$(NH_3)_6^{3+}$, $Co(acac)_3$, and $Co(edta)^-$. A more detailed investigation for $Co(NH_3)_6^{3+}$ has also demonstrated that $K$ and $k_{et}$ show little or no variation with pH. Metalloproteins containing uncoordinated histidines are expected to exhibit acid dissociation p$K_a$ values in this region of pH, and will affect the reactivity if situated close to the site at which electron transfer occurs. Proteins with no such histidines can also respond to pH changes in this region, however.[43] Interestingly no pH profiles have been detected with either the 2-Fe (parsley)[15] or 8-Fe (*C. pasteurianum*) proteins which have so far been investigated. No histidines are present in the 8-Fe protein. The amino acid composition of the parsley ferredoxin has not yet been reported, but spinach 2-Fe ferredoxin is known to contain a single histidine at position 90[44] which is conserved in at least five known 2-Fe amino acid sequences.

The trend of rate constants with ionic strength for the $Co(edta)^-$ oxidation of 8-Fe(rr) is in the direction expected for a reaction of two negatively charged reactants. Present understanding of ionic-strength dependences is such that we do not at this stage feel entitled to attempt to estimate the numerical value of the charge on the protein which is relevant to this reaction. The effect of ionic strength on $K$ and $k_{et}$ for the $Co(NH_3)_6^{3+}$ oxidation of the reduced 2-Fe protein has previously been reported,[15] when $k_{et}$ was shown to be independent of an increase in $I$ from 0.10 to 0.50 M.

**Acknowledgment.** We thank Dr. K. Rao for a sample of *C. pasteurianum* ferredoxin for preliminary studies in connection with this study. Discussions relating to statistical kinetic schemes with Dr. J. Chipperfield and Professor J. H. Espenson were particularly helpful. A Royal Society Research Grant for the purchase of an MSE Hi-spin 21 centrifuge is acknowledged, and also loan of equipment for the isolation of the metalloprotein from Dr. R. Herbert. Finally we are grateful to the Science Research Council (London) for postdoctoral (to R.A.H.) and postgraduate (to F.A.A.) awards. This work was carried out at the University of Leeds.

**Supplementary Material Available:** A listing of rate constants, Tables I, II, IV, and V (5 pages). Ordering information is given on any current masthead page.

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# Communications to the Editor

## Origin of Macrocyclic Enthalpy

*Sir:*

The extra stability imparted to complexes of ligands such as polyamines upon cyclization has been termed[1] the macrocyclic effect. The results of Paoletti et al.[2] indicate an equal contribution from enthalpy and entropy to the stabilization of the complex of cyclam (see Figure 1 for nature of ligands) relative to that of 2,3,2-tet with Ni(II). Busch et al.[3] explain the effect in terms of *multijuxtapositional fixedness*, which is a kinetic explanation, and not strictly applicable to thermodynamics. It is generally agreed that the entropy contribution arises from the smaller configurational entropy of the macrocycle, and it is the enthalpy contribution that requires explanation. Margerum et al.[4] suggested that it arose from steric hindrance to solvation of the nitrogen donor atoms, which are oriented in the "hole" in the center of the ligand. Paoletti et al.[2] and McDougall et al.[5] suggested that it arose because the ligand was 'preoriented' or 'prestrained', i.e., the unfavorable energy contribution arising from the increase in $U$, the conformational potential energy, of the ligand, normally accompanying complex formation, was smaller in the macrocycle because it was already in the conformation required for the complex. Metal ions experience a stronger ligand field (LF) from macrocycles than the linear analogues,[2,3] provided that the 'hole' is not too large for the metal ion. Busch et al.[3,6] explained this as constriction of the metal ion by the ligand.

