	6	337	38.1	224	13	CF_3CH_2OH	12	300	33.8	193
7	C_6H_5OH	21	334	38.1	205	14	$(CF_3)_2CHOH$	9	355	38.7	142
8	4-FC_6H_4OH	13	403	46.9	306	15	C_4H_4NH	10	176	19.6	110
9	4-ClC_6H_4OH	9	343	36.3	183	41	H_2O	9	183	16.2	57.8
10	3-FC_6H_4OH	7	368	39.4	211	44	4-BrC_6H_5OH	3	286	27.4	76.2
11	3-$CF_3C_6H_4OH$	19	378	42.4	220	45	CH_3OH	13	254	23.7	207
12	$(CH_3)_3COH$	14	175	21.2	124						

Base Parameters

no.	base[b]	no. of enthalpies	no. of shifts[c]	E_B	C_B	no.	base[b]	no. of enthalpies	no. of shifts[c]	E_B	C_B
1	C_5H_5N	30 (H)	11	1.30	6.69	25	$(CH_3)_2S$	6 (H)	2	0.57	7.17
2	NH_3	5 (H)		1.48	3.32	26	$(C_2H_5)_2S$	13 (H)	10	0.55	7.40
3	CH_3NH_2	5 (H)		1.50	5.63	27	$(CH_2)_3S$	4 (H)	2	0.57	6.49
4	$(CH_3)_2NH$	4 (H)		1.33	8.47	28	$(CH_2)_4S$	20 (H)	10	0.58	7.70
5	$(CH_3)_3N$	7 (H)		1.19	11.20	29	$(CH_2)_5S$	3 (H)	2	0.59	7.20
6	$(C_2H_5)NH_2$	3 (H)		1.51	5.91	30	C_5H_5NO	2 (C)		1.40	4.40
7	$(C_2H_5)_2NH$	2 (H)		1.11	8.59	31	4-$CH_3C_5H_4NO$	5 (C)		1.44	4.85
8	$(C_2H_5)_3N$	11 (H)	2	1.29	10.83	32	4-$CH_3OC_5H_4NO$	2 (C)		1.50	5.70
9	CH_3CN	13 (C)	8	0.90	1.34	33	$(CH_3)_3P$	7 (C)		1.11	6.51
10	$ClCH_2CN$	6 (C)	2	0.87	0.63	34	C_6H_6	4 (C or H)		0.40	0.85
11	$(CH_3)_2NCN$	4 (C)	2	1.06	1.74	35	$HC(C_2H_4)_3N$	7 (H)		1.14	12.71
12	$HC(O)N(CH_3)_2$	8 (C)	6	1.24	2.47	36	$C_6H_{10}O$	5 (C)		0.96	4.04
13	$CH_3C(O)N(CH_3)_2$	18 (C)	13	1.32[d]	2.48	37	$(CH_3)_2Se$	3 (H)		0.49	8.01
14	$CH_3C(O)OC_2H_5$	16 (C)	11	0.92	1.86	38	$C_9H_{18}NO$	6 (H)		1.08	6.05
15	$CH_3C(O)OCH_3$	7 (C)	2	0.92	1.79	39	$[(CH_3)_2N]_3PO$	8 (C)	6	1.60	2.87
16	$CH_3C(O)CH_3$	9 (C)		1.01	2.38	40	$C_2H_5C(CH_2O)_3P$	3 (H)		0.73	6.47
17	$(C_2H_5)_2O$	14 (C)	10	1.08	3.08	41	$(CH_3)_2O$	3 (H)		1.08	2.92
18	$(C_3H_7)_2O$	3 (C)	1	1.16	3.14	42	4-$CH_3C_5H_4N$	9 (C)	1	1.30	7.42
19	$(C_4H_9)_2O$	8 (C)	6	1.13	3.15	43	$(C_2H_5)_3PO_4$	2 (C)	3	1.37	1.84
20	$(CH_2)_4O_2$	6 (C)	7	1.07	2.43	44	$C_5H_{11}N$	6 (C)		1.28	9.00
21	$(CH_2)_4O$	14 (C)	7	1.06	4.12	45	CH_3-Im	7 (C)		1.12	9.30
22	$(CH_2)_5O$	4 (C)	3	1.07	3.81	46	3-$CH_3C_5H_4N$	1 (C)	1	1.29	7.04
23	$(CH_3)_2SO$	18 (C)	11	1.36	2.78	47	3-ClC_5H_4N	2 (C)	2	1.20	5.32
24	$(CH_2)_4SO$	4 (C)	1	1.40	3.10	48	DOE	3 (C)	3	1.10	3.68

