

radical reacts with a detergent molecule before it can diffuse away to oxidize another Cu(I).

Structural similarities between aqueous micelles and globular proteins have prompted the investigation of micelle systems as possible enzyme models.<sup>1b</sup> In general, micelle-associated species are poor models for enzymes because the dynamic equilibrium between monomer and aggregate does not allow duplication of critical protein-substrate interactions. Several iron and copper metalloproteins have kinetically accessible active sites which seem to transfer electrons as if they were simple transition-metal species.<sup>8b</sup> In these cases, where there appears to be no unique polypeptide contribution to the redox event, a metal-micelle complex may well mimic some of the features of the protein. Although we must exercise caution in drawing parallels between micelle and protein systems, the similarity in our aqueous and detergent rate data support Gray's arguments that metalloproteins with kinetically accessible sites should transfer electrons like simple inorganic complexes.<sup>8b</sup>

Studies with charged oxidants now in progress in our lab show, like this work, that aqueous and detergent rate constants usually agree within a factor of 10. This suggests that the metal center in the micelle is kinetically accessible and there is only a modest effect arising from association with amphipathic molecules.

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**Registry No.** Cu(phen)<sub>2</sub><sup>+</sup>, 17378-82-4; H<sub>2</sub>O<sub>2</sub>, 7722-84-1; Cu(phen)<sub>2</sub>HSO<sub>4</sub>, 73697-83-3.

**Supplementary Material Available:** A table, giving experimental kinetic data (3 pages). Ordering information is given on any current masthead page.

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## Parametric Correlation of Formation Constants in Aqueous Solution. 2. Ligands with Large Donor Atoms

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The equation  $\log K_1 = C_A^{aq}C_B^{aq} + E_A^{aq}E_B^{aq} - D_A D_B$  is used to correlate the formation constants in water of 266 different complexes involving 31 different Lewis acids with 16 different unidentate bases. The  $C$  and  $E$  parameters of each acid  $A$  and base  $B$  are identified with their tendency to undergo ionic or covalent bonding. The  $D$  parameters are identified with desolvation effects, brought about by both steric hindrance to solvation and also alteration of the strength of solvation at specific sites. The latter effect is envisaged as operating through an alteration of the tendency of the acid to undergo ionic bonding by attachment of very covalent donor atoms, thereby weakening the bonds to the remaining coordinated water molecules. Correlations of the  $C_B^{aq}$  parameters with the structural trans effect on infrared stretching frequencies and coupling constants in the NMR spectra are used to support the steric interpretation of the  $D$  parameters, while analyses of gas-phase proton basicities are used to support the specific solvation interpretation. The hardness of the methyl carbonium ion in water is estimated.

In the first paper in this series<sup>1</sup> it was shown that the formation constants of the fluoride, hydroxide, and ammonia complexes of Lewis acids in aqueous solution could be correlated by eq 1. This equation is similar to that developed

$$\log K_1 = E_A^{aq}E_B^{aq} + C_A^{aq}C_B^{aq} \quad (1)$$

by Drago and co-workers<sup>2</sup> for the correlation of heats of adduct formation in solvents of low dielectric constant.  $E$  and  $C$  represent the tendency toward ionic and covalent bonding of Lewis acid  $A$  and base  $B$ . We have used  $E^{aq}$  and  $C^{aq}$  to avoid confusion with Drago's  $E$  and  $C$  parameters, which are not interchangeable with our own.

It was shown<sup>1</sup> that, for ligands with second- or third-row donor atoms, eq 1 was incapable of adequate correlation, and the deviations from the predictions of eq 1 were interpreted as being caused by steric hindrance to solvation. In this paper we consider this aspect further and discuss means of modifying eq 1 so as to predict correctly the formation constants of all unidentate ligands.

### LFER Diagrams

There is a distinct pattern in the behavior of formation constants that has led, for example, to the classification of

Ahrland, Chatt, and Davies<sup>3</sup> into a- and b-type metal ions and Pearson's classification into hard and soft acids and bases.<sup>4</sup> At the same time, this pattern has led to many attempts at numerical correlation using four-parameter equations similar to eq 1, as in the pioneering work of Edwards.<sup>5</sup> This pattern can be illustrated conveniently in the LFER diagrams that we have developed.<sup>1,6</sup> In Figures 1-3 of the first paper in this series<sup>1</sup> we showed the LFER diagrams of  $\log K_1$  for Ag<sup>I</sup>, Bi<sup>III</sup>, and Fe<sup>III</sup> plotted against  $\log K_1$  for Hg<sup>II</sup> as a standard reference acid. In Figure 1 here is shown the LFER diagram for Cd<sup>II</sup>. It is typical of such diagrams in that the relative positions of the ligands on the diagram are what we should expect if our standard reference acid Hg<sup>II</sup> has a greater tendency to covalent bonding, or is softer, than Cd<sup>II</sup>. If all LFER diagrams were as "well-behaved" as Figure 1 (it is actually not completely "well-behaved", as will be seen in the following discussion), a four-parameter equation such as eq 1 would be adequate for the correlation of formation constants of all unidentate ligands. The problem is illustrated by a

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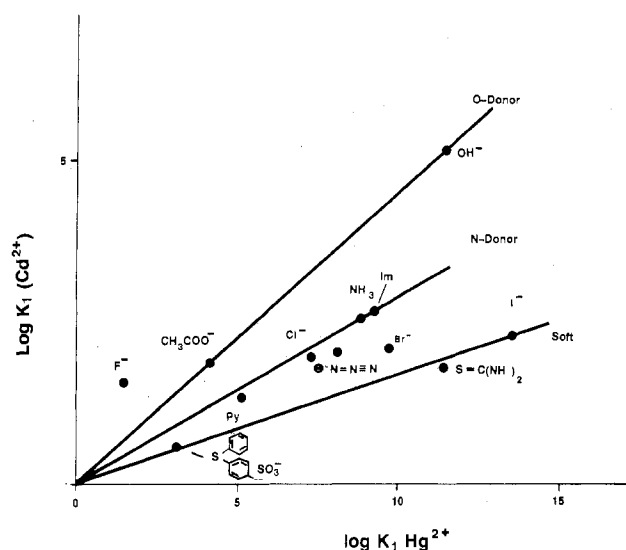


Figure 1. LFER diagram for Cd<sup>II</sup>.

