vanadium(II) reductions. The narrow range of second-order rate constants for the various carboxylate complexes indicates that the rate of substitution on vanadium(II) is governed principally by the loss of water and that there is little or no assistance by the incoming carboxylate.

Two of the most significant aspects of the present investigation pertain to the contrast between the rate laws for V^{2+} and Cr^{2+} reduction of *trans*-Co(en)$_2$(HCO$_2$)$_2^+$ and to the relative reactivities of cis and trans isomers toward reduction by V^{2+} or Cr^{2+}. The reaction of *trans*-Co(en)$_2$(HCO$_2$)$_2^+$ with V^{2+} is independent of [H$^+$], whereas the corresponding reaction with Cr^{2+} features an important term first order in H^+.[4] The reactions of the cis or trans isomers with V^{2+} are virtually identical; whereas a strong discrimination between the two isomers is observed for the Cr^{2+} reductions.[4] On the basis of eq 4–6 the contrasting behavior between reductions by V^{2+} and Cr^{2+} is readily understood. For the Cr^{2+} reactions, the electron-transfer step (eq 5) is rate determining. This step requires changes in the inner coordination shells and electronic energy levels of the two metal centers. Since protonation of the trans ligand on the oxidant appears to have the effect of facilitating such changes and lowering the energy of the acceptor orbital,[4,17] it is readily seen that the reactivity of the oxidant will increase on protonation. With V^{2+} as the reductant, the formation of the precursor binuclear complex appears to be rate determining (eq 4), and in this step no major reorganization is necessary in the coordination shell of the oxidant—only the ability of the bridging ligand to substitute into the coordination shell of V^{2+} is important—and consequently it is reasonable that no acceleration by H^+ obtains in this system. The difference in relative reactivities of the isomers toward V^{2+} or Cr^{2+} can also be understood on the basis of the shift in rate-determining step in going from one reductant to the other. In Cr^{2+} reductions, the nature of the ligand trans to the bridging group is important, since it changes the energy of the acceptor orbital and consequently determines the reactivity,[18] whereas for V^{2+} reductions the dissociative character of the rate-determining substitution makes these reactions rather insensitive to the nonbridging ligands in the oxidant.

Of three possible mechanistic classes, namely, inner-sphere rate-determining substitution, inner-sphere rate-determining electron transfer, and outer sphere, the presence or absence of an H^+ path for the trans isomers appears to provide a clear distinction between the two types of inner-sphere mechanisms and may provide a useful, but indirect, criterion for mechanistic assignment. However, until the patterns of hydrogen ion dependences for cis and trans isomers in outer-sphere reactions are established,[19] any mechanistic conclusions based on the presence or absence of an H^+ path must be considered tentative.

[17] A. Haim, *J. Amer. Chem. Soc.*, **86**, 2352 (1964).

[18] P. Benson and A. Haim, *ibid.*, **87**, 3826 (1965).

[19] It has been reported that the reductions of both *cis* and *trans*-Co(NH$_3$)$_4$(CH$_3$CO$_2$)$_2^+$ by the outer-sphere reductant Ru(NH$_3$)$_6^{2+}$ feature a term first order in [H$^+$]: J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964). However, the authors expressed some doubt about the reliability of the H^+-dependent term for the cis complex, and additional work is necessary.

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An Extended Hückel Study of the Conformational Dependence of the Contact Shifts of Ethylenediamine Complexes of Nickel(II)

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Extended Hückel molecular orbital calculations have been used to calculate the ratio of the equatorial to axial contact shifts for puckered ethylenediamine chelate rings in Ni(II) complexes as a function of ring pucker. The results indicate that the ethylenediamine rings are less puckered in H$_2$O solution than they are in the solid state. Substitution of a methyl group on one of the amino nitrogens is found to produce a larger contact shift for the α-methylene group while little effect is noticed at the β-methylene group.

Introduction

Recently there has been considerable interest in the study of the conformations of chelating ligand rings by nmr.[1-4] In particular, for paramagnetic complexes, the nmr contact shift has been observed to be quite different for the axial and equatorial protons of puckered chelate rings,[5,6] even though the rings are in rapid equilibrium between the δ and λ conformations. By the use of careful temperature measurements Reilley and coworkers have been able to extract the equilibrium constants for the conformational $\delta \leftrightarrow \lambda$ interconversion, as well as the contact shifts for the "frozen" conforma-

[1] J. K. Beattie and L. H. Novak, *J. Amer. Chem. Soc.*, **93**, 620 (1971).

[2] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, **10**, 317 (1971).

[3] J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

[4] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184, (1969).

