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Benjamin P. Hay<sup>a</sup>; Jim R. Rustad<sup>a</sup>

<sup>a</sup> Thermodynamic and Molecular Geochemistry Group, Earth and Environmental Sciences Center, Richland, Washington

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# Why the addition of neutral oxygen donor groups promotes selectivity for larger metal ions

BENJAMIN P. HAY\* and JIM R. RUSTAD

*Thermodynamic and Molecular Geochemistry Group, Earth and Environmental Sciences Center, Pacific Northwest Laboratory, P.O. Box 999, MSIN: K6-82, Richland, Washington 99352*

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The origin of selectivity enhancement for large metal ions that occurs on the addition of neutral oxygen donors to existing ligands in such a way as to form additional five-membered chelate rings is analyzed in terms of inductive and steric effects. Molecular mechanics calculations are used to examine the degree of strain that develops in five-membered, aliphatic chelate rings of ethers and amines as a function of the size and charge of the metal ion. Although five-membered chelate rings that contain saturated neutral oxygen donors are found to exhibit an inherent steric preference for large metal ions, experimental evidence suggests that for the majority of cases where enhanced selectivity for larger metal ions has been observed after the addition of neutral oxygen donors, the selectivity enhancement is largely the result of steric and inductive changes to other donor groups in the ligand, e.g. amines, rather than the result of increasing the denticity of the ligand.

## INTRODUCTION

It has been observed that while open-chain ligands containing saturated, neutral oxygen donor atoms, i.e. ethers and alcohols, form weak complexes with metal ions, the incorporation of such donor atoms in ligands which contain other, more strongly coordinating groups can markedly affect the strength of the mixed donor complexes.<sup>1</sup> Comparisons of aqueous stability constants for pairs of ligands, **a–I** in Figure 1, have been made to examine the influence of the neutral oxygen donor groups on complex stability.<sup>1–4</sup> A general pattern emerged from these comparisons. The addition of the neutral oxygen donor groups often resulted in an increase in stability for large metal ions such as Pb(II) and Ba(II) and a decrease in stability for small metal ions such as Cu(II) and Mg(II). Where sufficient data were available, **b, d, e, g–j**, plots revealed that the change in log K on addition of the neutral oxygen donor groups was linearly

