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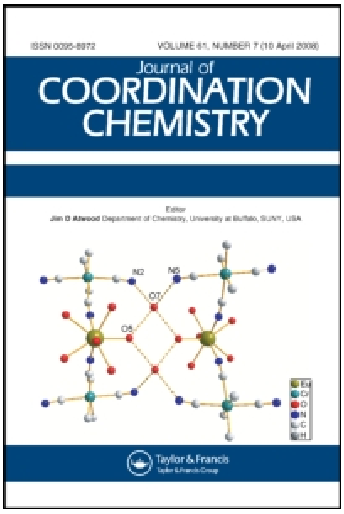

## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# STRUCTURE-REACTIVITY RELATION FOR THE COMPLEXATION OF Ni, Cd, Zn, AND Fe

Wesley R. Harris[a]
[a] Laboratory for Energy-Related Health Research, University of California, Davis, Davis, CA

**To cite this Article** Harris, Wesley R.(1983) 'STRUCTURE-REACTIVITY RELATION FOR THE COMPLEXATION OF Ni, Cd, Zn, AND Fe', Journal of Coordination Chemistry, 13: 1, 17 — 28
**To link to this Article: DOI:** 10.1080/00958978308079750
**URL:** http://dx.doi.org/10.1080/00958978308079750

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*J. Coord. Chem.*, 1983, Vol. 13, pp. 17–27
0095-8972/83/1301-0017 $18.50/0

# STRUCTURE-REACTIVITY RELATION FOR THE COMPLEXATION OF Ni, Cd, Zn, AND Fe[†]

WESLEY R. HARRIS
*Laboratory for Energy-Related Health Research, University of California, Davis, Davis, CA 95616*

*(Received August 10, 1982; in final form November 4, 1982)*

A structure-reactivity relationship is presented which predicts formation constants based solely on the structure of the organic ligand. This relationship has been evaluated using literature values of formation constants for Ni, Cd, Zn, and Fe. In most cases the root-mean-square deviation between observed and calculated log $K_{ML}$ values is less than 0.8 log units.

The relationship includes an adjustable parameter for each type of donor group coordinated to the metal ion, and the contribution of each donor atom is assumed to be independent of the other ligating groups. A separate term is included to account for the added stability due to the formation of chelate rings.

## INTRODUCTION

The introduction of synthetic organic chelating agents into the environment can have a marked effect on the translocation and bioavailability of trace metal ions.[1,2] The synthetic ligand may form complexes that are more soluble, more toxic, or more readily absorbed than the predominant naturally occurring species. Because these ligands must compete with natural complexing agents such as humic and fulvic acids, the impact of any synthetic chelating agent is clearly related to the formation constants of its metal complexes. If it is a much weaker chelator than natural ligands, then it is much less likely to cause any massive redistribution of trace elements. If it is a very strong chelator, it is likely to sequester metal ions and one must then consider the environmental toxicology of its metal complexes as well as the ligand itself. Similar considerations apply when a metal complex is released into the environment. It is necessary to consider whether or not the complex is likely to remain intact, since the mobility and toxicity of the complex is likely to be different from those of the dissociated ligand and metal ion.

It is obviously impossible to measure formation constants for the thousands of complexes that are released into the environment each year. A promising alternative is the use of structure-reactivity relationships to predict formation constants based on the structure of the organic ligand. In the past, many predictive equations have involved linear free energy relationships.[3–9] For multidentate ligands, these fall into two basic types, stability ratios and ligand basicity correlations. Stability ratios involve plotting the stability constants of the selected metal ion versus the corresponding constants of the same ligands with a reference metal ion.[3,7] The primary disadvantage of this approach is that the prediction of a stability constant for any given ligand requires that one already knows the constant for that ligand with the reference metal ion. In proton basicity correlations, it is

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[†]This work was supported by the Environmental Protection Agency and the U.S. Department of Energy. Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through Contract #68-01-6269 to Theodore Mill of SRI International, Menlo Park, CA, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

assumed that the stability constants of a series of ligands correlate with the $\sigma$ donating ability of the ligands, as measured by the sum of the ligand protonation constants.[8,9] In some cases this approach has been quite successful.[8] However, it is best suited to correlations involving similar types of ligands, for example all aliphatic polyamines or all aminocarboxylic acids. Problems have appeared when different types of ligands are included in the same correlation.[9] In addition, stability constants cannot be predicted without first measuring the ligand protonation constants.

The structure-reactivity relationship described in this paper is not a linear free energy relationship. Instead, the basic hypothesis is that the log $K_{ML}$ value can be calculated as the sum of fixed contributions for each type of donor atom, with a separate term to account for the chelate effect in multidentate ligands. The assumption is that a given type donor group, an aliphatic amine for example, will contribute a fixed increment to log $K_{ML}$ regardless of the number or identity of the other groups which may also be coordinated to the metal ion. However, since ethylenediamine complexes are almost invariably more stable than the corresponding *bis*(ammine) complexes, a separate term must be included to account for the enhanced stability that is associated with the formation of chelate rings.

