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## Relationship between Electronic Spectra and Heat of Formation of Some Copper-Polyamine Complexes and the Macrocyclic Effect

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The previously described relationship between  $\Delta H_{\text{aq}}$  and  $\nu(\text{d-d})$  for a series of tetragonal copper(II) complexes<sup>3,4</sup> has been greatly extended to include the ammonia complexes  $\text{Cu}(\text{NH}_3)_x^{2+}(\text{aq})$  ( $x = 1-4$ ), various monodiamine derivatives, some triamine complexes, and a macrocyclic derivative. In the light of the more extensive study, the significance of the relationship is reassessed. The good behavior of the copper complex with the macrocycle cyclen suggests that the "macrocyclic effect" is not due to an increased enthalpy contribution but rather to an increased entropy term. At least for the complexes studied here the difference in solvation enthalpy between open-chain and macrocyclic ligands does not seem to play an important role. This conclusion is also supported by data concerning the enthalpy of dehydration of hydrated open-chain and macrocyclic ligands. The strength of the copper-nitrogen bond in macrocyclic complexes may be greater than or less than the strength in analogous open-chain amine complexes depending upon details of the structure, in particular ring sizes.

### Introduction

In some preceding work<sup>3-5</sup> we have illustrated a linear relationship between the enthalpy of formation in water and the energy of the electronic maxima in some polyamine complexes of copper (containing four amine nitrogen atoms in the equatorial plane). The complexes in question were prepared by the reaction of aqueous copper ion with one molecule of the tetraamine or two molecules of diamine. Some conclusions concerning the significance of this work were drawn. In this work we have extended the relationship to polyamine complexes containing three atoms of nitrogen (tridentate amines), two atoms of nitrogen (complexes containing two ammonia groups or one diamine ligand), and one atom of nitrogen, namely, the species  $\text{Cu}(\text{NH}_3)_2^{2+}(\text{aq})$ . This series of complexes considerably extends the range of  $-\Delta H$  and  $\nu(\text{d-d})$  values and permits a more detailed discussion of the significance of the observations.

We have also observed that the macrocycle cyclen (1,4,7,10-tetraazacyclotetradecane) obeys the same linear relationship. This fact allows us to review current thinking on the stability of cyclic complexes and to propose an alternative explanation for the "macrocyclic effect". Margerum<sup>6</sup> maintained that the macrocyclic effect is due to a greater degree of solvation for the tetraamines, relative to the analogous macrocycles, and as a consequence attributed this effect solely to an exceptionally favorable enthalpy term, the entropy term being counterbalanced. The studies reported here led

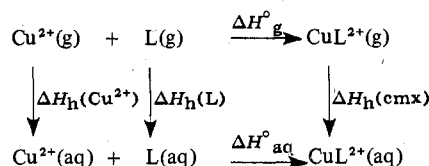
us to believe that ligand desolvation effects have been overestimated. It would appear that it is the entropy term,  $\Delta S$ , which makes the major contribution to the extra stability of macrocyclic complexes, at least for copper(II). The variations in  $\Delta H$  can favor or diminish the stability of macrocyclic complexes according to the sequence of chelate rings and the number of atoms contained therein. A combination of penta- and hexaatomic chelate rings is favorable. Macrocycles containing only five-membered rings (and presumably those containing only six-membered rings) have smaller  $\Delta H$  values. Similar arguments have been applied to explain the thermodynamic stability of open-chain derivatives.<sup>7</sup>

### Experimental Section

**Materials.** The amine ligands were obtained commercially (Fluka, Aldrich). The complexes, all as perchlorates, were obtained by reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with the ligand in ethanol solution followed by two recrystallizations from the same solvent. The analyses (C, H, N, and Cu) were satisfactory. The ligand *ms*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a) was prepared by the literature method.<sup>8</sup> Recrystallization from aqueous alcohol gave the dihydrate. The complex  $\text{Cu}(\text{tet a})(\text{ClO}_4)_2$  was obtained through reaction of tet a with copper perchlorate in anhydrous alcohol.