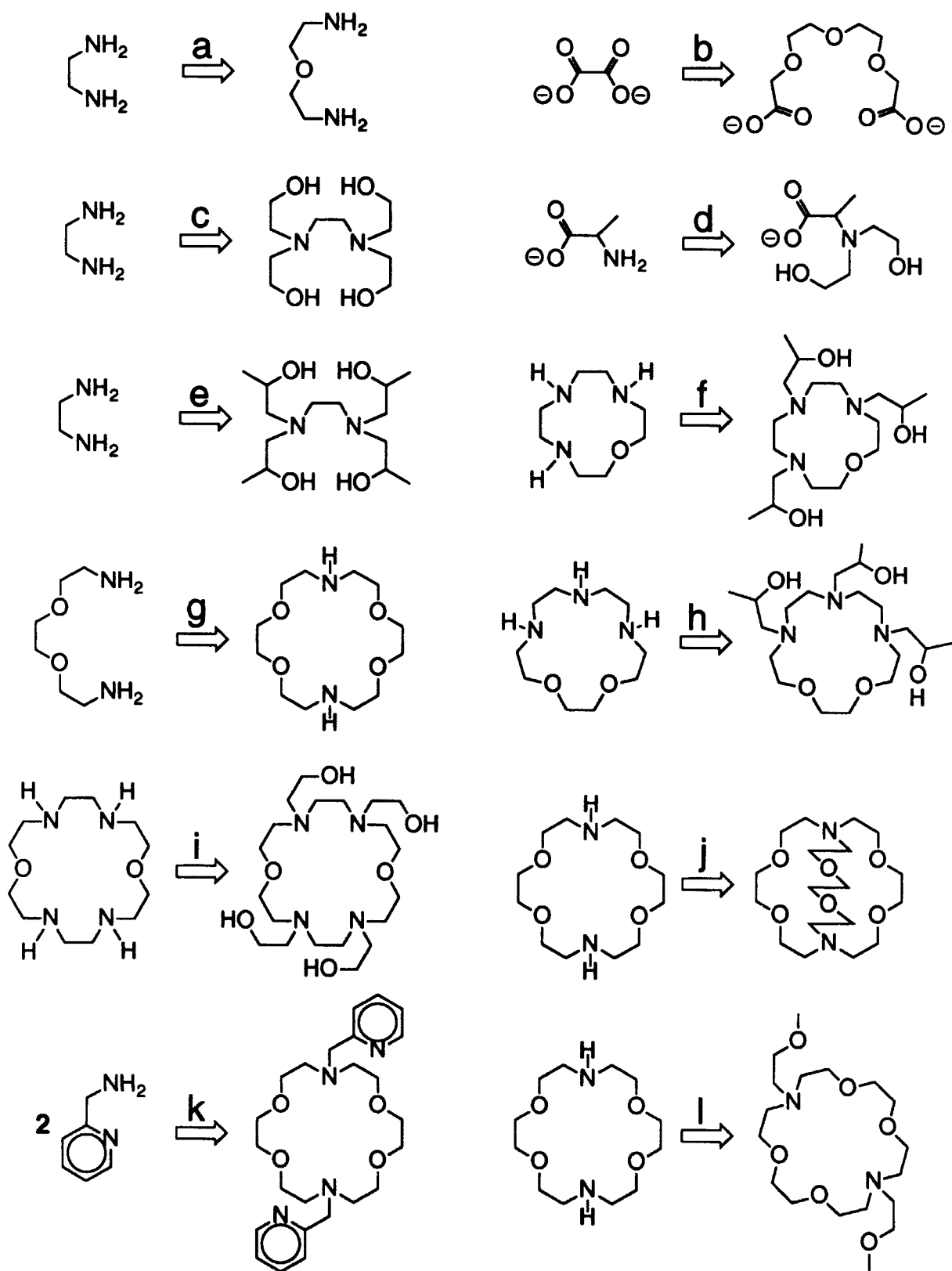
correlated with the ionic radius of the metal ion. This behavior led to the formulation of a rule for ligand design:<sup>2</sup> “Addition of groups containing neutral oxygen donor atoms to an existing ligand leads to an increase in selectivity of the ligand for large metal ions.”

The origin of metal ion selectivity associated with neutral oxygen donor addition has been discussed in terms of a balance between inductive and steric effects.<sup>1–4</sup> The relative donor strength of saturated, neutral oxygen donors increases in the order  $H_2O < ROH < ROR$ . Therefore, from an inductive point of view, one would expect all metal ions to show increased stability in aqueous solution when saturated, neutral oxygen donors are added to existing ligands. However, from a steric point of view, unfavorable steric interactions between ligands in the inner coordination sphere increases as the degree of alkylation at the donor atom increases. Initially it was argued that this steric crowding outweighs the favorable inductive effects with smaller metal ions and it was only the larger metal ions that could gain additional stabilization by complexation of the added neutral oxygen donors.<sup>1,2</sup>

Subsequently it was suggested that adverse steric effects were not limited to steric crowding.<sup>3</sup> For the ligands that were examined, Figure 1, the neutral oxygen donor groups are all added in such a way as to result in the formation of five-membered chelate rings on metal ion complexation. Analysis of chelate ring-strain in saturated nitrogen-donor ligands has shown that five-membered aliphatic chelate rings exhibit a steric preference for the complexation of large metal ions.<sup>5,6</sup> It was noted that the selectivity patterns exhibited by the ligands in Figure 1 are consistent with the existence of an analogous steric preference for five-membered aliphatic chelate rings bearing saturated neutral oxygen donors.

Metal ion size-selectivity resulting from chelate ring

\*To whom correspondence should be addressed.