With respect to possible environmental applications, the advantage of this approach for predicting log $K_{ML}$ values is that it requires no experimental data on the ligand or any of its metal complexes. Thus it can be easily applied to a large number of new compounds. Conversely, the primary limitation is that it cannot account for strong inductive effects. For example, aniline cannot be treated as a *phenyl*-substituted amine. The aromatic ring draws considerable electron density away from the nitrogen atom, and this is reflected in a drastic reduction in both the aniline protonation and metal-ligand stability constants. However, since no protonation constants enter into the structure-reactivity equation, it would predict identical log $K_{ML}$ values for aniline and ammonia.

Hancock has previously reported the functional group structure-reactivity relation shown below for aminocarboxylic acids[3,10,11], (*1*),

$$\log K_{ML} = n \cdot 1.152 \cdot \log K\,(\text{ammonia}) + m \cdot \log K\,(\text{acetate}) + (n+m-1)\log 55.5 - \Big(\sum_{i=1}^{n-1} i\Big)\lambda_N - \Big(\sum_{i=1}^{m} i\Big)\lambda_0 \qquad (1)$$

where n and m are the number of coordinated amine and carboxylate groups, respectively. In this equation the contributions for amine and carboxylate donor groups have been fixed at the log $K_{ML}$ values of ammonia and acetic acid, where the constant preceding the ammonia value is an adjustment for the increase in basicity of methylamine relative to ammonia. The chelate effect is represented as the sum of the log 55.5 term and the terms in $\lambda_N$ and $\lambda_0$ for amine and carboxylate donor groups. Log 55.5 is related to the theoretical increase in stability of a chelate ring due to the increase in the translational entropy of the system resulting from the displacement of coordinated water molecules from the initial metal aquo-ion reactant.[12] The $\lambda$ terms have no real theoretical basis, but rather are an attempt to account for a combination of factors such as strain energies, electrostatic repulsion, and increases in the $\Delta H$ for metal complexation upon going from primary to secondary to tertiary amines.[3] Hancock's equation can be expanded to include other types of donor groups, but it requires two $\lambda$ terms for each type of donor, one for five-membered chelate rings and another for six-membered rings.

This paper reports a new empirical structure-reactivity relationship which is also based on the concept of functional group additivity. The relationship has been evaluated using published formation constants for complexes of nickel(II), cadmium(II), zinc(II), and iron(III), with ligands that coordinate *via* various combinations of amine, carboxylate, pyridyl, imidazolyl, thioether, and phenolic donor groups. The root-mean-square deviations between observed and calculated log $K_{ML}$ values are $\sim$0.7–0.8 for nickel, cadmium, and zinc, with a higher value of 1.4 for ferric ion. The parameters used to construct this relationship and the values assigned to these parameters by least-squares refinement of the formation constant data are discussed in terms of fundamental principles of coordination chemistry. The results indicate that for donor groups such as pyridine and phenol, steric effects may have a very strong effect on chelate stability.

## EXPERIMENTAL

### *Formalism.*

The variables used in this structure-reactivity relationship include the types of donor groups (aliphatic amine, pyridyl, carboxylate, etc.), the number of each type of donor group, and the number of five and six membered chelate rings that are formed upon multidentate complexation. The full equation is shown below, (*2*),

$$\log K_{ML} = \sum_{i=1}^{a} n_i X_i + \left[r_5 + \sum_{i=2}^{n_5} (r_5 f_5^{\,i-1})\right]_{n_5 \neq 0} + \left[r_6 + \sum_{i=2}^{n_6} (r_6 f_6^{\,i-1})\right]_{n_6 \neq 0} \qquad (2)$$

where $X_i$ = functional group contribution of donor type i, $n_i$ = number of donor groups of type i, $n_x$ = number of x-membered chelate rings, $r_x$ = contribution of the initial x-membered chelate ring and $f_x$ = fractional contribution of successive x-membered rings.

The equation includes one adjustable parameter ($X_i$) to represent the intrinsic contribution of each type of donor atom, independently of any structural effects. The contribution of chelate rings is represented by four parameters. The initial chelate ring is represented by either $r_5$ or $r_6$. Previous strain energy calculations have indicated that the accumulation of ring strain should cause successive chelate rings to make smaller contributions to the log $K_{ML}$ value.[3] In addition, electrostatic repulsion between charged ligand donor groups may also decrease log $K_{ML}$ values for polydentate carboxylates. Thus the contribution of successive chelate rings is calculated as a fraction of the preceding ring, and the fraction is the adjustable parameter, $f_x$. For example, if $r_5 = 1$ and $f_5 = 0.9$, then a complex with four chelate rings would have a net contribution of 1.0 + 0.9 + 0.81 + 0.73 = 3.44 due to the chelate rings.