**Spectroscopic Measurements.** Visible spectra were obtained with a Beckman DK2A, using quartz cells thermostated at 25 °C, and ultraviolet spectra, with a Cary 14. Solutions of the copper-triamine derivatives and -bis(diamine) derivatives were obtained by dissolving the appropriate perchlorate salt in water. Solutions of the species  $\text{Cu}(\text{diamine})_2^{2+}$  (mono(diamine)derivatives) were prepared by dis-

## Scheme 1



solving a known quantity of the bis(diamine) derivative in water and adding an equimolar amount of aqueous  $\text{HClO}_4$ , enough to neutralize two  $-\text{NH}_2$  groups. This method is better than directly dissolving the mono(diamine) complex  $\text{Cu}(\text{diamine})(\text{ClO}_4)_2$  in water, which would give rise to a smaller percentage of the mono(diamine) in solution than that buffered by the perchloric acid. For example, in the case of  $\text{Cu}(\text{dieten})^{2+}$ , one may calculate from the formation constants<sup>9</sup> the following percentage compositions.

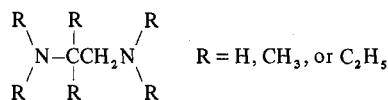
	$\text{CuL}^{2+}$	$\text{CuL}_2^{2+}$	$\text{Cu}_2\text{L}_2(\text{OH})_2$	$\text{CuL}(\text{OH})_2$	$\text{Cu}^{2+}$
Buffered soln	94%	2%	0%	0%	4%
Unbuffered	87%	1%	2%	3%	7%

Measured values of  $\nu(\text{d-d})$  in aqueous solutions are as follows (kK):  $\text{Cu}(\text{N,N,N',N'}$ -tetramethylethylenediamine) $^{2+}$ , 14.2;  $\text{Cu}(\text{N,N}$ -diethylethylenediamine) $^{2+}$ , 14.3;  $\text{Cu}(\text{N,N'}$ -diethylethylenediamine) $^{2+}$ , 14.8;  $\text{Cu}(\text{N,N'}$ -dimethylethylenediamine) $^{2+}$ , 14.9;  $\text{Cu}(\text{N,N}$ -dimethylethylenediamine) $^{2+}$ , 15.0;  $\text{Cu}(\text{N}$ -methylethylenediamine) $^{2+}$ , 15.2;  $\text{Cu}(\text{ethylenediamine})^{2+}$ , 15.2;  $\text{Cu}(\text{C-methylethylenediamine})^{2+}$ , 15.5;  $\text{Cu}(\text{C,C}$ -dimethylethylenediamine) $^{2+}$ , 15.6;  $\text{Cu}(1,5,9\text{-triazanonane})^{2+}$ , 16.3;  $\text{Cu}(1,4,7\text{-triazahexane})^{2+}$ , 16.6;  $\text{Cu}(1,4,8\text{-triazaoctane})^{2+}$ , 16.7.

**Calorimetric Measurements.** Thermogravimetric measurements with  $(\text{tet a}) \cdot 2\text{H}_2\text{O}$  using a Perkin-Elmer TGS-1B thermobalance showed that the compound lost two water molecules in the temperature interval 70–110 °C using a scan speed of 4 °C/min. The heat of reaction was obtained with a Perkin-Elmer Model DSC-1B differential scanning calorimeter using methods previously described.<sup>10</sup>

## Discussion

(i) **Extension of  $\Delta H$  vs.  $\nu(\text{d-d})$  Relationship.** Previous papers<sup>3-5</sup> have discussed the linear relationship observed between the heat of formation in aqueous solution,  $\Delta H_{\text{aq}}^\circ$ , and the frequency of the visible band maximum  $\nu(\text{d-d})$ ,<sup>3,4</sup> and charge-transfer maximum.<sup>5</sup> The study was limited to 1:1 complexes of the quadridentate ligands of general formula  $\text{H}_2\text{N}(\text{CH}_2)_p\text{NH}(\text{CH}_2)_q\text{NH}(\text{CH}_2)_r\text{NH}_2$  and to 1:2 complexes with diamines of the general type

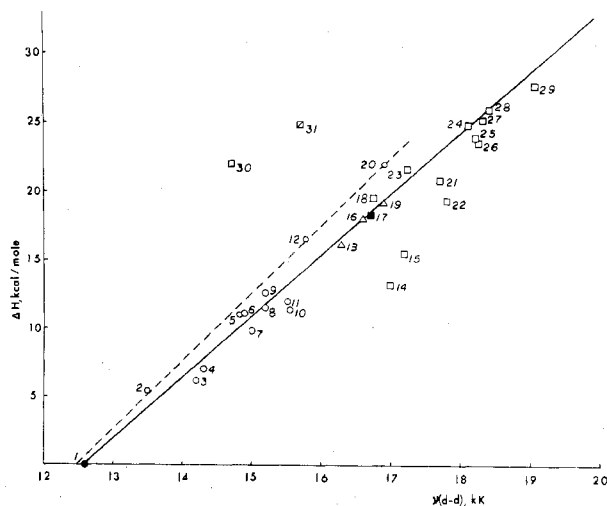


As may be observed in the thermodynamic cycle of Scheme I, the calorimetric value measured in the aqueous phase may be related theoretically to the corresponding value measured in the gas phase as in eq 1, where the  $\Delta H_h$  values are solvation

$$\Delta H_{\text{aq}}^\circ = \Delta H_g^\circ + [\Delta H_h^\circ(\text{cmx}) - \Delta H_h(\text{L}) - \Delta H_h(\text{Cu}^{2+})] \quad (1)$$