[a] *The parameters in this table must not be used in combination with any previously reported parameters.* [b] The numbers associated with the symbols are the same as the ones that are associated with the names. Acids: (1) iodine; (2) iodine bromide; (3) iodine chloride; (4) thiophenol; (5) 4-*tert*-butylphenol; (6) 4-methylphenol; (7) phenol; (8) 4-fluorophenol; (9) 4-chlorophenol; (10) 3-fluorophenol; (11) 3-(trifluoromethyl)phenol; (12) *tert*-butyl alcohol; (13) trifluoroethanol; (14) hexafluoroisopropyl alcohol; (15) pyrrole; (16) trimethylboron; (17) trimethylaluminum; (18) triethylaluminum; (19) triethylgallium; (20) trimethyltin chloride; (21) sulfur dioxide; (22) bis(hexafluoroacetylacetonato)copper(II); (23) antimony pentachloride; (24) chloroform; (25) 1-hydroperfluoroheptane; (26) isocyanic acid; (27) isothiocyanic acid; (28) trimethylgallium; (29) trimethylindium; (30) boron trifluoride (g); (31) bis(3-trifluoroacetyl-d-camphorate)nickel(II) dimer; (32) (1,5-cyclooctadiene)rhodium(II) chloride dimer; (33) (π-methylallyl)palladium(II) chloride dimer; (34) bis(bis(trimethylsilyl)amido)zinc(II); (35) bis(bis(trimethylsilyl)amido)cadmium(II); (36) molybdenum(II) perfluorobutyrate; (37) methylcobaloxime; (38) cobalt(II) protoporphyrin IX dimethyl ester; (39) bis(μ-chloro)tetracarbonyldirhodium(I); (40) zinc tetraphenylporphyrin; (41) water; (42) *n*-octanol; (43) perfluoro-*tert*-butyl alcohol; (44) 4-bromophenol; (45) methanol. Bases: (1) pyridine; (2) ammonia; (3) methylamine; (4) dimethylamine; (5) trimethylamine; (6) ethylamine; (7) diethylamine; (8) triethylamine; (9) acetonitrile; (10) chloroacetonitrile; (11) dimethylcyanamide; (12) dimethylformamide; (13) dimethylacetamide; (14) ethyl acetate; (15) methyl acetate; (16) acetone; (17) diethyl ether; (18) isopropyl ether; (19) *n*-butyl ether; (20) dioxane; (21) tetrahydrofuran; (22) tetrahydropyran; (23) dimethyl

Table I[a] (Footnotes Continued)

sulfoxide; (24) tetramethylene sulfoxide; (25) dimethyl sulfide; (26) diethyl sulfide; (27) trimethylene sulfide; (28) tetrahydrothiophene; (29) pentamethylene sulfide; (30) pyridine *N*-oxide; (31) 4-methylpyridine *N*-oxide; (32) 4-methoxypyridine *N*-oxide; (33) trimethylphosphine; (34) benzene; (35) quinuclidene; (36) oxabicyclo[2.2.1]heptane; (37) dimethyl selenide; (38) 2,2,6,6-tetramethylpyridine *N*-oxyl; (39) hexamethylphosphoramide; (40) 1-phospha-4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane; (41) dimethyl ether; (42) 4-methylpyridine; (43) triethyl phosphate; (44) piperidine; (45) *N*-methylimidazole; (46) 3-methylpyridine; (47) 3-chloropyridine; (48) Di-*n*-octyl ether. [c] Number of enthalpies and frequency shifts used to determine the specified acid or base. Any parameters determined from four or fewer data points should be considered tentative. The solvent recommended for obtaining data for comparison is indicated in parentheses; H stands for cyclohexane or gas phase and C represents carbon tetrachloride or gas phase. [d] Parameter is a standard.