### *Data Selection.*

Tabulated stability constants[13] were initially screened to identify ligands which coordinated to each metal ion *via* some combination of common donor groups. In practice one is limited to those donor groups for which a sufficiently large data base exists, since it is preferable to have several values for each type of donor group.

Those ligands which coordinated *via* the appropriate donor groups were then screened to remove compounds which contained strongly electron donating or withdrawing substituents. The main criterion for evaluating these inductive effects was a shift of $\sim$1 log

TABLE 1
Metal ion data bases.[a]

| | Ni | Zn | Cd | Fe |
|---|---|---|---|---|
| Total number of ligands | 148 | 190 | 191 | 99 |
| Redundant values | 28 | 66 | 53 | 14 |
| Excluded on steric grounds | 13 | 16 | 40 | 27 |
| Excluded on inductive grounds | 7 | 6 | 11 | 27 |
| Outliers | 10 | 5 | 0 | 0 |
| Included in refinement | 90 | 90 | 87 | 35 |

[a]Data are taken primarily from Martell and Smith.[13]

unit or more in the ligand protonation values from those of a prototypical molecule. For example, the pKa of methylamine is 10.7, whereas benzylamine has a pK of 9.5 and phenylamine has a pKa of only 4.7. The latter two compounds would thus be excluded. Similarly, ethylenediamine has pKa's of 9.9 and 7.1, while the corresponding *N*, *N*, *N'*, *N'*-tetra(2-hydroxyethyl) derivative has pKa's of only 9.4 and 4.7, and would thus be excluded from any correlations. Thus the exclusion is not based on the mere presence of any particular group within the ligand, but rather on an evaluation of the effect of any groups on the electron density at the donor atom.

An additional screening was based on steric effects, which are somewhat more difficult to rigidly define. Ligands which appeared likely to form seven-membered chelate rings were automatically excluded. This accounts for most of the data excluded in this category. Fused ring systems, such as 1,10-phenanthroline and 1,2-diaminocyclohexamine were also eliminated. A few ligands with very bulky substituents, such as 1-butyl- and 1-phenyl-ethylenediamine-*N,N,N',N'*-tetraacetic acid and *N,N,N',N'*-tetramethylethylenediamine, were also excluded. The main criterion for this type of exclusion was usually a comparison of the log $K_{ML}$ values to those of the unsubstituted form of the ligand. Alkylated derivatives usually had log $K_{ML}$ values that covered a range of about 1 log unit. Values well outside this range were frequently excluded, especially for "common" ligand types, such as glycine and ethylenediamine; here there are a number of ligands available to define the range of normal log $K_{ML}$ values.

The final screening involved the removal of redundant values. Certain types of ligands such as glycine and ethylenediamine, have a multitude of derivatives which frequently involve very minor changes in the ligand structure. A large share of these derivatives were omitted from the refinement to avoid inadvertently "weighting" the results to fit these special types of ligands. In a few cases stability constants were excluded because they were clearly inconsistent with the bulk of the data. A portion of these constants appear to represent inaccurate experimental data. However, certain types of ligands are overrepresented among these outliers, so that this group of ligands may indicate certain structural features which are poorly described by this structure-reactivity relationship. Table 1 lists the ligand categories in each metal ion data base.[†]

*Refinement.*

Table 2 lists additional information concerning the refinement for each metal ion structure reactivity relationship. Amine and carboxylate donor group parameters were evaluated for each metal ion. Because of the limited data bases, parameters for imidazolyl,

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[†] A complete listing of the data base has been deposited with the Editor and is available on request.

TABLE 2
Refinement parameters.

| | Ni | Zn | Cd | Fe |
|---|---|---|---|---|
| Donor groups | amine<br>pyridyl<br>imidazole<br>carboxylate | amine<br>pyridyl<br>imidazole<br>carboxylate<br>thioether | amine<br>pyridyl<br>carboxylate<br>thioether | amine<br>carboxylate<br>phenol |
| Chelate ring sizes | 5 & 6 | 5 & 6 | 5 & 6 | 5 only |
| Total number of adjustable parameters | 8 | 9 | 8 | 4 |
| Number of ligands included in correlation | 90 | 99 | 86 | 35 |
| No. ligands/ No. parameters | 11.3 | 11.0 | 10.9 | 8.8 |

pyridyl, thioether, and phenolate donor groups were not considered for all the metal ions. Both five- and six-membered chelate rings were considered for Cd, Ni, and Zn, but only five-membered rings were included in the ferric ion calculation. A total of eight or nine adjustable parameters were included in the refinement of the zinc, nickel, and cadmium data, but because of the larger data bases, we were still able to include at least ten data points for each adjustable parameter.