(hydration) energies. Given a proportionality relationship between  $\Delta H_g$  and  $\nu(\text{d-d})$ , there exists the possibility, through extrapolation of the linear relationship, of obtaining a value of the solvation energy terms in toto and of deducing the gas-phase metal-amine bond enthalpies. Our previous attempt to carry out such a calculation led to values which were lower than might reasonably be expected. Such a result might occur through the use of a too naive relationship between  $\Delta H_g$  and  $\nu(\text{d-d})$  and/or errors arising from the extrapolation process, the previous ranges of  $\Delta H$  and  $\nu(\text{d-d})$  being rather small.

This last consideration has been overcome by the extension of this study to include complexes of triamine ligands ( $\text{H}_2\text{N}(\text{CH}_2)_p\text{NH}(\text{CH}_2)_q\text{NH}_2$ ) and complexes containing only two nitrogen atoms. The resulting additional points lie in a satisfactory manner upon a line very close to that previously

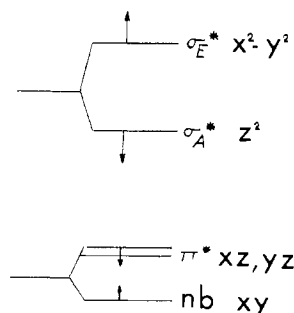


**Figure 1.** Plot of the heat of formation in aqueous solution,  $\Delta H_{\text{aq}}$ , vs. the frequency of the maximum of the visible band,  $\nu(\text{d-d})$ , for copper(II) complexes. The dashed line refers to ammonia complexes, and the solid line to other amine complexes. For the ammonia complexes the least-squares equation is  $-\Delta H = -61.01 + 4.90\nu(\text{d-d})$ . The least-squares equation for the polyamines is  $-\Delta H = -54.43 + 4.33\nu(\text{d-d})$ . Numbers in the figure refer to the following ligands: 1,  $6\text{H}_2\text{O}$ ; 2,  $\text{NH}_3$ ; 3,  $\text{N,N,N',N'}$ -tetramethylethylenediamine; 4,  $\text{N,N'}$ -diethylethylenediamine; 5,  $2\text{NH}_3$ ; 6,  $\text{N,N'}$ -dimethylethylenediamine; 7,  $\text{N,N}$ -dimethylethylenediamine; 8,  $\text{N}$ -methylethylenediamine; 9, ethylenediamine; 10,  $\text{C,C}$ -dimethylethylenediamine; 11,  $\text{C}$ -methylethylenediamine; 12,  $3\text{NH}_3$ ; 13,  $1,5,9\text{-triazanonane}$ ; 14, bis( $\text{N,N}$ -diethylethylenediamine); 15, bis( $\text{N,N'}$ -diethylethylenediamine); 16,  $1,4,7\text{-triazahexane}$ ; 17,  $1,4,7,10\text{-tetraazacyclododecane}$  (cyclen); 18,  $1,5,9,13\text{-tetraazatridecane}$  ( $3,3,3\text{-tet}$ ); 19,  $1,4,8\text{-triazaoctane}$ ; 20,  $4\text{NH}_3$ ; 21, bis( $\text{N,N'}$ -dimethylethylenediamine); 22, bis( $\text{N,N}$ -dimethylethylenediamine); 23,  $1,4,7,10\text{-tetraazadecane}$  ( $2,2,2\text{-tet}$ ); 24, bis( $\text{N}$ -methylethylenediamine); 25, bis( $\text{C}$ -methylethylenediamine); 26, bis( $\text{C,C}$ -dimethylethylenediamine); 27, bis(ethylenediamine); 28,  $1,5,8,12\text{-tetraazadodecane}$  ( $3,2,3\text{-tet}$ ); 29,  $1,4,8,13\text{-tetraazaundecane}$  ( $2,3,2\text{-tet}$ ); 30, tris(aminoethyl)amine (tren); 31,  $1,4,7,10,13\text{-pentaazatridecane}$  (teten). Enthalpy data for ammonia complexes have been taken from S. J. Ashcroft and C. T. Mortimer, "Thermochemistry of Transition Metal Complexes", Academic Press, London, 1970.