Table II

A. E_A and C_A Parameters for Substituted Phenols

X	σ^a	E_A(measd)[b]	E_A(calcd)[c]	C_A(measd)[b]	C_A(calcd)[c]
4-C(CH_3)$_3$	−0.15	4.32	4.46	0.250	0.280
4-CH_3	−0.14	4.47	4.47	0.263	0.282
H	0	4.54	4.54	0.302	0.302
4-F	0.15	4.54	4.62	0.301	0.324
4-Cl	0.24	4.60	4.66	0.331	0.337
3-F	0.34	4.70	4.71	0.353	0.351
3-CF_3	0.46	4.80	4.78	0.362	0.369

B. E_B and C_B Parameters for Substituted Pyridines

X	σ^a	E_B(measd)[b]	E_B(calcd)[d]	C_B(measd)[b]	C_B(calcd)[d]
4-CH_3	−0.14	1.30	1.33	7.42	7.24
3-CH_3[e]	−0.06	1.29	1.31	7.04	6.93
H	0	1.30	1.30	6.69	6.69
3-Cl[e]	0.37	1.20	1.22	5.32	5.23

[a] Reference 11b. Statistical σ constants are employed. [b] Data used to determine *E* and *C* are given in the supplementary material. [c] Calculated from eq 7 and 8 by using substituent constants from ref 11. The standard deviation is 0.14 for E_A and 0.033 for C_A. [d] Calculated from eq 9 and 10 using substituent constants from ref 11. The standard deviation is 0.02 for E_B and 0.12 for C_B. [e] Tentative values from limited data.

Table III. Substituted Phenol and *N,N*-Dimethylacetamide $\Delta\nu_{OH}$ Correlation

substituent or phenol	E_A[a]	C_A[a]	$\Delta\nu_{OH}$(calcd),[b] cm^{-1}	$\Delta\nu_{OH}$(measd),[c] cm^{-1}
4-C(CH_3)$_3$	4.46	0.280	323	320
4-CH_3[d]	4.47	0.282	325	327
4-OCH_3	4.47	0.284	326	328
3-N(CH_3)$_2$	4.49	0.287	329	336
3-CH_3	4.51	0.294	334	330
H[d]	4.54	0.302	341	341
4-F[d]	4.62	0.324	358	357
3-OCH_3	4.59	0.317	353	341
4-Cl[d]	4.66	0.337	369	377
4-Br[d]	4.67	0.340	371	369
3-F[d]	4.71	0.351	380	384
3-Cl	4.73	0.355	383	385
3-Br	4.73	0.355	383	384
3-CF_3[d]	4.78	0.369	394	391
3-CN	4.86	0.392	412	410
4-CN	4.91	0.405	423	432
3-NO_2	4.91	0.405	423	418
4-NO_2	4.95	0.420	434	431

[a] Calculated from eq 7 and 8 by using substituent constants from ref 11. Statistical σ values are employed. [b] Frequency shifts calculated from eq 11. [c] Measured frequency shifts from uncomplexed phenol in CCl_4 at 298 K from ref 12. Values estimated to be accurate to 5 cm^{-1}. [d] Used to calculate eq 11.

Table IV. Substituted Pyridine and Methanol $\Delta\nu_{OH}$ Correlation

substituent on pyridine[a]	E_B[b]	C_B[b]	$\Delta\nu_{OH}$(calcd),[c] cm^{-1}	$\Delta\nu_{OH}$(measd),[d] cm^{-1}
4-C(CH_3)$_3$	1.33	7.28	303	306
4-CH_3	1.33	7.24	302	294
4-OCH_3	1.32	7.17	298	312
3-CH_3	1.31	6.93	290	289
H	1.30	6.69	282	286
4-C_6H_5	1.29	6.49	274	294
3-C_6H_5	1.29	6.49	274	287
3-OCH_3	1.28	6.29	267	289
3-I	1.22	5.35	230	244
3-Cl	1.22	5.23	227	225
3-Br	1.22	5.23	227	241
3-CF_3	1.20	4.88	213	227
4-CF_3	1.18	4.60	202	228
3-CN	1.16	4.24	188	199*
4-CN	1.14	3.89	175	211*