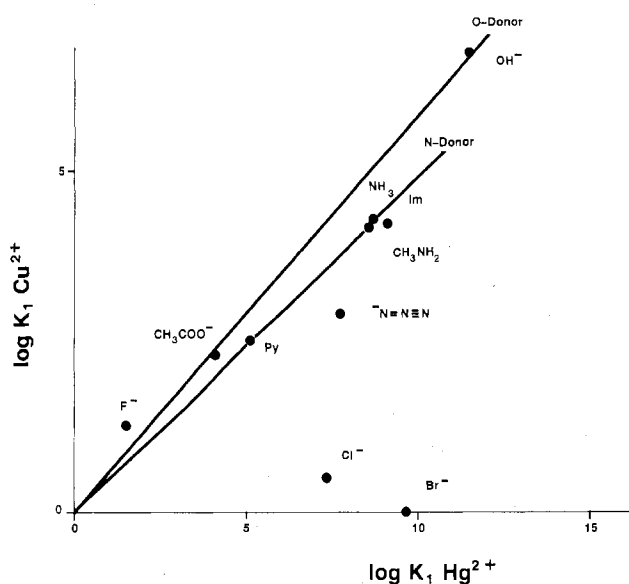


Figure 2. LFER diagram for Cu<sup>II</sup>, showing the displacement of the ligands with larger donor atoms, as compared with the diagram for Cd<sup>II</sup>.

comparison of Figure 1 with Figure 2, which shows the LFER diagram for Cu<sup>II</sup>. The Lewis acids Cu<sup>II</sup> and Cd<sup>II</sup> are fairly similar in hardness as judged by the relative positions of the points for fluoride, hydroxide, and ammonia. However, on the Cu<sup>II</sup> diagram, the points for the soft ligands appear to have been displaced markedly in a downward direction, in comparison with those on the Cd<sup>II</sup> diagram. It is this effect that equations of the form of eq 1 cannot correlate. Experimentation with eq 1 shows that, apart from the scaling effects of the absolute sizes of the  $E_A^{aq}$  and  $C_A^{aq}$  parameters, the points on the LFER diagram should behave like points on a fan that is opened or closed as the relative sizes of  $E_A^{aq}$  and  $C_A^{aq}$  are changed. No abrupt shifting of points such as those for the soft ligands on the Cu<sup>II</sup> diagram can be generated if "well-behaved" Lewis acids such as Cd<sup>II</sup> have been used in setting the  $E_B^{aq}$  and  $C_B^{aq}$  parameters. The proton shows the extreme of this displacement effect, with the positions of the fluoride point and the O- and N-donor lines being compatible with fairly soft behavior, whereas the points for the soft ligands are displaced right below the x axis to, for example,  $pK_a = -7$  for HCl. It is these displacement effects for ligands larger than F<sup>-</sup>, OH<sup>-</sup>, and NH<sub>3</sub> that must be explained and correlated.

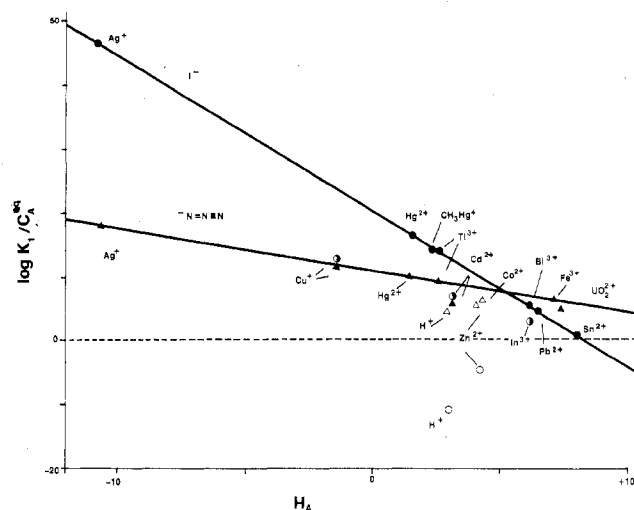


Figure 3. Plot of  $(\log K_1)/C_A^{aq}$  for iodide (O) and azide ( $\Delta$ ) ions against  $H_A$ . Filled points are for large Lewis acids with ionic radii greater than 1 Å which have small  $D$  values; half-filled ions are for acids of intermediate size that show moderate deviations from the lines drawn through the points for large acids; open points are for smaller acids that normally show large deviations.

#### Aqueous- and Gas-Phase Basicities

The organic chemist has at his disposal a considerable body of data on gas-phase proton basicities, which has provided a fairly detailed understanding of such phenomena as the reversal of relative basicity orders in passing from the gas to the aqueous phase. In this connection the work of Taft<sup>7</sup> is most useful. One finds that the reaction represented by eq 2 is  $(CH_3)_2OH^+ + (CH_3)_2S \rightleftharpoons (CH_3)_2SH^+ + (CH_3)_2O$  (2) favorable<sup>8</sup> in the gas phase by 8.0 kcal·mol<sup>-1</sup> but unfavorable in aqueous solution to the extent<sup>9</sup> of 6.1 kcal·mol<sup>-1</sup>. This reversal is attributed<sup>7</sup> to the far more favorable solvation by water of the proton attached to the base when the donor atom is oxygen instead of sulfur. This phenomenon is referred to<sup>7</sup> as specific solvation, where the solvent has specific sites of attachment to the solutes, as opposed to the nonspecific solvation provided by solvents of low dielectric constant as used by Drago and co-workers<sup>2</sup> in their studies. One must consider what contribution specific solvation might make to the breakdown of eq 1, as opposed to the contribution of steric hindrance suggested in our first paper.<sup>1</sup>