reported. *Very significantly the intercept of this line on the  $\Delta H$  axis ( $\Delta H = 0$ ) corresponds very well to the frequency,  $\nu(\text{d-d})$ , of the unsubstituted  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ion.* Moreover, the set of points corresponding to the ammonia complexes  $\text{Cu}(\text{NH}_3)_x^{2+}(\text{aq})$  ( $x = 1-4$ ) generates a line, also passing through  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  but deviating slightly from the polyamine line with increasing value of  $-\Delta H$  (see Figure 1). Note that the range of the two variables has now been extended to 27 kcal for  $\Delta H$  and  $6500\text{ cm}^{-1}$  for  $\nu(\text{d-d})$ . Nevertheless the best line through these points does not differ greatly from that previously demonstrated. This success prompts a more detailed discussion of the significance of this relationship.

In our previous Note<sup>4</sup> we made two simplifying suppositions. Implicitly it was assumed that the changes in energy of formation from one amine to another were due primarily to changes in in-plane bond energy. Further, it was assumed that the observed electronic bond maximum corresponded to the  $xy \rightarrow x^2 - y^2$  transition. The existence of a good straight-line correlation between these two quantities for the closely related series of complexes studied (all containing a  $\text{CuN}_4$  equatorial plane) suggests that the suppositions were substantially correct.

In the light of the extension of these data to other complexes, some of which contain only one or two nitrogen atoms in the equatorial plane, it is worthwhile to reconsider these simplifications. There is no doubt that as we change the in-plane ligands there is a complementary change in the axial copper-water interaction.<sup>5,11</sup> Therefore, as the in-plane field



**Figure 2.** Generalized d-orbital splitting diagram for tetragonal copper(II). The figure is not drawn to scale, and the order of the splitting of the lower orbital triplet is arbitrary; it will vary from one complex to another.<sup>12</sup> The arrows, and the relative sizes, indicate qualitatively the movement of the energy levels which would be expected as the axial field is diminished. The axial ligand is assumed to possess filled p orbitals capable of a  $\pi$  interaction with the copper  $d_{xz}$ ,  $d_{yz}$  orbitals (A = axial, E = equatorial, nb = nonbonding).

strength increases, we may anticipate that the axial interaction decreases and vice versa. Thus in a series of amines the observed heats of formation reflect the change in both in-plane and out-of-plane bond energy, as well as any variation in solvation energy, which will be considered later.

The electronic spectrum of these complexes consists, in the visible region, of a broad, often featureless band comprising the three possible transitions indicated in Figure 2 for an ideally tetragonal complex. The band maximum corresponds approximately to the energy of the  $xz, yz \rightarrow x^2 - y^2$  transition<sup>12</sup> for the  $\text{CuN}_4$  series. As previously discussed, the assumption that the  $xy \rightarrow x^2 - y^2$  transition was of energy comparable to that of the former transition was a reasonable proposition. For the greatly extended series of complexes reported here, such a general supposition is not valid since we may suppose that the in-plane  $xy \rightarrow x^2 - y^2$  transition will vary quite considerably. Because we can rarely discriminate this specific transition from the broad visible absorption, we are constrained to continue to utilize the main-band energy maximum. However this is no disadvantage if we now recognize that this will always correspond fairly well to the doubly degenerate (in  $D_{4h}$  symmetry) and presumably most intense visible transition.

Indeed, this transition,  $xz, yz \rightarrow x^2 - y^2$ , might be expected to be a better probe for the changes in the heat of formation than a direct observation of the in-plane  $xy \rightarrow x^2 - y^2$  transition. Thus, as the in-plane field strengthens, the axial interaction weakens. As a consequence, regarding the levels in a molecular orbital terminology, the in-plane  $x^2 - y^2$  orbital, being  $\sigma$  antibonding, will increase in energy, while the  $xz, yz$  orbitals, being  $\pi$  antibonding with respect to the axial ligand, will decrease in energy. As a consequence, an increase in the in-plane field strength will give rise to an increase in the observed absorption band maximum as indicated in Figure 2.