**Figure 1** Examples of additions of neutral oxygen donors to existing ligands that result in enhanced selectivities for larger metal ions.<sup>1-4</sup>

size is caused by the directional bonding preferences of the donor groups. In the case of amines, there is a preference for tetrahedral geometry in the coordinated nitrogen donor. Maximum stability is achieved only when the metal ion can approach the amine in the direction of the nitrogen lone pair. In the case of neutral oxygen donors, recent studies have established that there is also a significant directional bonding preference for the ether oxygen donor.<sup>7,8</sup> However, unlike the tetrahedral preference of the saturated nitrogen donor, ether oxygens prefer a trigonal planar geometry on coordination to a metal ion. As a consequence of the different donor atom geometry, it was shown that the metal ion size-selectivity exhibited by five-membered chelate rings depends on the geometric preference of the donor atoms.<sup>8</sup>

In this paper we further examine the metal size preferences of five-membered aliphatic chelate rings in terms of the donor atom type. The results of molecular mechanics calculations are presented to provide a quantitative comparison of the steric strain generated in five-membered chelate rings of ethers and amines on coordination of different sized metal ions. The selectivity for large metal ions associated with the addition of neutral oxygen atoms to the ligands shown in Figure 1 is discussed in the light of these findings.

## RESULTS

When coordinated to a metal ion, the amine nitrogen prefers a tetrahedral geometry while the ether oxygen prefers a trigonal planar geometry.<sup>8</sup> When these donor groups are incorporated in five-membered aliphatic chelate rings, the structural preferences within the backbone of the ligand act to prevent these donor groups from achieving their preferred geometries during complexation. This is illustrated in Figure 2 which shows the MM3 structures for the gauche conformations of the bidentate ligands that are formed by adding either  $-N(H)CH_3$  or  $-OCH_3$  groups to the termini of a  $CH_2-CH_2$  group. In addition, a 5 Å vector has been attached to each donor atom to illustrate the preferred line of approach for a metal ion. In a ligand that was preorganized to bind a certain size metal ion, these vectors would converge at the appropriate M-L distance. It can be seen, however, these vectors do not converge at any distance for either of these ligands.

On metal ion complexation, both of these ligands will undergo some structural reorganization as they attempt to attain the preferred geometries at the donor atoms at the expense of a loss of preferred geometry within the ligand backbone. This structural reorganization will result in the formation of steric strain within the ligand. It can be seen (Figure 2) that the approach vectors for the diether are

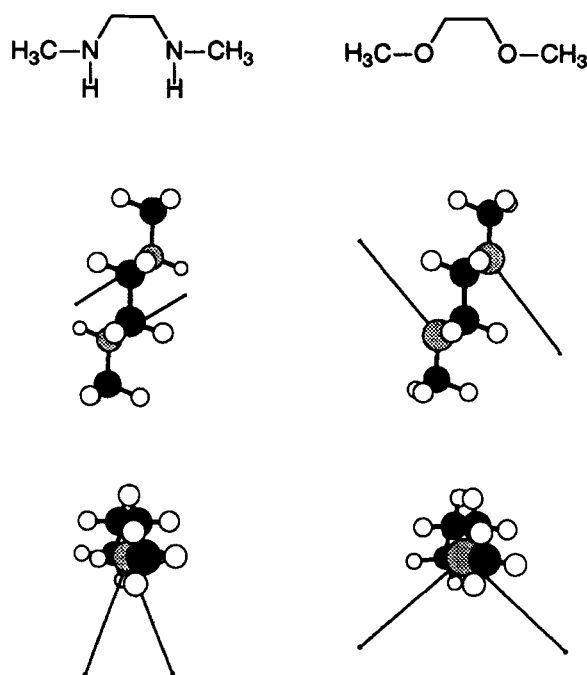


Figure 2 MM3 optimized structures for the gauche conformations of the diamine and diether. The 5 Å vector attached to each donor atom illustrates the preferred line of approach for a metal ion.

significantly more divergent than the approach vectors for the diamine. Thus, we can make the qualitative prediction that for the complexation of any given metal ion the diether will have to undergo greater structural reorganization than the diamine.