The simplest approach to acid-base reactions in aqueous solution is to regard them as the displacement of a coordinated water molecule by the incoming base. If the incoming base also has an oxygen donor atom, then the covalence of the bond to the acid, in this case the proton, is not much altered, so that its remaining bonds to other undisplaced coordinated solvent molecules are not affected. One might regard this specific solvation effect as a manifestation of *symbiosis*.<sup>10</sup> In other words, if the incoming base has a sulfur donor atom, it will increase the softness of the acid (proton) to which it attaches itself. This weakens the bonds to the remaining very hard water molecules also coordinated, which will be energetically unfavorable. It is quite possible that exactly the same mechanism may apply for a Lewis acid such as copper(II). In the first paper<sup>1</sup> we showed a graphical analysis of eq 1 in which  $(\log K_1)/C_A^{aq}$  for chloride was plotted against  $H_A$ , the

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tendency to ionic bonding, which is  $E_A^{aq}C_A^{aq}$ . The slope and intercept of the plot give  $E_B$  and  $C_B$  for the ligand. In Figure 3 of this paper we show similar plots for azide and iodide. For azide the deviations from the line drawn through the points for "well-behaved" Lewis acids are small, while they are very large for iodide. An interesting feature of the deviations is that they appear to peak at a definite  $H_A$  value, which might now be interpreted as being a critical covalence that produces unfavorable specific solvation effects. At more ionic  $H_A$  values than this the acid is not capable of responding to the potential covalence of the metal-to-ligand bond, while at more covalent  $H_A$  values the metal to solvent water bonds are already covalent, and in any case weak so that, once again, coordination to a very soft ligand does not have serious energetic consequences. One might summarize this view by saying that eq 1 fails because coordination takes place in competition with the very hard base water, and the coordination of ligands very much softer than the displaced water molecule tends to increase the softness of the Lewis acid, thus weakening its bonds to the remaining coordinated waters.

If this view is correct, what role can be assigned to steric hindrance? Here again the work of Taft<sup>11</sup> can be informative. In the gas phase, primary amines  $RNH_2$  show increased proton basicity in the order  $R = \text{methyl} < \text{ethyl} < \text{isopropyl} < \text{tert-butyl}$ . An important part of this stabilization comes<sup>11</sup> from polarizability effects, in which the positive charge of the proton is delocalized over the whole molecule. These effects are largely a function of the size of the substituent. In water this function is taken over by the highly polar solvent, and polarizability effects are completely quenched, so that it is probably not necessary to consider them further here. Inductive effects in the above series are quenched to an extent of about 50% in passing from the gas phase to water,<sup>11</sup> so that we should still expect to see the  $pK_a$  values in the above series increase according to the inductive effect order as they do in the gas phase. The  $pK_a$  values in the above series are almost invariant,<sup>12</sup> so that we must then have recourse to increasing steric hindrance to solvation along the series to account for this effect. The picture that emerges from studies of protonation equilibria is that steric hindrance to solvation can provide further modification of the observed aqueous-phase basicity orders. It is of considerable interest to note that  $\log K_1$  with  $Ag^I$  shows a strong increase along the above series with  $\log K_1 = 3.06$  (Me), 3.44 (ethyl), 3.64 (isopropyl), and 3.69 (tert-butyl).<sup>13</sup> Fitting the data for the  $pK_a$  values and  $\log K_1$  for  $Ag^I$  with these primary amines to the equation of Taft and Pavelich<sup>14</sup> for the separation of polar and steric effects indicates that the increase in  $\log K$  along the series for silver must be attributed to a smaller susceptibility to steric hindrance than is found to be the case for the proton. At this stage there are not sufficient data on gas-phase coordinating ability of acids other than the proton to allow us a detailed analysis as is possible for the proton, so that we can take our analysis no further than to say that the deviations must be primarily due to contributions from both specific solvation as well as steric hindrance effects.

#### Extension of the $E$ and $C$ Equation to Ligands with Large Donor Atoms

Pavelich and Taft<sup>14</sup> have very successfully correlated steric hindrance effects produced by various substituents using a single pair of parameters, where, as in the  $E$  and  $C$  equation,

one parameter is related to the acid and the other to the base. Although the range of our steric effects is likely to be very much larger than those considered by Pavelich and Taft,<sup>14</sup> one might hope to be able to correlate them, with perhaps a lesser degree of accuracy of prediction, with a single pair of parameters. The specific solvation effects are likely to be a function of the strength of interaction of the acid with water molecules, as well as the absolute value of the covalent interaction with the ligand, and this could possibly also be represented by a single pair of parameters. However, steric hindrance and strength of solvation are likely to be related to each other, so we have attempted to model the deviation seen in Figure 3 with a single pair of parameters,  $D_A$  and  $D_B$ , which are identified with desolvation effects brought about by the reduction of specific solvation and also steric effects, as in eq 3. The approach we used in fitting the parameters to eq 3

$$\log K_1 = E_A^{aq}E_B^{aq} + C_A^{aq}C_B^{aq} - D_A D_B \quad (3)$$

was to take the set of  $E$  and  $C$  parameters derived as described previously<sup>1</sup> by using  $\log K_1$  for fluoride, hydroxide, and ammonia, where  $D_B$  is presumed to make no contribution, and use these to derive  $E_B^{aq}$  and  $C_B^{aq}$  for ligands with large donor atoms by using only large metal ions such as  $Ag^I$ ,  $Hg^{II}$ ,  $Tl^{III}$ ,  $Pb^{II}$ , and  $Bi^{III}$ , where  $D_A$  is presumed to be zero. For the latter ligands a least-squares fit of  $(\log K_1)/C_A$  plotted against  $H_A$  gave  $E_B^{aq}$  as the slope and  $C_B$  as the intercept. The deviations from these relations exhibited by the smaller Lewis acids were then correlated by arbitrarily setting  $D_B$  as unity for the bromide ion, which gave trial values of  $D_A$  for the Lewis acids. These were used to calculate  $D_B$  values for the other ligands, after which  $D_A$  was adjusted to a best fit for all the ligands.