[5] K. I. Zamaraev, Yu. N. Molin, and G. I. Skubnevskaya, *Zh. Strukt. Khim.*, **7**, 798 (1966); *J. Struct. Chem.*, **7**, 740 (1966).

[6] (a) L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **65**, 915 (1969). (b) We will assume the Λ configuration for the metal ion. Since both enantiomers give the same nmr spectrum in the absence of an optically active solvent, our results for a δ ring in a Λ complex also apply to a λ ring in a Δ complex.

tions[7-9] of Ni(II) complexes of ethylenediamine and methyl-substituted ethylenediamines.

From a knowledge of the contact shifts for the axial and equatorial protons of the coordinated ethylenediamine ring one may obtain the electron-proton coupling constants by the use of the equation[10]

$$\frac{\Delta\nu}{\nu_0} = -\frac{A_i(g\beta)^2S(S+1)}{g_n\beta_n(3kT)} \qquad (1)$$

These coupling constants may then be related to the dihedral angle θ_i (see Figure 1) between the C-H bond and the N-Ni bond by the equation[11]

$$A_i = \beta_0 + \beta_2 \cos^2 \theta_i \qquad (2)$$

Using eq 1 and 2 and taking a ratio of the equatorial to axial contact shift, we find

$$\frac{\Delta\nu_{eq}}{\Delta\nu_{ax}} = \frac{\beta_0 + \beta_2 \cos^2 \theta_{eq}}{\beta_0 + \beta_2 \cos^2 \theta_{ax}} \qquad (3)$$

Now, since θ_{eq} and θ_{ax} are functions of the degree of ring pucker, we should be able to obtain the amount of ring pucker for these complexes in solution if we have values for β_0 and β_2. Ho and Reilley approached the problem by assuming $\beta_0 \ll \beta_2 \cos^2 \theta_i$ and by assuming tetrahedral HCH angles, *i.e.*, $\theta_{eq} = \theta_{ax} + 120°$, which allowed them to calculate $\theta_{ax} = 76 \pm 4°$ for $[Ni(en)_3^{2+}]$[8] and 80 ± 2° for $[Ni(N\text{-Meen})(H_2O)_4^{2+}]$.[7] While the assumption $\beta_0 \ll \beta_2 \cos^2 \theta_i$ is very good for small values of the θ_{ax}, it becomes less so as θ_{ax} approaches 90° where $\cos^2 \theta_{ax}$ vanishes. The values of θ_{ax} given above are rather large and $\cos^2 \theta_{ax}$ falls in the range 0.03-0.06 which makes the assumption $\beta_0 \ll \beta_2 \cos^2 \theta_i$ questionable. Further eq 3 has two solutions, one of which corresponds to θ_{ax} less than 90°, while the other corresponds to θ_{ax} greater than 90°.

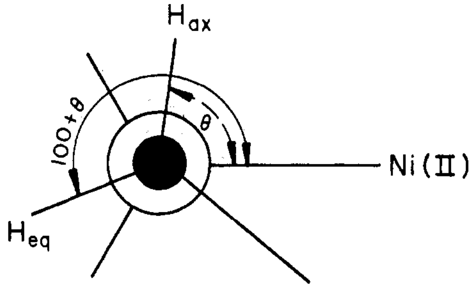

Figure 1.

In order to test eq 3 and to determine which of its two solutions is the correct one, we have carried out extended Hückel molecular orbital calculations on ethylenediamine and *N*-methylethylenediamine as a function of ring pucker. Extended Hückel molecular orbital calculations on free ligands have been used successfully to interpret the contact shifts of Ni(II) complexes in which the unpaired electrons are delocalized in σ orbitals[12] and in particular have been successful for primary alkylamines.[13]

By comparing the experimental ratio $\Delta\nu_{eq}/\Delta\nu_{ax}$ for the frozen conformations to the ratio A_{eq}/A_{ax} obtained from the extended Hückel calculation as a function of θ_{ax}, we hope to determine which two values of θ_{ax} are in agreement with the nmr contact shift results for the ethylenediamine complexes. Then by similar comparisons of the ratios $\Delta\nu_{eq}/\Delta\nu_{me}$ and $\Delta\nu_{me}/\Delta\nu_{ax}$ for the *N*-methyl-substituted ethylenediamine complexes, we hope to establish which of the two values of θ_{ax} produces the best agreement between experimental and calculated results and therefore most likely represents the degree of ring pucker in solution.