[a] Only those substituents that are not expected to undergo independent hydrogen-bonding interactions with methanol are included. 4-(Dimethylamino)pyridine, for instance, may act as a donor through both the aromatic and amine nitrogen lone pairs and is not included in the analysis. [b] Calculated from eq 9 and 10 by using substituent constants from ref 11. Statistical values used in all instances except 3-C_6H_5 (pK_A). [c] Frequency shifts calculated from eq 12. [d] Measured frequency shifts from uncomplexed methanol in CCl_4 at 298 K from ref 14. $\Delta\nu_{OH}$ values are estimated to be accurate to 5 cm^{-1} except for those indicated by an asterisk, which are less accurately known.

Table V. Cobalt–Carbon Bond Thermodynamic Data (kcal mol^{-1})

B	$-\Delta H^A$(measd)[a]	$-\Delta H^A$(calcd)[b]
4-$NH_2C_5H_5N$	21.2	20.8
4-$CH_3C_5H_5N$	20.1	20.3
C_5H_5N	19.5	19.9
4-CNC_5H_5N	17.9	17.7

[a] The enthalpy is defined by eq 13, and the values are reported in ref 15a. The reported experimental error is ±0.5 kcal mol^{-1}. [b] Calculated from the equation $-\Delta H^A = 4.27E_B + 0.54C_B + 10.7$.

effects upon the Co–C bond dissociation energy in B_{12} coenzyme model systems, the substituted pyridines examined here are sterically undemanding with respect to the glyoximato ligand, allowing prediction of the Co–C bond dissociation energy solely upon trans-bonding considerations.

This system bears a close resemblance to the spin-pairing description of O_2 binding to cobalt(II) complexes.[17] The model predicted increased strength of cobalt–oxygen binding as the ligands attached to cobalt(II) became better donors. The same trend is seen here for spin pairing an alkyl radical to cobalt(II). Coordination of O_2 to the cobalt(II) center (an increase in formal oxidation state from 2 to 3) was shown to lead to $\Delta E_A = 2.9$ and $\Delta C_A = 0.6$. One clearly has not transferred a full electron to the methyl group, and the similarity in the ΔC_A and ΔE_A values supports our position[16] that one has not transferred nearly a full electron when O_2 binds to cobalt(II) porphyrin.

The constant *W* indicates the enthalpy ($\Delta H = W \approx 11$ kcal mol^{-1}) that would be required to cleave the cobalt–carbon bond for the system in which there is no axial base. It is important to emphasize that we have gained additional insight by treatment of the data with eq 1. There is no way to determine the cobalt–carbon bond energy in the unligated complex (the quantity corresponding to *W*) from a pK_B correlation.[15] Furthermore, there is no way to quantify a change in acidity of the cobalt center upon methylation and oxygenation without the *E* and *C* analysis. This important information can only be obtained from an *E* and *C* analysis. Finally, we have gien ample testimony to the fact that pK_B data are at best a one-parameter relationship for Lewis acids with the same *C*/*E* ratio as the *aqueous* proton.[2] Accordingly, deviations in such plots do not indicate unusual electronic effects

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[17] Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353 and references therein.

but may simply mean the two quantities should not be plotted.

The *E*, *C*, and *W* analysis of these data reveals that more bases in the *E* and *C* correlation with a wider range of *C*/*E* values should be studied to accurately characterize the alkyl-substituted bis(dimethylglyoximato)cobalt(II) system. The problem is one of solving for three unknowns with four pieces of data. Thus, the parameters we reported above for the $(DH)_2CoR$ system are not well-defined and must be considered tentative. We do know from the value reported for the 4-CN derivative that the cobalt–carbon bond dissociation energy for the complex with no base attached must be less than 18 kcal mol^{-1}. We also note that both the covalent and electrostatic properties of the ligand are important in stabilizing the cobalt–carbon bond. If these conclusions on model compounds carry over to biological systems, hydration and dehydration could play an important role in stabilizing and destabilizing the cobalt–carbon bond.