All of the complexes possess, in common, two trans water molecules, whose energies are reflected in the energy of the  $xz, yz$  orbital (and also the  $z^2$  orbital, but the position of this level can rarely be unequivocally identified). In fact, the positions of these water molecules are monitored by the changes in the visible band energy maximum. This is supported by the observation that, for the limited series of complexes which have been studied, there is a direct correlation between  $g_{\parallel}$  and  $-\Delta H$ .<sup>13</sup> While this should not be unexpected, in view of the inverse dependence of  $g_{\parallel}$  upon the energy of the  $xz, yz \rightarrow x^2 - y^2$  transition,<sup>14</sup> it does provide further support for the assignment utilized.

Let us consider the magnitude of  $\Delta H_g$ . We may arbitrarily consider it to be the sum of two terms, one ( $E$ ) being non-

directional (spherical) and the other ( $C$ ) directional. Thus the first term is purely electrostatic and results from the spherical component, in a crystal field sense, of the cation-dipole interaction. It has no effect on the relative d-orbital energies but merely stabilizes all the d orbitals to the same degree. It therefore makes no contribution to the magnitude of  $\nu(\text{d-d})$ . The second term contains the covalent interaction energy and also the directional (crystal field) electrostatic terms. We can anticipate that these terms will contribute to the magnitude of  $\nu(\text{d-d})$  as indeed has been discussed for copper by Smith.<sup>15</sup> For simplicity, and because of the fact that experimentally it appears to be the case, we assume a linear relationship between  $\nu(\text{d-d})$  and  $C$ . Therefore we may write

$$\Delta H_g = E + C = E + f\nu(\text{d-d}) \quad (2)$$

Combining eq 1 and 2 and writing the set of solvation terms simply as  $\Delta H_{\text{solv}}$  we derive

$$\Delta H_{\text{aq}} = f\nu(\text{d-d}) + [\Delta H_{\text{solv}} + E] \quad (3)$$

The existence of the straight-line relationship in Figure 1 provides compelling evidence that the sum of the terms  $[\Delta H_{\text{solv}} + E]$  must remain essentially constant for the series studied. This last observation could be explained in two ways. First, we could assume that both  $E$  and  $\Delta H_{\text{solv}}$  are constant for all the complexes studied. The electrostatic spherical term  $E$  will depend solely on the metal-donor atom distance. Available x-ray data suggest that in the absence of steric effects, Cu-N distances in diamine complexes fall within a fairly narrow range of values.<sup>16</sup> However it is perhaps unlikely that complexes with water in the equatorial plane would also have the same value for  $E$  which is presumably a fairly large number. For  $\Delta H_{\text{solv}}$  to remain essentially constant, the difference (see eq 1) between the solvation of the complex and of the ligands must remain constant. In other words, as the capacity of the ligand to bind solvent molecules increases, so will the capacity of the complex, and vice versa. Alternatively, we could assume that the sum of the two quantities concerned rather than the individual components remains constant. This would imply that as the electrostatic term  $E$  increases, as a consequence, for example, of increasing effective charge on the nitrogen atoms, the solvation energy must decrease. On the other hand, with decreased electrostatic interaction as a consequence of a weaker donor atom to metal bond through a less negative nitrogen atom, the water molecule will feel an increased attraction to both the central metal atom and, in the second sphere, to the more positive protons on the nitrogen atoms.

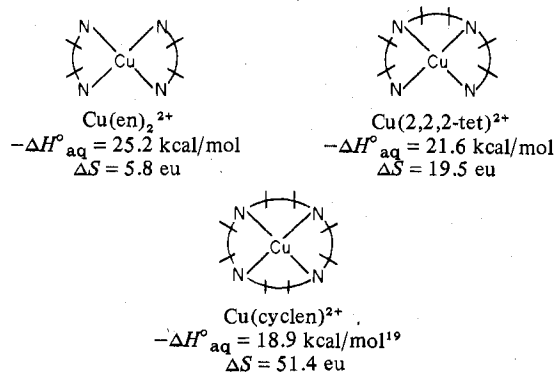
Given that the sum of the terms is constant as inferred from the experimental data, the second mechanism seems the more plausible and is perhaps not unreasonable in view of the fairly closely related series of complexes studied. The existence of the electrostatic term excludes the evaluation of  $\Delta H_{\text{solv}}$  through extrapolation of the line to  $\nu(\text{d-d}) = 0$ ; instead, the value of this intercept will be the sum of the two terms. The electrostatic term is strongly exothermic and balances, in part,  $\Delta H_{\text{solv}}$  which is strongly endothermic mainly as a consequence of the dehydration of the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ion,  $\Delta H_{\text{h}}(\text{Cu}^{2+})$  in eq 1.