This qualitative prediction is supported by the results of molecular mechanics calculations. The increase in strain within the ligand,  $\Delta$  ligand strain, was calculated for metal ion complexes of the diamine and diether shown in Figure 2 as a function of both M-L length and charge. The calculations did not include the influence of steric crowding in the inner coordination shell because the complexes consisted of only the metal ion and a single ligand and therefore did not have a full coordination shell. In addition, the calculations did not include any metal ion stereochemical preferences. Because both steric crowding and metal ion stereochemical preferences would result in higher steric strain in the ligand, the  $\Delta$  ligand strain values obtained in these calculations represent the minimum amount of strain present in an actual complex.

Figures 3 and 4 summarize the results as plots of  $\Delta$  ligand strain versus M-L length for +1 and +2 cations, respectively. In all cases, the magnitude of  $\Delta$  ligand strain decreases as the M-L length increases. Both types of five-membered aliphatic chelate rings are similar in that they both exhibit a steric preference for large metal ions. However, the magnitude of the effect is greater in the case of the diether. For +1 cations, the  $\Delta$  ligand strain for

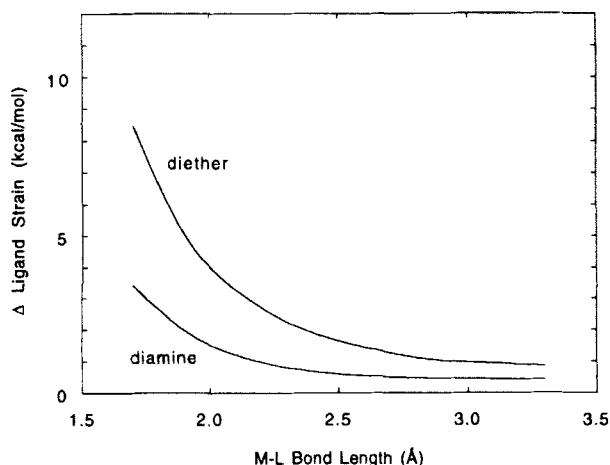


Figure 3 Plot of  $\Delta$  ligand strain versus M-L length for +1 cations.

the diamine increases from 0.5 kcal/mol at 3.0 Å to 1.5 kcal/mol at 2.0 Å while the  $\Delta$  ligand strain for the diether increases from 1.0 kcal/mol at 3.0 Å to 4.0 kcal/mol at 2.0 Å. As the charge on the cation increases, the magnitude of the effect becomes larger and the difference between the diamine and diether becomes more pronounced. For +2 cations, the  $\Delta$  ligand strain for the diamine increases from 0.5 kcal/mol at 3.0 Å to 2.3 kcal/mol at 2.0 Å while the  $\Delta$  ligand strain for the diether increases from 2.0 kcal/mol at 3.0 Å to 6.5 kcal/mol at 2.0 Å.

## DISCUSSION

As mentioned in the introduction, it is convenient to analyze changes in metal ion selectivity that accompany changes in ligand structure as a balance between inductive and steric effects. Inductive effects include the stability gained by the replacement of water by the ligand donor atoms and, therefore, a consideration of the donor

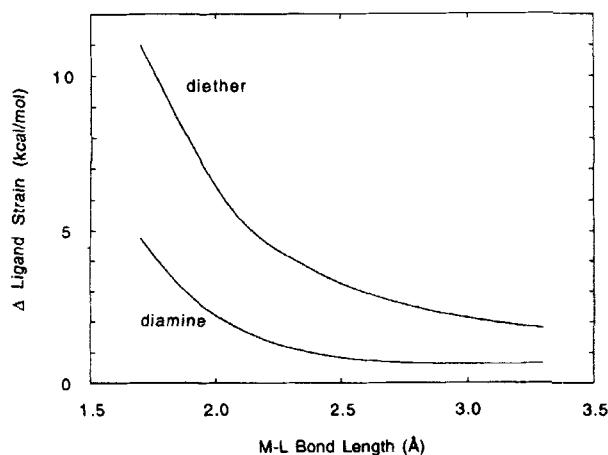


Figure 4 Plot of  $\Delta$  ligand strain versus M-L length for +2 cations.

atom strength. Steric effects may be divided into two categories, steric crowding resulting from interligand interactions and intraligand strain resulting primarily from structural reorganization to accommodate donor group geometry preferences. While it is often difficult to separate inductive and steric effects, we will now endeavor to apply this type of analysis to rationalize the enhanced selectivity for larger metal ions that is incurred by the addition of saturated neutral oxygen donors as shown in Figure 1.