In conclusion, we would emphasize that our treatment of the $(DH)_2CoR$ system clearly shows the need for more data to accurately define the parameters for this system and leads to confidence in the prediction of ΔH^{A} when any of the 48 different types of bases incorporated into the *E* and *C* equation are coordinated as axial bases. A more accurate definition of *E*, *C*, and *W* would also permit a more quantitative comparison of the influences of O_2 and methyl radical coordination to cobalt(II) on the acidity of the resulting compound. Our above analysis of the $(DH)_2CoR$ system indicates the insight in both the interpretation and design of experiments that can be accrued if one treats data of this sort with the *E* and *C* analysis.

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Registry No. DOE, 629-82-3; MoPFB, 5163-43-9; MeCoDMG, 36609-02-6; CoPPIXDME, 14932-10-6; ZnTPP, 14074-80-7; $Cu(HFAcAc)_2$, 14781-45-4; $[Ni(TFACCAM)_2]_2$, 62081-96-3; $[Rh(COD)Cl]_2$, 12092-47-6; $[Pd(\pi\text{-Allyl})Cl]_2$, 12081-18-4; $Zn[N(SiMe_3)_2]_2$, 3999-27-7; $Cd[N(SiMe_3)_2]_2$, 3323-04-4; $Rh_2(CO)_4Cl_2$, 14523-22-9; I_2, 7553-56-2; IBr, 7789-33-5; ICl, 7790-99-0; C_6H_5SH, 108-98-5; 4-*t*-$C_4H_9C_6H_4OH$, 98-54-4; 4-$CH_3C_6H_4OH$, 106-44-5; C_6H_5OH, 108-95-2; 4-FC_6H_4OH, 371-41-5; 4-ClC_6H_4OH, 106-48-9; 3-FC_6H_4OH, 372-20-3; 3-$CF_3C_6H_4OH$, 98-17-9; $(CH_3)_3COH$, 75-65-0; CF_3CH_2OH, 75-89-8; $(CF_3)_2CHOH$, 920-66-1; C_4H_4NH, 109-97-7; $B(CH_3)_3$, 593-90-8; $Al(CH_3)_3$, 75-24-1; $Al(C_2H_5)_3$, 97-93-8; $Ga(C_2H_5)_3$, 1115-99-7; $(CH_3)_3SnCl$, 1066-45-1; SO_2, 7446-09-5; $SbCl_5$, 7647-18-9; $HCCl_3$, 67-66-3; $CF_3(CF_2)_6H$, 375-83-7; HNCO, 75-13-8; HNCS, 3129-90-6; $Ga(CH_3)_3$, 1445-79-0; $In(CH_3)_3$, 3385-78-2; BF_3, 7637-07-2; H_2O, 7732-18-5; C_8OH, 111-87-5; $(CF_3)_3COH$, 2378-02-1; 4-BrC_6H_5OH, 106-41-2; CH_3OH, 67-56-1; C_5H_5N, 110-86-1; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; $(C_2H_5)NH_2$, 75-04-7; $(C_2H_5)_2NH$, 109-89-7; $(C_2H_5)_3N$, 121-44-8; CH_3CN, 75-05-8; $ClCH_2CN$, 107-14-2; $(CH_3)_2NCN$, 1467-79-4; $HC(O)N(CH_3)_2$, 68-12-2; $CH_3C(O)N(CH_3)_2$, 127-19-5; $CH_3C(O)OC_2H_5$, 141-78-6; $CH_3C(O)OCH_3$, 79-20-9; $CH_3C(O)CH_3$, 67-64-1; $(C_2H_5)_2O$, 60-29-7; $(C_3H_7)_2O$, 111-43-3; $(C_4H_9)_2O$, 142-96-1; $(CH_2)_4O_2$, 123-91-1; $(CH_2)_4O$, 109-99-9; $(CH_2)_5O$, 142-68-7; $(CH_3)_2SO$, 67-68-5; $(CH_2)_4SO$, 1600-44-8; $(CH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2; $(CH_2)_3S$, 287-27-4; $(CH_2)_4S$, 110-01-0; $(CH_2)_5S$, 1613-51-0; C_5H_5NO, 694-59-7; 4-$CH_3C_5H_4NO$, 1003-67-4; 4-$CH_3OC_5H_4NO$, 1122-96-9; $(CH_3)_3P$, 594-09-2; C_6H_6, 71-43-2; $HC(C_2H_4)_3N$, 100-76-5; $C_6H_{10}O$, 279-49-2; $(CH_3)_2Se$, 593-79-3; $C_9H_{18}NO$, 2564-83-2; $[(CH_3)_2N]_3PO$, 680-31-9; $C_2H_5C(CH_2O)_3P$, 824-11-3; $(CH_3)_2O$, 115-10-6; 4-$CH_3C_5H_4N$, 108-89-4; $(C_2H_5)_3PO_4$, 78-40-0; $C_5H_{11}N$, 110-89-4; CH_3-Im, 616-47-7; 3-$CH_3C_5H_4N$, 108-99-6; 3-ClC_5H_4N, 626-60-8; 4-$OCH_3C_6H_4OH$, 150-76-5; 3-$N(CH_3)_2C_6H_4OH$, 99-07-0; 3-$CH_3C_6H_4OH$, 108-39-4; 3-$OCH_3C_6H_4OH$, 150-19-6; 3-ClC_6H_4OH, 108-43-0; 3-BrC_6H_4OH, 591-20-8; 3-CNC_6H_4OH, 873-62-1; 4-CNC_6H_4OH, 767-00-0; 3-$NO_2C_6H_4OH$, 554-84-7; 4-$NO_2C_6H_4OH$, 100-02-7; 4-$NH_2C_5H_4N$, 504-24-5; 4-$C(CH_3)_3C_5H_4N$, 3978-81-2; 4-$OCH_3C_5H_4N$, 620-08-6; 4-$C_6H_5C_5H_4N$, 939-23-1; 3-$C_6H_5C_5H_4N$, 1008-88-4; 3-$OCH_3C_5H_4N$, 7295-76-3; 3-IC_5H_4N, 1120-90-7; 3-BrC_5H_4N, 626-55-1; 3-$CF_3C_5H_4N$, 3796-23-4; 4-$CF_3C_5H_4N$, 3796-24-5; 3-CNC_5H_4N, 100-54-9; 4-CNC_5H_4N, 100-48-1.