We have reported[7-9] a series of empirical force-field (EFF) calculations on polyamine complexes of Ni(II), and report here calculations aimed at understanding the macrocyclic effect by using the same program, which is that determined by Boyd[10] as modified by Snow.[11] Since there are no low-spin Ni(II) complexes with simple unidentate nitrogen-donor ligands, for example, it is difficult to estimate an 'ideal' low-spin Ni–N bond length. Thus, $U$ was scanned for each complex as a function of ideal, i.e., strain-free initial, M–N, and final adjusted M–N bond lengths from the EFF calculations. All parameters for the EFF were as used previously,[8] except for the varying ideal M–N length.

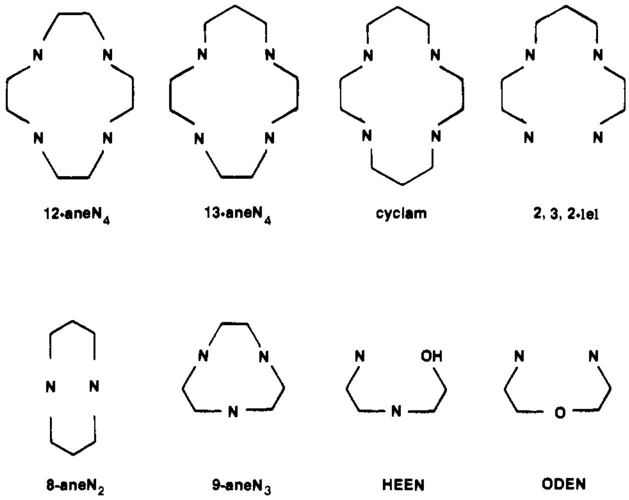

**Figure 1.** Ligands discussed in this paper.

Before discussing the EFF calculations, we will consider constrictive effects. 8-aneN$_2$ shows[12] in its complexes the properties associated with the macrocyclic effect, enhanced stability as

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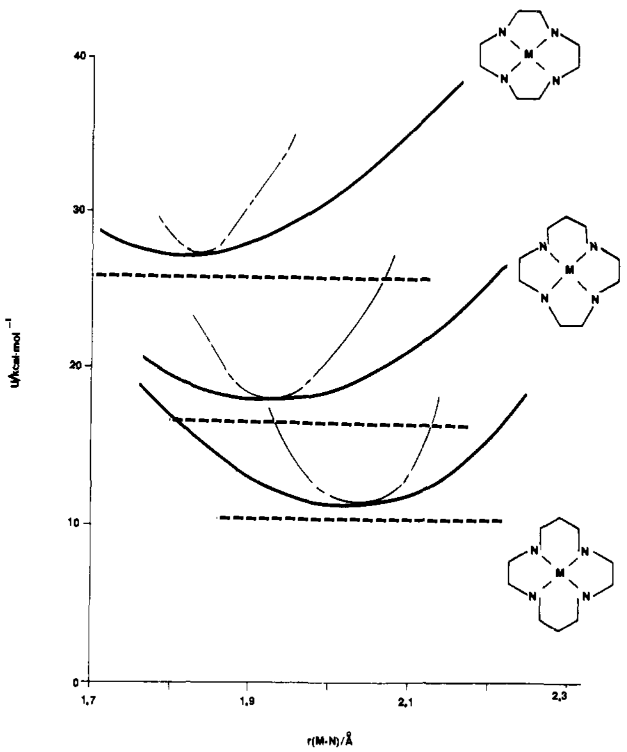

**Figure 2.** Conformational potential energy ($U$) as a function of $r$(M–N), with the ideal (–) and final energy-minimized (– – –) values for complexes of the tetrazamacrocycles indicated. The horizontal lines indicate $U$ for the free ligand corresponding to the complex immediately above it. $U$ for any of the macrocyclic complexes may be determined as a function of $r$(M–N) (ideal), and the distance of the solid line at that point above the broken line for the free ligand gives an indication of the increase in $U$ upon complex formation that will result.