There are some complexes which lie off the line (Figure 1). One of these is  $\text{Cu}(\text{tren})^{2+}$  (tren is tris(aminoethyl)amine). In this case the amine has a tripodlike structure and cannot dispose its donor atoms in a quadratic equatorial plane. We expect the relationship to be valid only for amines capable of forming tetragonal complexes with the nitrogen atoms in the quadratic plane and for cases where two water molecules can be coordinated axially. It is probable that five-coordinate square-pyramidal complexes with one axial water molecule will also lie on the line, though as yet we have no direct ev-

idence to support this contention. The complex with tetradentate tetren (tetraethylenepentamine), for example, does not lie on the line. In this case one of the amine nitrogen atoms occupies an axial position and influences the energy of the  $xz, yz \rightarrow x^2 - y^2$  transition and also, of course, the total enthalpy of formation. We have already noted how alkyl substitution on the nitrogen atoms in the diamines causes deviation from the line, especially with increasing size of the alkyl group. This was attributed to the fact that the hydrophobic alkyl groups resulted in greater desolvation of the complexes relative to the unsubstituted ligands. As a consequence,  $\Delta H_{\text{aq}}^{\circ}$  decreases and we find the complexes below the line in Figure 1. The largest deviations are seen with the 1:2 diamine complexes where presumably there is the greatest desolvation effect. Steric hindrance of the axially coordinated water molecules may also contribute to their bad behavior. Moreover, an increase in Cu-N bond length through steric hindrance<sup>17</sup> will decrease the value of  $E$ . The importance of desolvation in the substituted diamine complexes is demonstrated by their  $\Delta S$  values. In general the  $\Delta S$  value increases with decreasing magnitude of  $-\Delta H_{\text{aq}}^{\circ}$  in related series of mono- and bis(diamine) complexes.<sup>4</sup> This is fully consistent with a greater loss of water both from the inner sphere (axially bound water) and from the second sphere with increasing alkyl substitution. Although it is too early to make definitive statements, we speculate that these data also provide implicit information concerning the number of water molecules bound to the ligands.

(ii) **Macrocyclic Effect.** It is most interesting to note that the macrocyclic ligand, cyclen, lies very satisfactorily on the  $\Delta H_{\text{aq}}^{\circ}$  vs.  $\nu(\text{d-d})$  line.<sup>18</sup> Thus the combined solvation and electrostatic term for cyclen cannot be very different from that of the other ligands and, in particular, not very different from the corresponding open-chain ligand 2,2,2-tet. If the electrostatic term for these two clearly related complexes could be considered approximately equal, then we could conclude that the differential solvation term ( $\Delta H_{\text{h}}(\text{cmx}) - \Delta H_{\text{h}}(\text{L})$ ) is the same for both the macrocycle cyclen and the open-chain 2,2,2-tet. This does not provide information about the *individual* solvation energies of open-chain and macrocyclic ligands, only the difference between ligand and complex. Nevertheless, this would weaken Margerum's viewpoint that it is the solvation term which is responsible for the macrocyclic effect at least in Cu(cyclen), since it is the *differential* solvation term which contributes to the experimental heat of formation. Clearly, however, further macrocyclic complexes must be studied before this conclusion may be unequivocally drawn. Such studies are in progress but present special difficulties because of the high kinetic stability of macrocyclic systems.

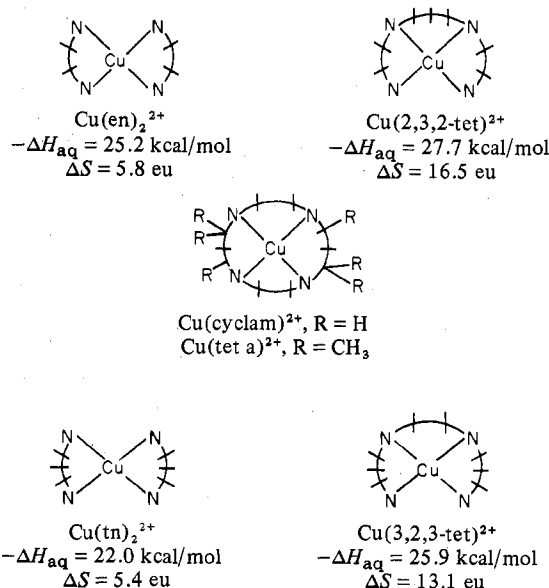
Let us consider the enthalpy of formation of tetraamine complexes containing a constant number of atoms in each ring, e.g., pentaatomic rings in complexes involving two ethylenediamine ligands, one 2,2,2-tet ligand, or one cyclen ligand.