Supplementary Material Available: Tables of thermodynamic and spectroscopic data for an updated *E* and *C* fit (18 pages). Ordering information is given on any current masthead page.

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Experimental and Theoretical Study of the Nascent Photoredox Behavior of the Aqueous Hexachloroplatinate(IV) Ion

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The nascent photoredox behavior of aqueous ammonium hexachloroplatinate(IV) has been studied following picosecond laser excitation at 355 nm. The observed species exhibits two absorption bands with peaks near 640 and 440 nm, which decay via a first-order rate law with a common lifetime of 210 ± 10 ps. The quasi-relativistic version of the multiple-scattering $X\alpha$ molecular orbital theory has been used to predict the absorption spectra for various possible transients for comparison to the experimental observations. The experimental and calculated information leads to the assignment of the transient as being $PtCl_5^{2-}$ of a square-pyramidal structure with elongated Pt–Cl bond lengths although the possibility exists that the species could be an electronically excited state of $PtCl_6^{2-}$.

The increased use of fast reaction techniques such as flash laser photolysis and pulse radiolysis has opened up broad new horizons to the study of the chemical and physical properties of short-lived species. In many instances, these techniques afford unique opportunities to investigate substances of unusual formal oxidation states and of less common structures; however, the evolution of our capacity to achieve faster resolution in time has been inevitably accompanied by an increase in the difficulty of identifying in a specific manner what species is being observed. This arises in part because the species becomes more closely associated with its mode of generation as one progresses to shorter time scales, and the use of alternative experimental routes to its formation (and thus to an aid in its identification) is less feasible. Consequently for studies involving ever shorter time scales, alternative means, particularly those based upon theoretical predications and interpretations as employed in this work, will assume an increasingly important role in the characterization of transitory entities.

Viewed in this context, the principal objectives of this study are twofold. First, we have used picosecond flash photolysis

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