compared with its linear analogue, 1,3-diaminopropane, and high LF strength. While one can imagine cyclam constricting a too large metal ion, it is difficult to see how 8-aneN$_2$, or even 9-aneN$_3$, could achieve this. One would expect that any strain would first be taken up in N–M–N angle deformation. The M–N length best suited for fitting into the hole in 13-aneN$_2$ is 1.92 Å (Figure 2), close to the ideal M–N bond length of 1.9 Å[13] in low-spin Ni(II). The d–d transitions occur at highest energy in this complex, the energy being lower in 12-aneN$_4$ and 14-aneN$_4$. As Fabbrizzi[13] points out, the expected compression in the 12-aneN$_4$ complex has led to a *decrease* in LF strength. Co–N values range from about 1.92 to 2.1 Å for Co(III). However, the Co–N bond length in the Co(III) hexammine is 1.936 Å,[14] and EFF calculations carried out by Snow et al.[11] on polyamine complexes of Co(III) with the Co–N ideal bond length of 1.92 Å satisfactorily account for longer Co–N values in the polyamine complexes examined. EFF calculations[9] on the tris(ethylenediamine) complexes showed that below the M–N bond length of 2.00 Å, interligand repulsion became so large that considerable bond stretching occurred, and the Co–N bond length of 1.98 Å observed cannot be regarded as the ideal value. Both EFF calculations and Dreiding models indicate a best-fit M–N length for 13-aneN$_4$ of 1.92 Å so that the occurrence of the highest LF for Co(III) in its complex with this ligand must be due to a better fit than with cyclam, which requires a M–N distance equal to 2.05 Å, rather than to the suggested[6] compression. Very low LF strengths in large macrocycles are caused by stretching of the M–N bond.

**Table I.** Final Energy Terms from the Empirical Force-Field Calculations[a]

| | L = 2,3,2-tet | | L = cyclam[b] | |
|---|---|---|---|---|
| | L | [NiL-($H_2O$)$_2$]$^{2+}$ | L | [NiL-($H_2O$)$_2$]$^{2+}$ |
| $U_b$[c] | 0.33 | 0.50 | 0.77 | 0.94 |
| $U_{nb}$ | 4.01 | 1.82 | 7.07 | 4.07 |
| $U_\theta$ | 0.54 | 3.31 | 1.67 | 4.41 |
| $U_\phi$ | 0.04 | 1.62 | 0.64 | 1.83 |
| $\Sigma U$ | 4.92<br>(3.0)[d] | 7.25 | 10.15<br>(5.3) | 11.26 |
| $U_L - U_{ML}$ | −2.33 | | −1.11 | |
| $\Delta U_{cyclic} - \Delta U_{noncyclic}$[a] | 1.22 (−1.7) | | | |
| add 1.7 per extra secondary N[e] | 4.6 (0.5) | | | |
| obsd[2] diff in $\Delta H$ between cyclam and 2,3,2-complex | 4.9 | | | |

[a] Differences in the total strain energies and enthalpies of complex formation for various tetraaza ligands and their high-spin Ni(II) complexes, illustrating how the macrocyclic enthalpy may be accounted for in terms of the presence of secondary nitrogens and a lower increase in $U$ upon complex formation for the macrocycle; units are kcal·mol$^{-1}$. [b] γ-Cyclam, which is the most stable conformational isomer. [c] Symbols: $U_b$, contribution from bond stretching or compression; $U_{nb}$ bond-angle deformation; $U_\theta$, bond-angle deformation, $U_\phi$, torsion; $\Sigma U$, total conformational potential energy of molecule/ion; $U_L - U_{ML} = \Delta U$, increase in $U$ of L on forming complex ML($H_2O$)$_2$; $\Delta U_{cyclic} - \Delta U_{noncyclic}$ is the difference in increase of $U$ on complex formation between the macrocycle and its open-chain analogue. [d] Value obtained, ignoring dipoles altogether as described in the text. [e] The Ni-N bond is 1.7 kcal·mol$^{-1}$ more exothermic when N is secondary than primary,[8] so 3.4 kcal·mol$^{-1}$ must be added to obtain the final predicted difference in $\Delta H$ between the Ni(II) complex of cyclam and 2,3,2-tet.