The result of fitting eq 1 to the available data on formation constants of Lewis acids with unidentate Lewis bases is shown in Tables I and II. The  $E_A$  and  $C_A$  values of the Lewis acids are mostly unchanged from those given in our first paper.<sup>1</sup> A change for  $Ag^I$  has been produced by adoption of  $\log K_1(OH^-) = 2.00$ , taken from Smith and Martell's critical compilation,<sup>15</sup> instead of the higher value used previously.<sup>1</sup> This has altered most of the  $E_B^{aq}$  and  $C_B^{aq}$  values reported,<sup>1</sup> since the point for  $Ag^I$  is slope determining in the plots of  $(\log K_1)/C_A$  vs.  $H_A$  used to evaluate  $E_B^{aq}$  and  $C_B^{aq}$ . Other small changes have been produced by revision of  $\log K_1(NH_3)$  estimated from correlations involving the chelate effect.<sup>16</sup> This was occasioned by the realization<sup>17</sup> that the terms in  $\lambda$  in the equations used to estimate  $\log K_1(NH_3)$  were related to the increase in the conformational potential energy,  $U$ , on complex formation, instead of having a statistical significance, as might have been expected from the way the equations were derived. In order to improve one's estimate of  $\log K_1(NH_3)$ , one should avoid having to estimate  $\lambda$ . The revised  $\log K_1(NH_3)$  values were estimated from linear relations of  $\log K_1(NH_3)$  vs.  $\log K_1(L) - \log K_1(L')$ , where  $L$  and  $L'$  are ligands that differ only in  $L$  having one oxygen donor atom of  $L'$  replaced by a nitrogen donor. The difference in  $U$  between the two ligands and their complexes with any one metal should then be minimal. Thus,  $L$  might be iminodiacetate and  $L'$  oxydiacetate or  $L$  aspartic acid and  $L'$  malic acid. On this basis,  $\log K_1(NH_3)$  for  $La^{III}$  was revised downwards from 0.7 to 0.2, and for  $Sc^{III}$  from 1.5 to 0.7. These revised estimates of  $\log K_1(NH_3)$  will be more fully discussed in a future paper.

Examination of Tables I and II shows that the predictive ability of eq 3 is acceptable. Table II contains calculated and

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Table I.  $\log K_1$  for a Variety of Unidentate Ligands, Calculated As Described in the Text and Observed<sup>a</sup>

	$H_A$	$C_A^{aq}$	$D_A$	$\log K_1$ (F <sup>-</sup> )		$\log K_1$ (OH <sup>-</sup> )		$\log K_1$ (CH <sub>3</sub> COO <sup>-</sup> )		$\log K_1$ (N=N=N)		$\log K_1$ (NH <sub>3</sub> )	
				calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
Ag <sup>+</sup>	-10.6	0.143	0.0	0.26 <sup>b</sup>	0.37	2.00	2.00	0.68	0.73	2.50	2.49	3.40	3.31
Cu <sup>+</sup>	-1.3	0.43	2.5	0.26 <sup>b</sup>		6.00	(6.00) <sup>c</sup>	2.04		4.3	(4.6)	5.93	5.98
Hg <sup>2+</sup>	1.63	0.826	0.0	1.45	1.50	11.57	11.51	3.93	4.2	7.67	7.80	8.74	8.80
CH <sub>3</sub> Hg <sup>+</sup>	2.5	0.64	0.0	1.66	1.70	9.0	9.2	3.04	3.50	5.58		6.2	7.2
Tl <sup>3+</sup>	2.66	0.96	0.0	2.55	<4	13.4	13.4	4.56		8.21	8.35	9.2	(9.1) <sup>d</sup>
Cu <sup>2+</sup>	2.68	0.466	6.00	1.27	1.37	6.52	6.66	2.22	2.25	2.80	2.86	4.41	4.27
H <sup>+</sup>	3.04	1.009	20	3.07	3.19	14.12	14.00	4.80	4.76	4.44	4.65	9.14	9.26
Cd <sup>2+</sup>	3.31	0.300	0.6	0.99	1.06	4.20	3.9	1.43	1.93	2.33	1.77	2.63	2.65
Ni <sup>2+</sup>	3.37	0.300	4.5	1.20	1.26	4.20	4.11	1.43	1.43	1.54	1.46	2.62	2.71
Co <sup>3+</sup>	3.77	0.875	7.0	3.30		12.25	12.20	4.17		5.49		7.3	7.25
Zn <sup>2+</sup>	4.26	0.312	4.0	1.43	1.26	4.37	4.60	1.48	1.57	1.55	1.36	2.41	2.18
Co <sup>2+</sup>	4.34	0.276	3.0	1.33	(1.33) <sup>e</sup>	3.87	3.90	1.43	1.46	1.46	1.32	2.13	2.10
Fe <sup>2+</sup>	5.94	0.256	2.0	1.59	1.40	3.58	(3.7) <sup>e</sup>	1.36	1.40	1.24		1.53	(1.4) <sup>f</sup>
VO <sup>2+</sup>	5.97	0.664	3.5	3.97	3.97	9.30	9.30	3.16	(3.28) <sup>f</sup>	3.55		3.91	
In <sup>3+</sup>	6.30	0.714	0.5	4.49	4.60	10.00	10.0	3.39	4.06	4.31		4.0	(4.0) <sup>d</sup>
Bi <sup>3+</sup>	6.39	0.926	0.0	5.91	5.84	12.96	12.90	4.41		5.67		5.06	(5.0) <sup>d</sup>
Pb <sup>2+</sup>	6.69	0.413	0.0	2.76	2.08	5.78	6.3	1.97	2.68	2.44		2.11	(1.6) <sup>d</sup>
Mn <sup>2+</sup>	7.09	0.223	1.0	1.64	1.40	3.12	3.41	1.25	1.40	1.06		1.07	(0.8) <sup>g</sup>
Cr <sup>3+</sup>	7.14	0.721	1.5	5.15	5.20	10.10	10.05	3.43		2.74		3.35	(3.4) <sup>d</sup>
Fe <sup>3+</sup>	7.22	0.841	1.5	6.07	6.04	11.77	11.80	4.00	4.05	4.4	4.9	3.83	(3.8) <sup>d</sup>
Ga <sup>3+</sup>	7.69	0.788	1.5	6.06	5.86	11.03	11.33	3.75		3.84		3.20	(3.0) <sup>d</sup>
U <sup>4+</sup>	7.80	0.968	3.0	7.55	7.9	13.55	13.2	4.61		4.41		3.80	(4.2) <sup>d</sup>
Sn <sup>2+</sup>	8.07	0.700	0.0	5.65	4.8	9.80	10.40	3.33	3.3	3.50		2.50	(1.4) <sup>d</sup>
UO <sub>2</sub> <sup>2+</sup>	8.40	0.589	1.0	4.95	5.0	8.25	8.20	2.81	3.05	2.1	~3	1.93	(2.0) <sup>d</sup>
Lu <sup>3+</sup>	10.07	0.454	0.0	4.57	4.5	6.36	6.6	2.16	2.51	1.66		0.66	(0.7) <sup>d</sup>
La <sup>3+</sup>	10.30	0.379	0.0	3.90	3.6	5.31	5.7	1.81	2.55	1.33		0.46	(0.2) <sup>d</sup>
Mg <sup>2+</sup>	10.46	0.178	1.5	1.86	1.82	2.50	2.58	1.13	1.27	0.30		0.32	0.26
Sc <sup>3+</sup>	10.49	0.671	0.0	7.03	7.04	9.39	9.4	3.19		2.26		0.68	(0.7) <sup>d</sup>
Al <sup>3+</sup>	10.50	0.657	2.0	6.90	7.00	9.20	9.1	3.13	2.41	1.81		0.71	(0.8) <sup>d</sup>
Y <sup>3+</sup>	10.64	0.447	0.0	4.76	4.8	6.26	6.2	2.13	2.34	1.46		0.38	(0.4) <sup>d</sup>
Ca <sup>2+</sup>	12.16	0.081	0.0	1.19	1.1	1.29	1.3	0.96	1.14	0.18		-0.05	-0.2