Saturated neutral oxygen donors are weak ligands, being only slightly better bases than water. Even when steric effects are at a minimum, as in unidentate alcohols and ethers, they do not form strong metal ion complexes in aqueous solution.<sup>9</sup> Therefore, one would expect that the modest gain in stability that would accompany the formation of M-O bonds to be easily overcome by adverse steric effects. Steric crowding alone, i.e. strain from interligand interactions as donor groups from different ligands attempt to coordinate the metal,<sup>5</sup> will act to prevent all but the largest metal ions from utilizing the additional donor groups. In addition to steric crowding effects, the results obtained in this study have established when the neutral oxygen donor groups are present in five-membered, aliphatic chelate rings, there is a strong intraligand preference to complex large metal ions.<sup>10</sup> We are led to the conclusion that for small metal ions, the neutral oxygen donors added to the existing ligands in Figure 1 will not coordinate to the metal ion in aqueous solution. Only with larger metal ions may coordination take place. Even then, gains in complex stability from the replacement of water by neutral oxygen donors in five-membered aliphatic chelate rings are expected to be small. This is especially true when the extra neutral oxygen donors are added to a ligand of high denticity.

This conclusion is supported by the behavior of macrocyclic ethers that form five-membered, aliphatic chelate rings on metal ion complexation.<sup>11,12</sup> In aqueous solution, 12-crown-4 complexes only weakly with large metal ions such as Pb(II) ( $\log K = 2.0$ ) and very weakly with small metal ions such as Li(I) ( $\log K = -0.1$ ) and Mg(II) ( $\log K = 0.2$ ). Similar behavior is observed with 15-crown-5 and 18-crown-6. The strongest reported aqueous  $\log K$ 's for 15-crown-5 and 18-crown-6 are 3.4 for In(III) and 4.3 for Pb(II), respectively.

From the preceding discussion, we predict that the addition of neutral oxygen donors to an existing ligand should result in a small increase in stability for larger metal ions and no change in stability for smaller metal ions. A comparison of  $\Delta \log K$  values<sup>1-4</sup> for representative examples from Figure 1 is given in Figure 5. An examination of the  $\Delta \log K$  values reveals that while the expected stability increases do occur for the large Pb(II) ion, there does not appear to be any correlation between the  $\Delta \log K$  and the number of added neutral oxygen

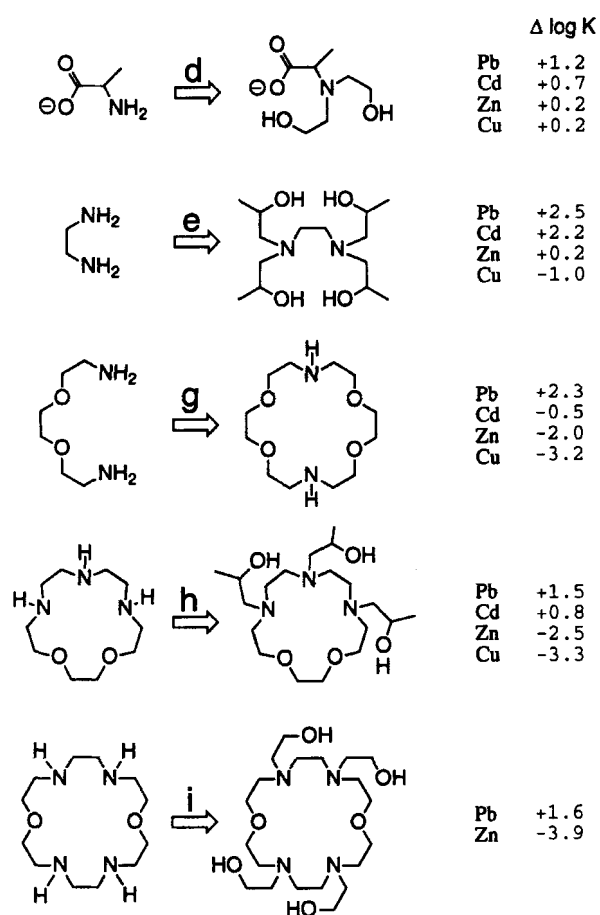


Figure 5  $\Delta \log K$  values<sup>1-3</sup> for the addition of a neutral oxygen donors to representative ligands from Figure 1.