The entire set of parameters, $X_i$, $r_x$, and $f_x$, were varied simultaneously by standard non-linear least-squares techniques to minimize the sum of the squares of the residuals between the observed and calculated values of log $K_{ML}$. Each refinement was characterized by $\sigma_y$, defined

$$\sigma_y = \left[\frac{\Sigma[\log K_{ML}(\text{obsvd}) - \log K_{ML}(\text{calcd})]^2}{\text{NO} - \text{NP}}\right]^{1/2} \qquad (3)$$

in (*3*), where NO and NP represent the number of observations and the number of adjustable parameters, respectively.

## RESULTS

Values of log $K_{ML}$ for the complexes of each of the metal ions were calculated from equation (*2*) after the set of adjustable parameters had been varied by non-linear least-squares to minimize the sum of the squares of the residuals between the observed and calculated log $K_{ML}$ values. The overall precision of each set of calculations is visually represented by plots of log $K_{ML}$ (calculated) versus log $K_{ML}$ (observed). An ideal fit would have a perfect line with a slope of 1.00 and zero y-intercept. Figures 1-4 show the actual plots for the four metal ions included in this study, along with a list of the slope, intercept, and correlation coefficient for each line. The slopes are very tightly bunched between 0.974 and 0.983, obviously very near the ideal value of 1.00. Likewise the intercepts bunched together near zero, ranging from 0.16 to 0.22. Although the slopes are consistently below 1.00 and the intercepts are consistently above zero, the deviations are so small that little significance can be attached to these trends. The scatter in the data is quite small, with correlation coefficients of $\sim$0.99 for all the plots.

TABLE 3
Functional group parameters ($X_i$).

| Donor Group | Ni | Zn | Cd | Fe |
|---|---|---|---|---|
| Amine | 3.0(2) | 2.5(2) | 2.6(1) | 4.7(7) |
| Carboxylate | 2.1(2) | 1.6(2) | 1.7(1) | 3.4(4) |
| Imidazole | 2.6(2) | 1.7(2) | | |
| Pyridyl | 2.7(2) | 1.5(2) | 1.5(2) | |
| Thioether | | -1.6(2) | -0.1(2) | |
| Phenol | | | | 9.4(4) |

TABLE 4
Chelate ring parameters.

| | Ni | Zn | Cd | Fe |
|---|---|---|---|---|
| $r_5$ | 0.8(2) | 0.9(3) | 0.09(8) | 0.4(5) |
| $f_5$ | 1.0(1) | 1.1(1) | 2.4(6) | 1.0 |
| $r_6$ | -0.3(3) | -0.2(3) | -0.9(2) | |
| $f_6$ | 0.9(5) | 1.7(16) | 1.4(2) | |
| $r_5 - r_6$ | 1.1 | 1.1 | 1.0 | |

The final values for the functional group parameters ($X_i$'s) and the chelate ring parameters ($r_x$'s and $f_x$'s) are listed in Tables 3 and 4, respectively. The errors in the $X_i$ parameters are typically 0.1 to 0.2 log units, with the exception of the ferric ion values. Errors in the ring parameters are much more variable. The $r_5$ and $f_5$ parameters are fairly well defined, with the exception of the cadmium $f_5$ value of $2.4 \pm 0.6$. However, the $r_5$ value for cadmium is only 0.09, so that large changes in $f_5$ will obviously have little impact on the overall calculation of log $K_{ML}$. The $r_6$ parameters also appear to have reasonable error limits, but the uncertainties associated with the $f_6$ parameters tend to be rather large.

The data sets for cadmium and nickel were also split into two subsets, one containing ligands with either one or zero carboxylate groups and one subset of ligands which had two or more carboxylates. The purpose was to determine whether intramolecular electrostatic repulsions between charged carboxylate groups would be reflected in a significant difference in the results for each subset. The results of these refinements are shown in Table 5. The $X_i$ values for carboxylate and amine groups do not shift by any significant amount. However, there are wide fluctuations in some of the chelate ring parameters. Both the $r_5$ and $r_6$ values of the nickel polycarboxylate subset increase by about 0.8 log units. In contrast, the $f_5$ and $f_6$ values for nickel are fairly constant. The results for cadmium are exactly reversed. The $r_5$ and $r_6$ parameters do not shift significantly between subsets, but there are large changes in the $f_5$ and $f_6$ values.

## DISCUSSION

It was intended that the functional group parameters would represent the contribution to log $K_{ML}$ of each isolated metal-ligand bonding interaction, apart from any enhanced stability due to chelate effects. If this separation of effects is achieved, then the $X_i$ value should be very similar to the log $K_{ML}$ values of corresponding monodentate ligands. For example, the $X_i$ value for amine groups should be close to the stability constant for ammonia. Thus the success of this approach can be gauged to a first approximation by the magnitude of the residuals between $X_i$ values and the appropriate stability constants.