<sup>a</sup> At 25 °C and  $\mu = 0$ . The  $H_A$ ,  $C_A^{aq}$ , and  $D_A$  parameters are for use in eq 3 in the text. For base parameters  $E_B^{aq}$ ,  $C_B^{aq}$ , and  $D_B$ , see Table III. Estimated values are in parentheses. <sup>b</sup> Constants refer to predominantly outer-sphere complexes calculated by using the Fuoss equation. <sup>c</sup>  $\log K_1$  values for Cu<sup>I</sup> estimated from known  $\log \beta_2$  values by comparison with other Cu<sup>I</sup> complexes with both  $K_1$  and  $\beta_2$  known. <sup>d</sup>  $\log K_1$ (NH<sub>3</sub>) and  $\log K_1$ (pyridine) estimated by using chelate-effect equations. <sup>e</sup> Estimated by interpolation in "Irving-Williams" stability

observed results for the ligands with large donor atoms for which data are rather scarce except with the larger Lewis acids included. Experimentation with this equation shows that, even when data are not available, the predictions accord with chemical experience; e.g., complexes between Ni<sup>2+</sup> and thio-urea should be weak, and it is found that they do not form in aqueous solution. We have included predictions where no experimental values are reported in the hope that they can be compared with the experimental values if, and when, these become available but have not included predictions for the very large number of bromide and iodide complexes that are expected to be outer-sphere in nature. The Fuoss<sup>18</sup> equation, which was used as discussed earlier<sup>1</sup> to generate values for outer-sphere complexes, does not appear to generate satisfactory  $\log K$  values for Br<sup>-</sup> and I<sup>-</sup> complexes, which possibly relates to inappropriate choice of  $a$  values ( $a$  is the charge separation) for the complexes of these ions. We did not wish to clutter up Table I with predictions not directly related to eq 3 and so have left these out. As discussed before,<sup>1</sup> changes of coordination number must have an adverse effect on the performance of eq 3, and so we find the poor agreement between the predicted and observed  $\log K_1$  value for (diphenylphosphino)benzenesulfonic acid and cadmium in Table II:  $\log K_1$  is 0.9 and  $\log K_2$  2.48, which can only reflect a change in coordination number on adding the first ligand.

We have used<sup>1</sup>  $pK_a$ (OH<sup>-</sup>) equals 14 rather than the 15.74 that might logically be expected. This was because, in an LFER diagram such as Figure 4, 14.00 is indicated as being the correct value. Use of the 15.74 value upsets the application of eq 3 to the correlation of formation constants for RO<sup>-</sup> ligands. The rationale for the value of 14.00 might be that,

unlike other RO<sup>-</sup> ligands, the OH<sup>-</sup> ion can utilize Grotthuss conduction to react with the proton and so gains by the amount of its translational entropy in the absence of this effect, which is the  $\log 55.5$ , which was added to  $pK_w$  to obtain a  $\log K_1$  of 15.74 in the first place. Figure 4 raises the question of choice of units. The LFERs in Figure 4 pass through the origin of the diagram, which means that ligands of the same type, e.g., RO<sup>-</sup> ligands, are all of the same hardness. If we change units, or switch to constants expressed as mole fractions, since  $\Delta G$  is not a unitary function, the LFERs no longer pass through the origin, and this convenient feature is lost. It could be a real effect that not all RO<sup>-</sup> ligands are of the same hardness, but since there is no *a priori* reason for choosing one scale over another, we currently favor retention of the molarity scale because of its greater simplicity.

An important test of an equation such as eq 3 is the extent to which the parameters utilized follow intuitive ideas on the chemistry involved. In Table III the order of  $H_B$  of the ligands follows very well the order of increasing electronegativity of the donor atom, in keeping with the idea that increasing softness of the bond involves greater covalence. The  $C_B^{aq}$  values would normally in themselves be of no special chemical significance. It can be shown<sup>19</sup> that if one can reliably conclude that  $C_B^{aq}$  is zero for any ligand, and set it as such, as we have done here, then the order of increasing  $C_B^{aq}$  represents the order of increasing absolute covalent bond strength. Relative to water, it seems reasonable that the fluoride ligand that

(19) From ref 2, a new  $C_B$  value,  $C'_B$  can be obtained from  $C'_B = 1/|A|(a_{11}D_B - a_{12}E_B)$ , where  $a_{ij}$  are the parameters in the transformation matrix. If we have reliable evidence that  $C_B$  is really zero for F<sup>-</sup>, then it means that  $C_B = C'_B = 0$  for F<sup>-</sup>, which can only be true if  $a_{12}$  were zero in the above equation. If  $a_{12}$  were zero, then for all ligands  $C'_B = \text{constant} \times C_B$ . From this it follows that the order of  $C_B$  is unique and is a measure of the order of increasing absolute covalent bond strength.