Musker and Hussain[12] suggested that the properties of 8-aneN$_2$ could be due in part to the 'enhanced basicity of the secondary amine—not reduced by intramolecular steric reactions.' We suggested[8] that the M–N bonds where N is secondary were stronger than those where N is primary on the basis of EFF calculations. The EFF could not be used to rationalize observed stability orders in Ni(II) complexes, unless the Ni–N bond with secondary nitrogen was taken as 1.7 kcal·mol$^{-1}$ more stable than with primary nitrogen.[8] To create a secondary nitrogen from a primary one, one causes steric destabilization by either adding alkyl groups or creating another chelate ring. With macrocycles, one creates two extra secondary nitrogens at the expense of only one extra ring. For HEEN and ODEN (see Figure 1), a primary nitrogen is replaced by a secondary one without adding an extra ring, and here the Ni(II) complex of HEEN is 1.6 kcal·mol$^{-1}$ more stable than with ODEN.[8] With the series of primary amines MeNH$_2$, EtNH$_2$, $i$-PrNH$_2$, and $t$-BuNH$_2$, the p$K_a$ is almost invariant while log $K_1$ increases steadily along this series with Ag(I),[15] showing that proton basicity is not always a good guide to inductive effects. Similar effects are found for C-substituted ethylenediamines,[15] from which it is clear why Hald and Rasmussen[16] were not able to rationalize differences in stability of the Co(III) complexes of C(methyl)-substituted ethylenediamines by using EFF calculations where inductive effects are ignored.

The modeling of the electrostatic repulsive forces due to the charges on dipoles is not reliable in EFF calculations.[17] The difference in $U$ between cyclam and its Ni(II) complex is large (see Table I), disregarding both the purely electrostatic component, and also those parameters which treat the dipole as a small atom. Although models had shown that the 'hole' was the correct size, it was not noticed[5] that the orientation of the dipoles was not good for coordination to the metal ion. If the M–N–C bending constants are set at zero, $U$ for the complex drops considerably. The $U$ value for cyclam becomes high (≈18 kcal·mol$^{-1}$) when all the

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interaction parameters, including the electrostatic charge-charge repulsion components according to Allinger,[17] are added. Although not accurate, this indicates that in the gas phase 'prestraining' of the ligand would be caused by dipole-dipole repulsion. An attempt was made to 'solvate' cyclam by placing a hydrogen atom on each nitrogen in place of the dipole, so as to simulate hydogen-bonded water. This gave a $U$ value similar to that obtained with dipoles present so that steric hindrance to solvation must occur as suggested.[4] How much this would decrease strain is not clear, however, since it would expose the dipoles, which might attract the remaining water of solvation more strongly, or else replace steric strain with dipole-dipole repulsion.

We initially[7] chose to neglect the electrostatic charge-charge repulsion component of the dipoles so as to minimize the influence of uncertain parameters on our calculations, but include other parameters relating to interactions with dipoles. This choice of parameters reproduces the macrocyclic enthalpy quite well (Table I), which probably relates to the quenching of purely electrostatic dipole-dipole interactions by solvation in aqueous solution. In summary, the main contributions to the macrocyclic enthalpy are (1) more secondary nitrogen-donor atoms unaccompanied by the usual large increase in $U$ normally associated with changing a primary into a secondary nitrogen and (2) the high value of $U$ for the free ligand, caused by dipole-dipole repulsion in the gas phase, which may be somewhat modified by steric hindrance to solvation in aqueous solution. The high LF strengths of the macrocycles are caused by the secondary nitrogens, and are highest in those into which the metal ion fits best; 13-aneN$_4$ (best-fit ionic radius 1.92 Å) for Co(III) (M-N ideal length 1.92-1.94 Å) and low-spin Ni(II) (M-N ideal length $\sim$1.9 Å), and cyclam (best-fit M-N length 2.05 Å) with high-spin Ni(II) (M-N ideal distance 2.05-2.12 Å).