donors. In addition, only one of the five examples, **d**, exhibits the anticipated behavior with respect to the smaller metal ions. In the other examples, we find that the addition of neutral oxygen donors results in a decrease in stability for smaller metal ions. In the last three examples, **g**, **h**, and **i**, it can be seen that it is this decrease in stability for the smaller ions that is the major component of the selectivity enhancement for Pb(II) over Cu(II) and Zn(II). What is the origin of this effect?

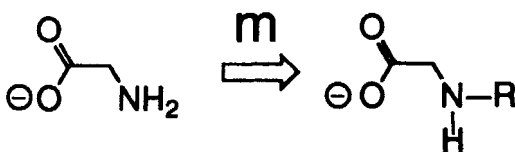


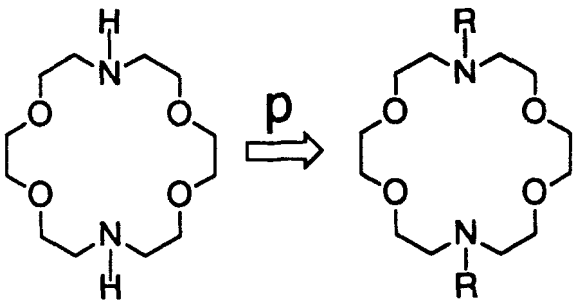
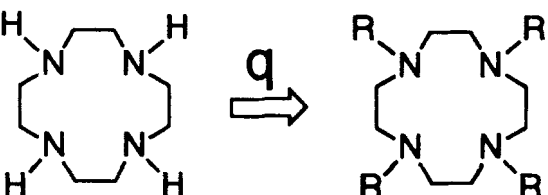
For every example in Figure 5, and the majority of examples in Figure 1 (c-l), the neutral oxygen donor groups are added to the ligand via alkylation of amine donor groups. The influence of increasing the alkyl substitution of a ligand's amine donors on the stability of metal ion complexes has been thoroughly analyzed for smaller metal ions, i.e. Ni(II) and Co(III), and has been rationalized as a balance of inductive and steric effects.<sup>2,5</sup> While increasing substitution results in a more basic, and thus stronger donor group (increase in log K), the increased bulk of the substituents leads to steric crowding (decrease in log K). In smaller metal ions, e.g. Ni(II), steric effects overcome inductive effects and alkyl substitution leads to a decrease in stability in aqueous

solution.<sup>5</sup> In larger metal ions, e.g. Ag(I), inductive effects can overcome steric effects and alkyl substitution of the amine donor can lead to increases in stability.<sup>13</sup> Thus, one might expect that alkylation of amine donor groups in existing ligands could result in a stability increase for large metal ions and a stability decrease for small metal ions, i.e. an enhanced selectivity for larger metal ions.

In several cases, sufficient data are available to compare the  $\Delta \log K$  values that result on amine substitution by  $\text{CH}_2\text{-C(R)H-OR}$  groups to the  $\Delta \log K$  values that result on amine substitution by simple alkyl groups.<sup>12,14</sup> Examination of this data, summarized in Figure 6, reveals that the  $\Delta \log K$  values associated with the attachment of neutral oxygen donor groups to amine nitrogens, are primarily the result of N-alkylation rather than the result of adding extra oxygen donor sites. Consistent with our earlier conclusions regarding the neutral oxygen donor in a five-membered aliphatic chelate ring (vide supra), any stability gained through coordination of the alcohol groups is small to non-existent.