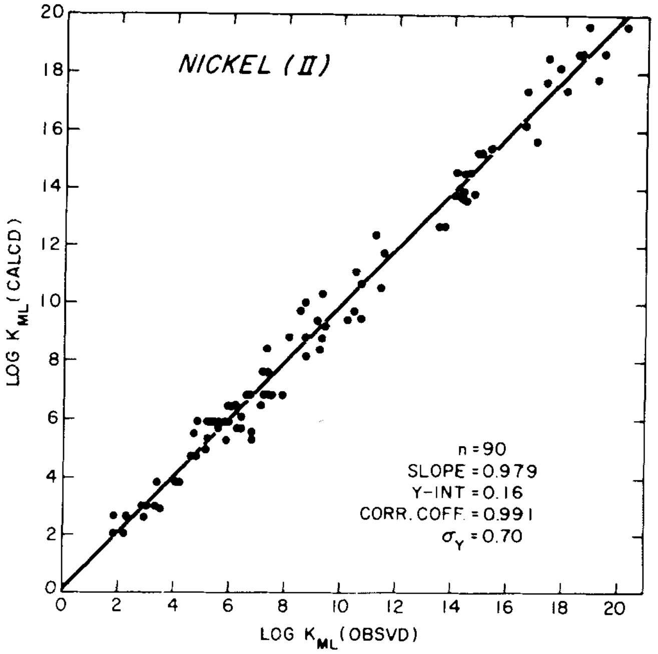

FIGURE 1 Plot of the observed log $K_{ML}$ values for $Ni^{2+}$ versus the values calculated using the structure-reactivity relationship described by equation (*2*).

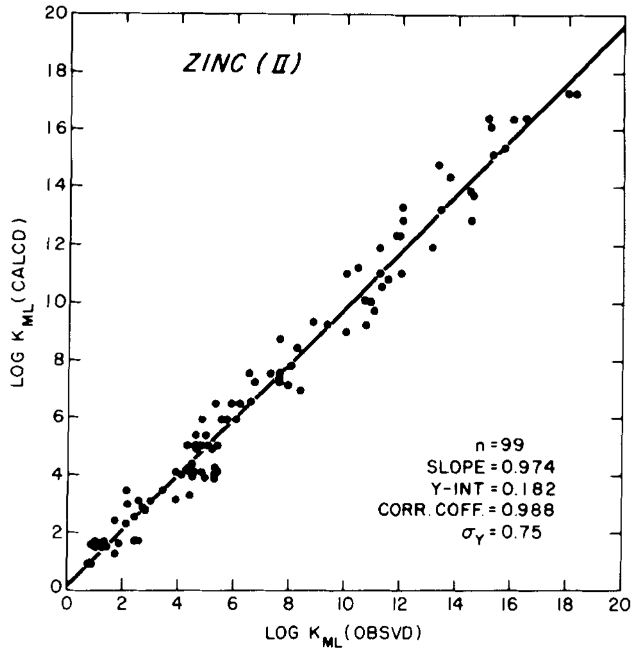

FIGURE 2 Plot of the observed log $K_{ML}$ values for $Zn^{2+}$ versus the values calculated using the structure-reactivity relationship described by equation (*2*).

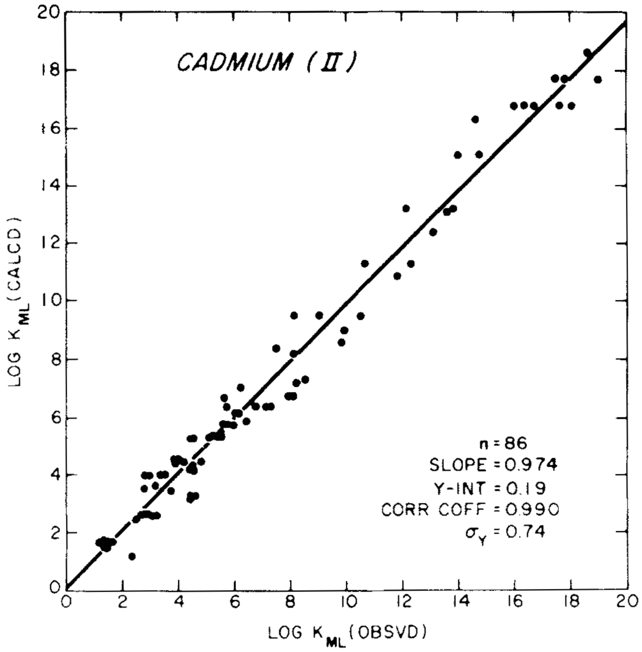

FIGURE 3 Plot of the observed log $K_{ML}$ values for $Cd^{2+}$ versus the values calculated using the structure-reactivity relationship described by equation (*2*).