In this series of compounds with an increase in the number of five-membered rings, we observe a decrease in *both*  $-\Delta H_{\text{aq}}^{\circ}$

and  $\nu(\text{d-d})$  and an increase in  $\Delta S_{\text{aq}}^{\circ}$ . We cannot assume that the copper atom will necessarily lie exactly in the center of each of the planes defined by the nitrogen atoms in the preceding (and following) compounds. There may be some distortions, especially in the macrocyclic systems; however we do not feel that this will invalidate our conclusions. In this case formation of the macrocycle is *unfavorable* from the point of view of enthalpy, relative to formation of the open-chain analogue. The greater free energy of formation of the macrocycle clearly arises from the increased entropy change. The decreased enthalpy of formation of cyclen may be attributed to poorer overlap in the copper-nitrogen bonds through steric strain in the rings of the cyclic ligand. The alternative explanation that the bonding is stronger than in the open-chain ligand but that increased desolvation of the ligand results in a more endothermic heat change can be eliminated on the basis that the observed  $\nu(\text{d-d})$  does place the complex on the line rather than markedly below it.

Now consider a series of complexes in which the ring size alternates with five- and six-membered rings.



As can be seen in this case, alternating ring size causes an increase in  $-\Delta H_{\text{aq}}^{\circ}$  in passing from the bis(diamines) to the open-chain tetraamines. Measured values of  $\Delta H_{\text{aq}}^{\circ}$  for the macrocyclic ligands cyclam and tet a with copper(II) are not yet available. However, if the trend indicated above continues to include the macrocycles, values of  $-\Delta H_{\text{aq}}^{\circ}$  of 29–31 kcal/mol would be anticipated. Alternatively, if we assume that the  $\text{Cu}(\text{tet a})^{2+}$  complex obeys the linear relationship between  $\Delta H_{\text{aq}}^{\circ}$  vs.  $\nu(\text{d-d})$ , then the measured value of  $\nu(\text{d-d})$  (18.53 kK)<sup>20</sup> leads to a value of 30–31 kcal/mol for the heat of formation of this complex. Using the relationship<sup>5</sup> between  $\Delta H_{\text{aq}}^{\circ}$  and the high-energy ultraviolet  $\sigma\text{-}\sigma^*$  charge-transfer transition observed for many of these complexes in aqueous media, the measured value of 45.45 kK for the  $\text{Cu}(\text{tet a})^{2+}$  complex yields  $-\Delta H_{\text{aq}}^{\circ} = 31 \text{ kcal/mol}$  on the assumption, of course, that the complex is well behaved. There seems little doubt, in the circumstances, that the measured value, when it becomes available, will lie near 30 kcal/mol. Therefore, for macrocycles containing alternating five- and six-membered rings, formation of the copper complex is favored by an increased enthalpy of formation due primarily to an increase in Cu-N bond energy relative to the analogous open-chain ligand. Note, however, that using a value of  $-30 \text{ kcal/mol}$  for  $\Delta H$  together with the recorded  $\Delta G$  value (38 kcal/mol)<sup>21</sup> leads to a calculated  $\Delta S$  of 27 eu. Hence the high stability of this complex would also seem to be due to entropy.

Margerum has recorded values of  $-\Delta H = 31$  and  $28$  kcal/mol for the nickel complexes of cyclam and tet a, respectively.<sup>6</sup> These values, when compared with those of  $\text{Ni}(\text{en})_2^{2+}$  ( $-\Delta H_{\text{aq}} = 17.9$  kcal/mol)<sup>22</sup> and  $\text{Ni}(\text{2,3,2-tet a})^{2+}$  ( $-\Delta H_{\text{aq}} = 16.8$  kcal/mol),<sup>6</sup> seem rather elevated compared with the corresponding copper complexes. The results discussed above suggest that solvation enthalpy cannot be utilized to explain the macrocyclic effect, at least for copper compounds, though it may make some contribution. Margerum commented that the macrocyclic effect arises from a *decreased* enthalpy of hydration for macrocyclic ligands relative to their open-chain analogues. It is supposed that an open tetraamine binds four water molecules while a macrocycle binds only two. There seems little doubt that this is correct; however it does not necessarily follow that the dehydration enthalpies for the two types of ligand will differ greatly, if at all. Binding of the two water molecules by the four nitrogen atoms in a macrocycle ring ligand could conceivably be of energy similar to the total binding energy of the four water molecules by the open-chain tetraamine.