In the first three examples, **m-o**, N-alkylation to convert a primary amine donor group to a secondary amine donor group results in a decrease in stability for all metal ions the size of Cu(II) through Cd(II). No specific trend in metal ion size-selectivity is observed. However, the last two examples in Figure 6, **p** and **q**, reveal that N-alkylation to convert a secondary amine donor group to a tertiary amine donor group yields selectivity enhancements similar to those exhibited in Figure 1. In the first case, **p** (similar to **j** and **k**, and identical to **l** in Figure 1), it can be seen that while the addition of  $\text{CH}_2\text{CH}_2\text{OCH}_3$  groups to the nitrogens leads to an enhanced selectivity for Ba(II) over Cd(II) of +2.1 log units, the addition of methyl groups has essentially the same effect, yielding an enhancement in selectivity for Ba(II) over Cd(II) of +1.9 log units. Similar behavior is observed in the second case, **q** (similar to **f** in Figure 1). Here enhanced selectivities for Pb(II) over Cu(II) of +3.0 and +2.9 log units are obtained after the addition of  $\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$  groups and methyl groups, respectively.

It can be seen from the foregoing discussion that the addition of neutral oxygen donors to an existing ligand does much more than increase the ligand's potential denticity. The addition also effects the inductive and steric character of the other donor groups in the ligand. Because these other groups, e.g. amines, are usually much stronger donors than the added oxygens, structural modifications that affect their ability to coordinate with metal ions have a much greater impact on complex stability. For example, we have presented evidence that it is the increase in N-alkylation, rather than the presence of neutral oxygen donors, that is the predominant cause

		$\Delta \log K$		
	$\xrightarrow{m}$	$R = \text{CH}_2\text{CH}_2\text{OH}$	$R = \text{CH}_3$	
		Zn	-0.9	-1.1
		Ni	-0.7	-0.9
		Cu	-0.6	-0.4
	$\xrightarrow{n}$	$R = \text{CH}_2\text{CH}_2\text{OH}$	$R = \text{CH}_2\text{CH}_2\text{CH}_3$	
		Cd	-0.5	-0.4
		Ni	-0.5	-0.7
		Cu	-0.5	-0.5
	$\xrightarrow{o}$	$R = \text{CH}_2\text{CH}_2\text{OH}$	$R = \text{CH}_3$	
		Cd	-0.2	-0.3
		Zn	-0.2	-0.9
		Ni	-0.6	-0.7
		Cu	-0.5	-0.8
	$\xrightarrow{p}$	$R = \text{CH}_2\text{CH}_2\text{OCH}_3$	$R = \text{CH}_3$	
		Ba	+0.8	+1.0
		Pb	+0.6	+1.5
		Sr	+0.7	+1.7
		Cd	-1.3	-0.9
	$\xrightarrow{q}$	$R = \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$R = \text{CH}_3$	
		Pb	-0.8	-2.0
		Zn	-2.8	-2.2
		Cu	-3.8	-4.9

**Figure 6** Comparison of  $\Delta \log K$  values<sup>4,12,14</sup> for the attachment of either neutral oxygen donors or alkyl groups to the amine nitrogens of existing ligands.

of the enhanced selectivity for larger metal ions exhibited in examples c-1.

Although amine alkylation does not occur in examples a and b of Figure 1, the selectivity enhancements for larger metal ions exhibited in these two cases is again primarily the result of decreases in stability for smaller metal ions rather than increased stability for larger metal ions. This behavior is not explained by the increased

denticity of the ligand and implies that modifications to the existing donor groups also play a major role here. In case a, the spatial relationship of the amine groups is altered from a five-membered chelate ring to an eight-membered chelate ring. In case b, both the basicity and the spatial relationship of the two carboxylate donor groups are modified. The effect of these structural modifications remains to be clarified.

## CONCLUSIONS

(1) Ligands that form five-membered aliphatic chelate rings must undergo structural reorganization on metal ion complexation leading to the development of strain in the ligand. This is true regardless of the size of the metal ion. Because of this structural reorganization, such ligands are not preorganized, even when the cavity size matches the metal ion size.