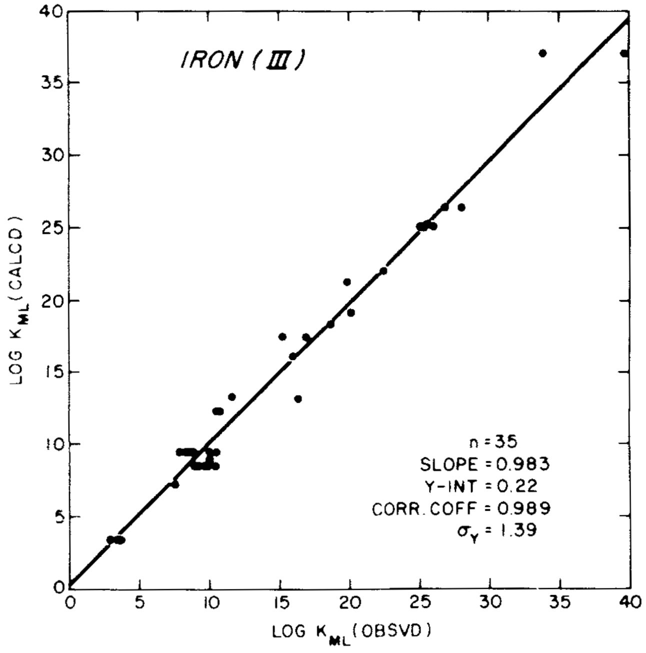

FIGURE 4 Plot of the observed log $K_{ML}$ values for $Fe^{3+}$ versus the values calculated using the structure-reactivity relationship described by equation (*2*).

TABLE 5
Refined values for nickel and cadmium data subsets.

| | Ni | | | Cd | | |
|---|---|---|---|---|---|---|
| Parameter | Set I[a] | Set II[b] | Δ | Set I[a] | Set II[b] | Δ |
| $X_i$(ammine) | 3.0 ± .2 | 2.8 ± .8 | 0.2 | 2.4 ± .2 | 2.3 ± .4 | 0.1 |
| Carboxylate | 1.9 ± .2 | 1.6 ± .7 | 0.3 | 1.6 ± .2 | 1.7 ± .3 | −0.1 |
| Imidazole | 2.6 | | | | | |
| Pyridine | 2.7 | | | 1.6 ± .3 | | |
| Thioether | | | | −0.2 ± .4 | | |
| $r_5$ | 0.9 ± .3 | 1.8 ± .1 | −0.9 | 0.5 ± .4 | 0.3 ± .3 | 0.2 |
| $f_5$ | 0.9 ± .1 | 0.9 ± .1 | 0 | 0.9 ± .2 | 1.7 ± .4 | −0.8 |
| $r_6$ | −0.2 ± .3 | 0.6 ± .9 | −0.8 | −1.4 ± .5 | −1.0 ± .5 | −0.4 |
| $f_6$ | 1.1 ± .7 | 1.3 ± 1.7 | −0.2 | 0 ± .6 | 1.3 ± .2 | −1.3 |
| $\sigma_y$ | 0.68 | 0.70 | – | 0.70 | 0.77 | – |

[a] Ligands with either one or no carboxylate donor groups. [b] Ligands with two or more carboxylate donor groups.

These differences are listed in Table 6. In general the agreement between the $X_i$'s and the modentate log $K_{ML}$ values is quite good. The log $K_{ML}$ value for ferric ion with ammonia is not known. Therefore the Δ value in Table 6 is based on the value of the log $K_{ML}$ predicted by Hancock[10] using his own structure reactivity relationship.

Despite the generally good agreement between $X_i$ and the monodentate log $K_{ML}$ values, some large deviations are observed for a few of the $X_i$ values of pyridyl, imidazolyl, and phenolic donors. It is likely that these deviations are due partly to the incomplete separation of functional group and chelate effects by the refinement. However, a common feature of the pyridyl, imidazolyl, and phenolic donors is the cyclic organic structures associated with the ligating atom. This will affect the ligand bond angles and conformational freedom, which may alter chelate stability compared with fully saturated, flexible chelate rings. If this were the case, then the added stability of complexes of this type of ligand would be associated with the $X_i$ parameter, which is related to the specific donor group, rather than with the $r_5$ parameter, which is related to all chelate rings regardless of the donor groups involved.