log $K_1$ (pyridine)		log $K_1$ ( $\text{N}=\text{C}=\text{S}/\text{SCN}$ )		log $K_1$ ( $\text{Cl}^-$ )		log $K_1$ ( $\text{Br}^-$ )		log $K_1$ ( $\text{I}^-$ )		log $K_1$ ( $\text{S}_2\text{O}_3^{2-}$ )	
calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
2.12	2.05	4.91	4.80	3.06	3.04	4.36	4.38	6.54	6.58	8.56	8.82
3.42	3.17	4.67	(5.0)	3.55	(3.3)	4.5	(4.0)	5.7	(5.3)	10.4	10.8
4.78	5.10	9.35	9.68	7.19	7.37	9.66	9.66	13.25	13.50	17.7	(18.2) <sup>h</sup>
3.45		6.22	6.32	4.99	5.47	6.62	6.71	8.91	8.82	11.92	11.19
5.1	(4.1) <sup>d</sup>	9.52		7.32	7.72	9.70	9.7	12.99	(13.5) <sup>i</sup>	17.40	
2.34	2.50	2.23	2.33	0.5 <sup>b</sup>	0.5					2.38 <sup>b</sup>	
4.79	5.23	3.1	1.0	-4.7	(-7)	-10.4	(-9)	-21	(-11)	1.88 <sup>j</sup>	1.60
1.37	1.34	1.92	1.89	1.73	2.00	2.13	2.14	2.57	2.38	4.16	3.92
1.35	1.78	1.15	1.76	0.5 <sup>b</sup>	0.60					2.25 <sup>b</sup>	2.06
3.68		4.23		1.47	1.42					5.10	
1.20	1.0	1.12	1.33	0.5 <sup>b</sup>	0.43					2.25 <sup>b</sup>	2.35
1.05	1.19	1.06	1.35	0.5 <sup>b</sup>	0.55					2.25 <sup>b</sup>	2.05
0.67	0.6	0.83	1.31	0.5 <sup>b</sup>						2.25 <sup>b</sup>	
1.71		2.32	2.46	0.64	0.68					2.25 <sup>b</sup>	
1.67	(1.8) <sup>d</sup>	3.12	3.15	2.45	3.10	2.71	2.83	2.51	1.83	4.22	
2.10		2.36	2.21 <sup>h</sup>	3.19	3.13	3.59	3.3	4.14	4.53	5.90	
0.85	(0.9) <sup>d</sup>	0.85	0.91 <sup>h</sup>	1.42	1.59	1.61	1.83	1.55	1.92	2.55	2.42
0.39	0.14	0.67	1.23	0.5 <sup>b</sup>	0.48					2.25 <sup>b</sup>	1.95
1.24		2.56	2.77	1.24						3.5 <sup>b</sup>	
1.39	(1.9) <sup>d</sup>	2.99	3.02	1.51	1.49	0.75	0.60			3.5 <sup>b</sup>	3.3
1.03	(1.6) <sup>d</sup>	2.42	2.15	0.99	0.96					3.5 <sup>b</sup>	
1.19		2.66	2.23	1.48	1.50					4.9 <sup>b</sup>	
0.72		2.22	1.53	1.41	1.51	1.24	1.16	0.34	0.43	2.25 <sup>b</sup>	
0.46	(0.7) <sup>d</sup>	1.52	1.35	0.38	0.21					2.25 <sup>b</sup>	
-0.21	(0.2) <sup>d</sup>	0.75	1.10	0.99 <sup>b</sup>	0.6					3.5 <sup>b</sup>	
-0.24	(-0.1) <sup>d</sup>	0.56	1.02	0.99 <sup>b</sup>	0.8					3.5 <sup>b</sup>	2.99
-0.13	(-0.1) <sup>d</sup>	0.0		0.5 <sup>b</sup>						2.25 <sup>b</sup>	1.85
-0.51		0.89	1.14	0.99 <sup>b</sup>	0.99					3.5 <sup>b</sup>	
-0.51		0.47	0.42	0.99 <sup>b</sup>						3.5 <sup>b</sup>	
-0.39	(-0.1) <sup>d</sup>	0.54	0.88	0.99 <sup>b</sup>	0.80					3.5 <sup>b</sup>	
-0.16	(-0.3) <sup>d</sup>	0.0		0.5 <sup>b</sup>						2.25 <sup>b</sup>	1.98

order. <sup>f</sup> Estimated from log  $K_1$  (formate). <sup>g</sup> Estimated by other authors. <sup>h</sup> Estimated from known  $\beta_2$  by comparison with the  $\text{Cd}^{\text{II}}$  system. <sup>i</sup> Estimated from log  $\beta_4$  ( $\text{I}^-$ ) by comparison with the  $\text{Tl}^{\text{III}}\text{Cl}^-$  and  $\text{Tl}^{\text{III}}\text{Br}^-$  systems. <sup>j</sup> Bonding through O not S. <sup>k</sup> Bonding through S not N, although the latter gives a slightly higher log  $K_1$ .