(2) The degree of structural reorganization depends on the size and charge of the metal ion. Complexation of large, low valent metal ions causes the least amount of structural reorganization (least ligand strain). Complexation of small, high valent metal ions causes the greatest amount of structural reorganization (greatest ligand strain).

(3) The degree of structural reorganization also depends on the geometry preferences of the donor groups. For a metal ion of a given size and charge, five-membered aliphatic chelate rings that contain saturated oxygen donors undergo more structural reorganization and develop larger amounts of ligand strain than those that contain amine donor groups.

(4) Because saturated neutral oxygen donors are inherently weak ligands, steric effects dominate their ability to coordinate a metal ion. Both experiment and theory reveal that when present in five-membered aliphatic chelate rings, these donor atoms tend to weakly complex only large metal ions in aqueous solution.

(5) Both theory and experiment indicate that much of the observed selectivity enhancement that has been associated with the addition of neutral oxygen donors to existing ligands results from inductive and steric changes that occur to the other donor groups in the ligand rather than from the increased denticity of the ligand.

## METHODS

The increase in ligand strain that accompanies metal ion complexation,  $\Delta$  ligand strain, was calculated as a function of metal ion size and charge for the diether and diamine ligands shown in Figure 2. For each metal ion, the calculations were performed as follows. Metal-dependent parameters corresponding to the size and charge of the metal ion were assigned. A molecular mechanics geometry optimization was done on the metal ion-ligand complex. The metal ion was then removed and, without allowing any of the ligand atoms to move, the steric strain of the ligand in its binding configuration was determined. The  $\Delta$  ligand strain was then obtained by subtracting the steric strain of the geometry optimized, uncomplexed ligand from this value.

Molecular mechanics calculations were performed on a Sun SparcII workstation using the MM3 program.<sup>15</sup>

The molecular graphics program, Chem3D Plus,<sup>16</sup> was used on a Macintosh IICI personal computer to build initial sets of molecular coordinates for MM3 to plot energy-minimized molecular coordinates obtained from the calculations. The points-on-a-sphere method<sup>17,18</sup> was used to model the metal complexes in which L-M-L bends are replaced with L-L nonbonded interactions. Torsions about the M-L bond and non-bonded interactions involving the metal ion were removed from the calculation. The desired M-L bond lengths were obtained by setting stretching force constants to 99 mdyne/Å. MM3 parameters for the diether and its metal complexes were taken from previous work.<sup>8</sup> Default MM3 parameters were used for the diamine. MM3 parameters for the diamine-metal complexes were derived as described below.

In prior calculations of steric strain as a function of metal ion size,<sup>1,5,6,19-22</sup> it is generally assumed that the bending and torsional parameters for amine-metal ion interactions remain constant as a function of M-L length and charge. In our development of a valence bond force field for ether complexes,<sup>8</sup> we have found that the bending and torsional parameters depend upon both the size and the charge of the metal ion. The trend is for the strength of donor orientation preferences, defined by M-L-X bends and M-L-X-X torsions (X=any atom), to become weaker as the M-L length increases and as the charge decreases. To make the best comparison in Figures 3 and 4, we decided to scale the parameters for the amine complexes by assuming that they would change in the same direction and with the same magnitude as the ether parameters.<sup>23</sup> For a +2 cation with an M-N length of 2.0 Å (e.g. Ni(II), M-N-C and M-N-H bending interactions were assigned an ideal angle of 109.5° and force constants of 0.6 and 0.3 mdyne-Å/rad<sup>2</sup>, respectively.<sup>4</sup> M-N-C-C and M-N-C-H torsional interactions were assigned the default MM3 parameters for C-N-C-C and C-N-C-H torsions. As a rough approximation, these bending and torsional parameters for other +2 cations were scaled linearly with M-L length to give a 30% decrease in bending force constant and a 60% decrease in torsional parameters as the M-L length is increased by 1.0 Å. For any given M-L length, the bending and torsional parameters for the amine-metal ion interactions of +1 cations were assigned values of 0.5 times those of the corresponding +2 cations.

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