One of the factors that affects chelate stability constants is the strain energy that results from distorting the ligand from its ideal geometry to fit the steric requirements imposed by coordination to the metal ion.[14,15] Clearly the incorporation of a donor atom into a structure such as a pyridine ring will change not only the ideal ligand geometry, but will also alter the energy required to distort the ligand. Thus, depending on how the geometry of a partially-fused structure such as aminomethylpyridine matches the ionic radius of a particular metal ion, chelate stability may be either enhanced or decreased.

TABLE 6
Δ Values.[a]

| Donor group | Ni | Zn | Cd | Fe |
|---|---|---|---|---|
| Amine | 0.2 | 0.1 | −0.2 | 0.4 (est)[b] |
| Carboxylate | 0.3 | 0.5 | 0.1 | 0 |
| Imidazole | 0.3 | −0.8 | | |
| Pyridyl | 0.9 | 0.5 | 0.2 | |
| Phenol | | | | 1.6 |

[a] $\Delta = X_i - \log K_{ML}$ [b] Reference 10.

Strain energy calculations have been performed on the cobalt(III) complexes of a few multidentate aliphatic amines and pyridylamines.[16–18] Two aliphatic amine complexes, triethylenetetramine-*S*-prolinatocobalt(III)[18] and chlorotetraethylenepentaminecobalt (III),[17] have total strain energies of 99.2 and 75.7 kJ $mol^{-1}$, respectively. Thus the stability produced by the cobalt-nitrogen bonding interactions is partially offset by these positive strain energies. Since the separate strain energy of the prolinate ligand was not reported for the first compound, it is not possible to consider just the strain energy of the amine ligand. However, if one assumes that the strain energy associated with a chloro group of the second compound is small, then the tetraethylenepentamine value indicates a strain energy of roughly 18.8 kJ $mol^{-1}$ per chelate ring.

Strain energies have also been calculated for the mixed-ligand cobalt(III) complex of oxalate and the tetradentate ligand *N, N'*-bis(2-pyridylmethyl)-1,2-*S*-propanediamine, and these indicate that only ∿38.5 kJ $mol^{-1}$ of strain energy are associated with the pyridylamine ligand.[16] If one subtracts 18.8 kJ $mol^{-1}$ for the one aliphatic ethylenediamine chelate ring in the complex, this leaves only ∿10.0 kJ $mol^{-1}$ for each of the two aminomethylpyridine chelate rings. This decrease of about 8.8 kJ $mol^{-1}$ per ring would correspond to an increase of 1.5 log units/ring in the stability constant of the complex.

Such calculations are not intended to be quantitative, but to show that the stability of metal complexes may be markedly enhanced by decreases in the strain energy of pyridyl ligands. We feel that the large $\Delta$ values for both the nickel-pyridyl and iron-phenolate $X_i$ parameters are due to such an effect. However, one might expect a similar effect for the zinc-pyridyl $X_i$ value, since the zinc(II) ionic radius is very similar to that of nickel(II). In fact, calorimetric studies have reported[19] $\Delta H$ values for complexation of both nickel and zinc by multidentate pyridylamines which are much more negative than one observes for saturated polyamines of similar basicity. For the nickel complex this leads directly to unusually large log $K_{ML}$ values. However, in the zinc system this favorable enthalpic effect is largely offset by an unfavorable entropy term, so that the net change in log $K_{ML}$ is rather small. This could explain the smaller $\Delta$ value for zinc-pyridyl compared to the nickel value. The lower value for the cadmium-pyridyl $X_i$ value is presumably due to an increased steric strain caused by the much larger ionic radius of the cadmium ion.

Since the imidazole $\Delta$ values are not exceptionally large, it appears that not all organic ring structures have a favorable effect on chelate stability. This observation tends to argue against any major contribution to log $K_{ML}$ from the increase in entropy of complexation that one might expect due to the hindered ligand rotation within the organic ring. In fact, the zinc-imidazolyl $\Delta$ value is quite negative, indicating the imidazole ring structure may actually have a destabilizing effect on the complex. However, the data base for zinc is such that the imidazolyl $X_i$ value is strongly influenced by a high proportion of six-membered chelate rings. Since the effects of these larger rings are rather poorly described by this structure-reactivity relation, the low $X_i$ is more difficult to interpret. A second factor which complicates the fitting of the zinc data is the possibility of shifts from four-coordinate, tetrahedral geometry for smaller ligands to six-coordinate, octahedral geometry for larger ligands. Such a shift can change the ionic radius of the zinc by 0.14 Å,[20] which could affect the ligand strain energies.

Hancock has shown that ligand strain energies are also important in establishing the relative stabilities of five- and six-membered chelate rings.[14,15] Calculations on nickel(II) complexes showed a net difference of 1.1 log units in the stabilities of the two ring sizes, which matched very well with the observed differences in the actual log $K_{ML}$ values of several nickel polyamine complexes. In our treatment, this net difference between the two ring sizes should appear at $r_5$-$r_6$. Although the magnitude of both $r_5$ and $r_6$ shifts markedly for the various metal ions, the differences hold very steady at 1.1, 1.1, and

1.0 for Ni, Zn, and Cd, respectively. These values obviously agree quite well with the strain energy calculations.