Table II. log  $K_1$ , Calculated by Using Eq 3 and Observed, for Large Lewis Acids plus the Proton<sup>a</sup>

		ligand				
		$\text{S}=\text{C}(\text{NH}_2)_2$	$\text{SR}_2^b$	$(\text{C}_6\text{H}_5)_2^-$ $\text{PC}_6\text{H}_5\text{SO}_3^-$	$\text{CN}^-$	$\text{RS}^-$
Ag <sup>+</sup>	calcd	6.33	3.51	7.88	11.08	11.3
	obsd	6.46	3.33	8.15	(11.1) <sup>c</sup>	13.2
Hg <sup>2+</sup>	calcd	11.72	6.51	14.99	18.81	27.0
	obsd	11.40	6.37	14.30	18.6	(25) <sup>e</sup>
Bi <sup>3+</sup>	calcd	2.28	1.31	3.38	1.57	13.8
	obsd	2.28	1.63	3.70		13.4 <sup>f</sup>
Pb <sup>2+</sup>	calcd	0.61	0.41	1.13	0.15	5.7
	obsd	0.21	0.25			6.0
In <sup>3+</sup>	calcd	1.68	1.17	2.44	1.30	10.31
	obsd	1.98				9.8
Cd <sup>2+</sup>	calcd	2.42	1.32	3.47	4.37	8.26
	obsd	1.82	(1.40) <sup>d</sup>	0.9 <sup>g</sup>	5.48	8.0
H <sup>+</sup>	calcd	0.85	-6	-0.21	9.08	9.72
	obsd	~0.5	-6.8 <sup>h</sup>	0.15	9.15	9.8

<sup>a</sup> At 25 °C and  $\mu = 0$ . <sup>b</sup> R =  $\text{CH}_2\text{CH}_2\text{OH}$ . <sup>c</sup> Estimated from log  $\beta_2$  value by comparison with other Ag<sup>+</sup> systems. <sup>d</sup> Estimated from log  $K_1$  for (phenylthio)benzenesulfonic acid. <sup>e</sup> Estimated from  $\beta_2$  of mercaptoacetic acid. <sup>f</sup> R. D. Hancock and G. Jackson, unpublished results. <sup>g</sup> Significance of this discrepancy is discussed in the text. <sup>h</sup> Bonding through S.

replaces it to form the complex has zero covalence, especially in the light of the reasonable success obtained<sup>20</sup> by using simple electrostatic correlations for predicting log  $K_1$  for fluoride complexes. An area of research that is particularly concerned with covalence is the structural trans effect.<sup>21</sup> The consensus of opinion is that this effect is caused by increasing covalent bond strength of one ligand weakening the bond to the ligand

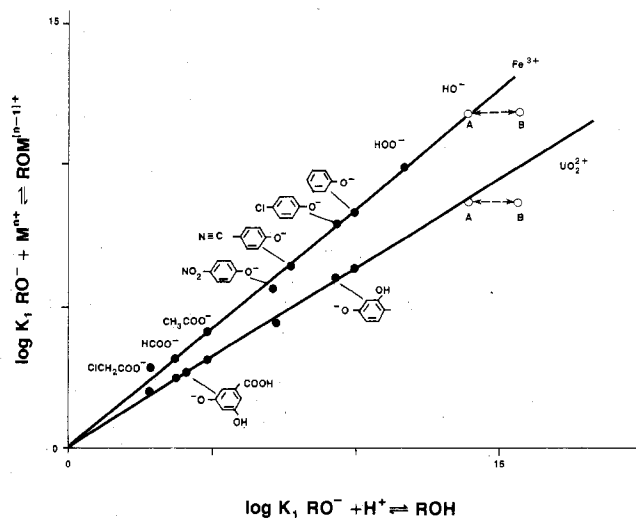


Figure 4. LFER of log  $K_1$  for  $\text{Fe}^{3+}$  or  $\text{UO}_2^{2+}$  vs. ligand  $\text{pK}_a$  for  $\text{RO}^-$ -type ligands. The points at A on each LFER represent the positions if the  $\text{pK}_a$  of the hydroxide ion is taken to be 14.00 and those at B the positions if it is taken to be 15.74.

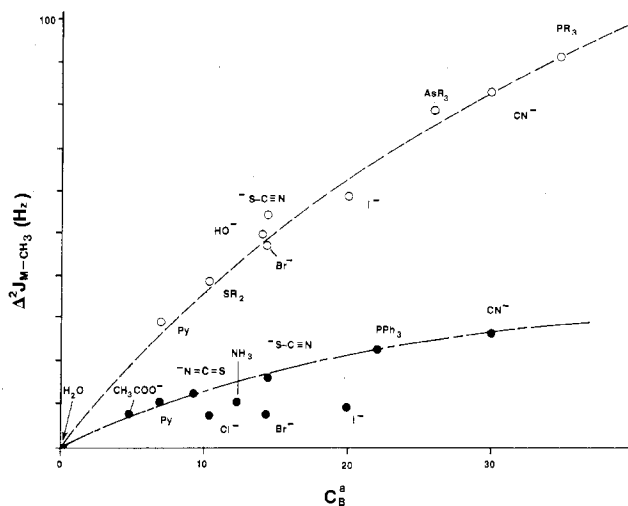
trans to it. One finds a good correlation of  $C_B^{\text{aq}}$  with parameters used to quantify the strength of the structural trans influence of ligands. Very reasonable correlations are obtained with  $C_B^{\text{aq}}$  and the infrared stretching frequencies  $\nu_{\text{M-X}}$ , where X is the ligand trans to that being varied in a series of otherwise isostructural complexes, with, for example, X in a particular series being  $\text{H}^-$ ,  $\text{Cl}^-$ ,  $\text{CH}_3^-$ , or  $\text{PR}_3$ . In Figure 5 we have reproduced the graphical correlation of  $C_B^{\text{aq}}$  with the coupling constants  ${}^2J_{\text{M-CH}_3}$  for  $\text{CH}_3\text{Hg}^{\text{II}}\text{L}$  or  $(\text{CH}_3)_3\text{Pt}^{\text{IV}}(\text{bpy})\text{L}$ , taken from ref 21. The correlations in Figure 5 and those for the infrared stretching frequencies are important in

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(21) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

**Table III.**  $H_B$ ,  $E_B^{aq}$ ,  $C_B^{aq}$ , and  $D_B$  Values for a Variety of Lewis Bases Calculated As Described in the Text<sup>a</sup>