We have measured the enthalpy of reaction 4 and find a

$$(\text{tet a}) \cdot 2\text{H}_2\text{O}(\text{c}) \rightarrow (\text{tet a})(\text{c}) + 2\text{H}_2\text{O}(\text{g}) \quad (4)$$

value of  $26.4$  kcal/mol which is very high. This energy is not a direct measure of the hydration energy of the water molecules bound to the macrocycle since it will contain a term depending upon the differences in the lattice energies of the hydrated and dehydrated compounds. However, since the lattice energies of organic compounds are generally rather small ( $10$ – $40$  kcal/mol), it seems improbable that the lattice energies of the hydrated and anhydrous compounds can differ by more than a few kilocalories.

One may conclude from (4) that the heat of hydration of tet a is near  $13$  kcal/mol of bound water. Unfortunately we are unable to find a literature value for the enthalpy of one  $\text{N} \cdots \text{H} - \text{OH}$  bond. There is, however, a calculated value of  $5.8$  kcal/mol reported by Margerum for ammonia–water<sup>6</sup> and a similar value calculated by Allen.<sup>23</sup> The heat of reaction 5



has been reported.<sup>24</sup> It is probable that the difference in heat required to vaporize the two liquids is small (they have similar boiling points) so that the reported value will lie close to the actual binding energy of the water molecule. It is significant that this value is very close to that for reaction 4, expressed per water molecule. When compared with the calculated value for one hydrogen bond noted above, these results infer that both reactions 4 and 5 involve the breaking of *two* hydrogen bonds per water molecule, presumably bonding to two different nitrogen atoms. In general, an open-chain amine will bind as many molecules of water as there are nitrogen atoms in the amine.<sup>25</sup> We, therefore, can anticipate that in aqueous solution an open-chain tetraamine binds four water molecules, each through one hydrogen bond. The macrocycle tet a and, presumably, cyclam, cyclen, etc. bind only two water molecules because of steric constraints, but yet in total may still involve four hydrogen bonds. Naturally we may expect the second hydrogen bond to be weaker than the first, but the thermodynamic results indicated here suggest that the differences are not great. In the circumstances it seems unlikely that the macrocyclic effect, at least in copper complexes, can be due

primarily to differences in hydration energy of open-chain and macrocyclic ligands.

Certainly for the complexes reported in this study, the macrocyclic effect seems to be due primarily to a favorable entropy term. The relative contribution of the enthalpy reflects the stability of the copper–nitrogen bond and may increase or decrease  $\Delta G$  depending on whether or not there are alternating five- and six-membered rings.

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**Registry No.**  $\text{Cu}(\text{N,N,N',N'}$ -tetramethylethylenediamine) $^{2+}(\text{aq})$ , 58452-34-9;  $\text{Cu}(\text{N,N}$ -diethylethylenediamine) $^{2+}(\text{aq})$ , 58919-04-3;  $\text{Cu}(\text{N,N'}$ -diethylethylenediamine) $^{2+}(\text{aq})$ , 58919-05-4;  $\text{Cu}(\text{N,N'}$ -dimethylethylenediamine) $^{2+}(\text{aq})$ , 58452-30-5;  $\text{Cu}(\text{N,N}$ -dimethylethylenediamine) $^{2+}(\text{aq})$ , 58452-32-7;  $\text{Cu}(\text{N}$ -methylethylenediamine) $^{2+}(\text{aq})$ , 58919-06-5;  $\text{Cu}(\text{ethylenediamine})^{2+}(\text{aq})$ , 15227-16-4;  $\text{Cu}(\text{C-methylethylenediamine})^{2+}(\text{aq})$ , 58919-07-6;  $\text{Cu}(\text{C,C}$ -dimethylethylenediamine) $^{2+}(\text{aq})$ , 58919-08-7;  $\text{Cu}(1,5,9\text{-triazanone})^{2+}(\text{aq})$ , 58452-36-1;  $\text{Cu}(1,4,7\text{-triazheptane})^{2+}(\text{aq})$ , 55528-71-7;  $\text{Cu}(1,4,8\text{-triazaoctane})^{2+}(\text{aq})$ , 58452-38-3;  $\text{Cu}(\text{trisaminoethylamine})^{2+}(\text{aq})$ , 38985-27-2;  $\text{Cu}(1,4,7,10,13\text{-pentaazatridecane})^{2+}(\text{aq})$ , 58919-09-8;  $\text{Cu}(\text{OH})_2^{2+}$ , 14946-74-8.

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