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## Mechanism of Ejection of Organic Molecules from Surfaces by keV Ion Bombardment

*Sir:*

The application of secondary ion mass spectrometry (SIMS) to the analysis of nonvolatile, high molecular weight compounds is a rapidly evolving research field.[1-4] Of special interest is (i) that the observed fragmentation is similar to other methods of ionizing molecular solids,[5,6] (ii) that the parent ion (± one proton) is often the most intense peak,[1] and (iii) that large organic fragments have been observed to form complexes with a variety of metals,[2] both from the substrate holding the organic film and from metal salts mixed into the organic film. In this work, we examine for the first time the possible nuclear motion in the solid that can lead to the ejection of these fragments and illustrate how they can retain simple and direct structural information about the original surface.

The major question is this: if the primary ion has energy of $\sim$500-10000 eV, how is it possible to eject molecular fragments with individual chemical bonds whose strength is on the order of 2-10 eV? This process should be contrasted to the formation of clusters from the ion bombardment of clean metals and metals with atomic adsorbates such as oxygen. Theoretical calculations have shown that these clusters, which can have from 2 to 12 constituent atoms, form from atoms which eject individually and establish their identity as a cluster in the near surface region.[7-10] As a consequence, the constituent atoms do not necessarily originate from neighboring sites on the surface. Extrapolating this concept to larger molecules seems statistically improbable, suggesting that another mechanism must dominate. From our theoretical calculations, three factors favor ejection of molecular fragments. First, a large molecule has many internal degrees of freedom and can absorb energy from an energetic collision without dissociating. Second, in the more massive framework of a large organic molecule, individual atoms will be small in size compared to a metal atom (Figure 1); thus, it is possible to strike several parts of the molecule in a concerted manner so that the entire molecule moves in one direction. Finally, by the time the organic molecule is struck, the energy of the primary ion has been dissipated so that the kinetic energies are tens of eVs rather than hundreds or thousands of eVs.

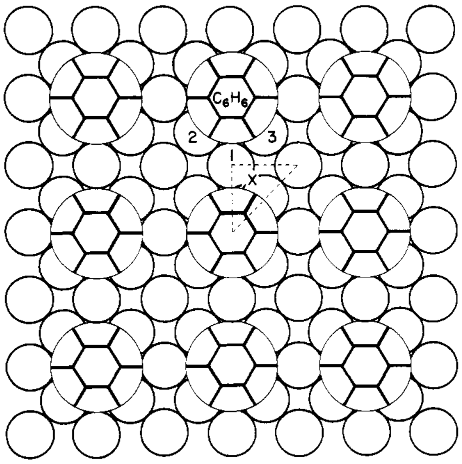

**Figure 1.** Ni(001) with a $c(4 \times 4)$ overlayer of benzene. The dashed triangle is the impact zone for normal incidence ion bombardment. The numbered atoms correspond to the atoms shown in Figure 2. The X is the impact point for the Ar$^+$ ion which leads to the motion depicted in Figure 2. The circle around each C$_6$H$_6$ is the radial extent of the hydrogen position, 2.5 Å.

We choose to examine the ejection mechanisms with a classical dynamics procedure developed in order to study in detail the ion bombardment process and subsequent ejection of particles.[7-12] The model system to be studied is benzene, which forms an ordered $c(4 \times 4)$ overlayer on the (001) face of nickel.[13,14] Briefly, the theoretical model consists of approximating the solid by a finite microcrystallite. In this case, the Ni(001) crystal has three layers of 85 atoms per layer. Nine benzene molecules are then placed on the surface in a $c(4 \times 4)$ configuration. With the assumption of a pairwise interaction potential among all the atoms,[15] Ham-

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