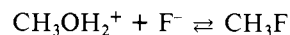
ligand	$H_B$	$E_B^{aq}$	$C_B^{aq}$	$D_B$
F <sup>-</sup>	∞	1.00	0	0
CH <sub>3</sub> COO <sup>-</sup>	0	0	4.76	0
OH <sup>-</sup>	0	0	14.00	0
N≡N=N	-0.064	-0.67	10.4	0.2
S=C=N <sup>-</sup>	-0.082	-0.76	9.3	0.2
NH <sub>3</sub>	-0.088	-1.08	12.34	0.0
C <sub>5</sub> H <sub>5</sub> N	-0.102	-0.74	7.0	0.0
Cl <sup>-</sup>	-0.100	-1.04	10.4	0.6
SO <sub>3</sub> <sup>2-</sup>	-0.107	-1.94	18.2	0.4
Br <sup>-</sup>	-0.108	-1.54	14.2	1.0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	-0.119	-3.15	26.5	1.1
I <sup>-</sup>	-0.122	-2.43	20.0	1.7
N≡C-S <sup>-</sup>	-0.128	-1.83	14.3	1.0
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S	-0.135	-1.36	10.1	0.6
PPh <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>-</sup>	-0.132	-3.03	23.0	0.7
As(C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup>	-0.135	-1.93	14.3	
(NH <sub>2</sub> ) <sub>2</sub> C=S	-0.135	-2.46	18.2	0.6
HOCH <sub>2</sub> CH <sub>2</sub> -PEt <sub>2</sub>	-0.141	-4.89	34.7	0.6
CN <sup>-</sup>	-0.148	-4.43	30.0	0.38

<sup>a</sup> The ligands are arranged in order of decreasing  $H_B$ .**Figure 5.** Plot of the change in coupling constant  $\Delta^2J_{M-CH_3}$  relative to the value found in the complex where L is water, for M = Hg in the series of complexes  $CH_3Hg^{II}L$ , or M = Pt in  $(CH_3)_3Pt^{IV}L(bpy)$ , against  $C_B^{aq}$  values derived from eq 1. Where a ligand is indicated as SR<sub>2</sub> or PR<sub>3</sub>, for example, this means that R in the complex from which J was obtained, e.g., S(CH<sub>3</sub>)<sub>2</sub> or PEt<sub>3</sub>, was slightly different from that used to derive  $C_B$ , e.g., S(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> or Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OH. PPh<sub>3</sub> indicated on the diagram refers to  $C_B^{aq}$  for Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>. J values (Hz) are from ref 21.

that they support the argument in favor of steric hindrance. In linear complexes such as those of the  $CH_3Hg^{II}L$  series, one would expect steric interactions to be at a minimum, and so no deviations for the correlations in Figure 5 are found for these complexes. For the Pt<sup>IV</sup> series, however, the octahedral coordination would be expected to promote steric hindrance, and a deviation for the larger halides is observed, being small for chloride and being at a maximum for iodide. This tendency to deviate found for the heavier halide ions is typical of such correlations. For  $\nu_{M-H}$  vs.  $C_B^{aq}$  for  $M^{II}H(PR_3)_2L$  complexes it is found to be small for M = Pd or Pt, but very large for M = Ni<sup>II</sup>, in keeping with the large  $D_A$  value for Ni<sup>II</sup>. It has been suggested<sup>21</sup> that this tendency to deviate from structural trans effect orders on the part of the halide ions, in particular

may be related to steric crowding. The  $D_B$  values in Table III give a good relationship with the van der Waals radii of the ligand donor atom, in keeping with their interpretation in terms of steric effects. On the other hand, the  $D_B$  values do not seem to tie in very well with the specific solvation idea in that cyanide, which must surely form the strongest covalent bond in Table III, does not have a very large  $D_B$  value. If anything, the  $D_B$  parameters appear to follow the nephelauxetic series.

We have attempted to extend the application of eq 1 and 3 to organic chemistry and estimated the hardness of the methyl carbonium ion in water. It is true that  $CH_3^+$  does not exist in water but neither does  $Ni^{2+}$  as such. By writing  $Ni^{2+}$ , we mean  $[Ni(H_2O)_6]^{2+}(aq)$ , and, by analogy,  $CH_3^+$  must be  $CH_3OH_2^+(aq)$ . One can then write the "formation constants" for the  $CH_3^+$  ion as follows, with water formed omitted in keeping with convention:



The free energies of the individual species were estimated<sup>22</sup> and the "formation constants" for  $CH_3^+$  with F<sup>-</sup>, OH<sup>-</sup>, NH<sub>3</sub>, and CH<sub>3</sub>COO<sup>-</sup> calculated. Fitting eq 1 to the data below gave  $H_A$  equals 0.2, corresponding to a very soft acid, with  $E_A^{aq} = 0.5$  and  $C_A^{aq} = 1.16$ , indicating very strong bonding. The calculated and observed  $\log K_1$  values were:

ligand		F <sup>-</sup>	CH <sub>3</sub> COO <sup>-</sup>	OH <sup>-</sup>	NH <sub>3</sub>
$\log K_1(CH_3^+)$	calcd	0.2	5.5	16.3	14.1
	obsd	0.5	5.6	15.7	14.9

The aqueous chemistry of  $CH_3^+$  appears to be consistent with  $D_A \approx 13$ , i.e., if one wishes to reproduce the ease of replacement of I<sup>-</sup> by Cl<sup>-</sup> or OH<sup>-</sup> in aqueous solution, and so on. It is difficult for this large  $D_A$  value to be reconciled with steric hindrance, and it agrees with the very large body of data supporting the specific solvation theory for the proton.

In conclusion, it appears that eq 3 gives a satisfactory quantitative account of formation constant data, and it is hoped that in this regard it will prove useful in providing estimates of unknown constants. The most important aspect for further work would be further investigation of the nature of the  $D$  parameters. The way in which we have derived the  $E$ ,  $C$ , and  $D$  parameters imposes restrictions on eq 3. It is quite probable that more accurate correlation might have been achieved with the same number of parameters using abstract factor analysis, as was done<sup>23</sup> for formation constants of complexes with ethylenediamine derivatives. In this approach there are no restrictions on the parameters. However, we feel that it is important to keep some physical model in mind while fitting the equation. To this end, other physical models may be imposed on eq 3 by multiplication of the acid parameters by a three-square matrix where the elements  $a_{ij}$  may be arbitrarily chosen, provided that the determinant of  $A$  is nonzero, and multiplication of the base parameters by  $A^{-1}$ , in the same way as was done<sup>2</sup> for eq 1.

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**Registry No.**  $CH_3^+$ , 14531-53-4.

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