The standard deviations in log $K_{ML}$ values ($\sigma_y$) are somewhat large compared to those usually reported for linear free energy relationships (LFER). However, most LFER contain only five to ten closely related ligands. We have sacrificed some precision to include as many ligands as possible in a single correlation. The errors for the Cd, Ni, and Zn systems of 0.74, 0.70 and 0.75 log units are quite reasonable. This is comparable to the range in log $K_{ML}$ values that one measures for essentially identical ligands such as glycine and dimethylglycine. Thus it is unlikely that further refinement in the structure reactivity formalism will significantly reduce the overall $\sigma_y$ term.

There are a few ligands which obviously do not behave according to the predictions of this structure-reactivity relationship. Rather than bias the overall results, we have exercised some judgement as to which ligands should be included within the data base for each metal ion. Some of the excluded data probably reflect inaccurate determinations of log $K_{ML}$. However, there are patterns among the outliers that suggest some factors for which this structure-reactivity relationship simply cannot account. Polyamines, particularly those which form a mixture of both five-and six-membered chelate rings, are greatly overrepresented among the outliers, as are propionic acid derivatives. Thus it appears that the inclusion of six-membered chelate rings is probably the most difficult feature of metal ion coordination chemistry to model effectively.

The standard error for the ferric ion refinement is much higher than that of any of the other data sets. This is partly due to the rather limited data base available for the ferric ion. The data base is limited primarily by the fact that the ferric ion does not form hydrolytically stable complexes with the regular series of polyamine ligands. In addition, the phenolic and catecholate ligands involve significant steric factors which might be considered reason to exclude such ligands from this correlation. However, phenols form very stable ferric ion complexes,[13] so we felt that it was important to include such ligands, even at the expense of a decrease in the precision of the structure reactivity relationship.

An additional problem in the evaluation of this relationship was the selection of standard conditions of temperature and ionic strength. Rigid adherence to any one set of conditions substantially reduced the available data base. Initially we attempted to alleviate this problem by correcting all values of log $K_{ML}$ to zero ionic strength. However, the standard Debye-Huckel corrections are most accurate for low ionic strengths and monovalent ions. The corrections for highly charged species such as $EDTA^{4-}$ were unreasonably large, and the correlations were consistently worse when corrected values of log $K_{ML}$ were used. Therefore, we have used log $K_{ML}$ values measured at 25° and 0.10 M ionic strength whenever possible. However, we have included values which fall within the ranges of 0 to 0.5 M ionic strength and 20 to 30°. These ranges are regrettably wide and almost certainly contribute to the scatter of the data, but none of the outliers can be ascribed to "nonstandard" conditions.

The parameters in this correlation are presented as empirical parameters with no direct theoretical definition. However, it is interesting to compare this equation to the one proposed by Hancock (equation *1*). Obviously, the log K values for ammonia and acetic acid correspond to the amine and carboxylate $X_i$ values. The 1.152 factor in Hancock's equation is to compensate for the difference in the basicity of a primary amine *versus* ammonia. The log 55.5 term has the usual significance in terms of the increase in $\Delta S$ due to the increase in translational entropy of water molecules released by chelate ring formation. The $\lambda$ term represents the favorable $\Delta H$ contribution fron ring strain and electrostatic repulsion terms.

Since the log 55.5 and the $\lambda$ terms are related only to chelate ring formation, their sum corresponds to the chelate ring term $(r_5 + \Sigma(r_5(f_5)^i))$. Since $\lambda_N$ and $\lambda_0$ differ by $\sim$0.2 log units,[3] Hancock's function essentially has two different ring contributions, one for diamines and one for amino acids. The equation used in this study treats all rings identically, regardless of the identity of the donor groups involved. The net value of log 55.5 $- \lambda$ is larger than our parameter $r_5$. However, Hancock's ring term decreases quite rapidly for successive chelate rings. In this study, since $f_5$ is consistently close to 1.0, we in effect use an average value for the chelate ring contribution with little variation between successive rings.

We are currently using the information obtained in this study to modify the proposed relationship. Possible improvements include the elimination of $r_6$ as an adjustable parameter by setting $r_6 = r_5 - 1.1$. It may also be necessary to include an electrostatic term to improve the simultaneous fit of both polyamine and amino acid ligands. Finally, because of the generally low values of $\Delta$, it may be possible to fix the $X_i$ values at the appropriate log $K_{ML}$ value, if some mechanism can be developed to account for variations in steric factors associated with the formation of chelate rings by donor atoms contained in cyclic organic ring structures.

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