Calculations

The extended Hückel molecular orbital calculations were of the self-consistent charge type and were carried out using the same parameters and programs which we have found to be successful in the past.[12,13] The electron-proton coupling constants were evaluated by calculating the values of $[\psi(0)]^2$ in the equation

$$A_i = \frac{K}{2S}[\psi(0)]^2 \qquad (4)$$

using the value of *K* found by Drago and Peterson.[14] It is assumed that, upon formation of the metal-ligand bond, orbitals which correspond to the two nitrogen lone pairs will mix to a small extent with the metal orbitals which contain the unpaired electrons and that this mixing will not significantly alter the *ratios* of the coupling constants. Thus the ratios of the coupling constants calculated for the free ligand will closely approximate the ratios of the contact shifts for the complex.

Since ethylenediamine has two lone pairs, it must have two molecular orbitals which correspond to these two lone pairs. The two highest filled orbitals can be identified as the nitrogen lone-pair orbitals and are close in energy ($\Delta E < 0.3$ eV), so that it is reasonable to assume that they will be equally populated with unpaired electrons. Then the total coupling constant felt at each proton of the methylene group will be the sum of the coupling constants for that proton in each of the two highest filled orbitals.

The bond lengths and angles for the ethylenediamine ligand were those determined from the X-ray structure of $Ni(en)_3SO_4$.[15] The value of θ_{ax} was varied from 65 to 120° in such a way that the C_2 axis passing through the midpoint of the C-C bond and the Ni^{2+} ion was preserved. In the case of *N*-methylethylenediamine, the methyl carbon-nitrogen bond length was 1.48 Å and the methyl group was assumed to be tetrahedral. For the methyl group of *N*-methylethylenediamine, the coupling constants of the three methyl protons were averaged to account for free rotation. Two rotamers of the methyl group were calculated, and no dependence of the average coupling constant of the methyl protons was found. A similar result has been reported for methylamine.[13]

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[7] F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969).

[8] F. F.-L. Ho and C. N. Reilley, *ibid.*, **42**, 600 (1970).

[9] R. F. Evilia, D. C. Young, and C. N. Reilley, *Inorg. Chem.*, **10**, 433 (1971).

[10] B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **87**, 2372 (1965).

[11] C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

[12] R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970).

[13] R. J. Fitzgerald and R. S. Drago, *ibid.*, **90**, 2523 (1968).

[14] R. S. Drago and H. Peterson, *ibid.*, **89**, 3978 (1967).

[15] M. U. Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970). The C-H bond length in this structure is 1.11 Å. A check calculation shows that a C-H distance of 1.09 Å produces the same results, and we have used the 1.11-Å distance.

The final parameter in this work is the choice of the HCH angle. One's first guess would be the tetrahedral value of 109.5°. However, examination of crystal structures of ethylenediamine complexes in which the protons have been located and refined shows that the HCH angle has been significantly compressed, presumably due to steric interactions which occur as a result of ring puckering. For example, in the structure of $Ni(en)_3SO_4$[15] the HCH angle is 93° and the HNH angle is 97°, both of which are significantly less than tetrahedral. Further, the molecule bis[2,2'-iminobis(acetamidoxime)]nickel(II) has puckered five-membered chelate rings in which both donors are nitrogen. This molecule has two crystallographically independent methylene groups adjacent to a coordinated alkylamine, and the HCH angles are 92 ± 3 and 99 ± 2°.[16] In the structure of $Cu(en)_3SO_4$,[17] in which the ethylenediamine rings are not as puckered as they are in $Ni(en)_3{}^{2+}$, we find that the HCH angle is 105 ± 3° while the HNH angle is 103 ± 4°. While both of these values are close to tetrahedral, they are still slightly smaller than tetrahedral. From these data we conclude that the HCH angle is not tetrahedral. We have used the value 93° found for $Ni(en)_3SO_4$.[18] Choice of some other value which would be more in keeping with chemical dogma would have to be considered arbitrary.

Corey and Bailar, in a classic paper,[19] were able to predict the stable conformation of ethylenediamine complexes by finding the conformation in which interatomic repulsions are minimized. The important interactions turn out to be those which involve a hydrogen on one chelate ring and another hydrogen on another chelate ring. This model has since been refined by considering various van der Waals repulsive functions and including entropy considerations.[2,20,21] In addition, almost every independent geometrical parameter involved in the chelated ring has been varied in order to determine the most stable geometry of the ring. Remarkably all of this work has assumed tetrahedral HCH and HNH angles. Certainly this sort of analysis will be very sensitive to the choice of these angles, and in view of the X-ray results, which do not show tetrahedral angles, the current results of those studies may be suspect.

Results

In the case of ethylenediamine the extended Hückel molecular orbital calculation yields two orbitals with energies between −11.5 and −11.8 eV which are the two highest filled orbitals and which can be identified as the nitrogen lone pairs. The next filled orbital lies at about −14.00 eV and can be considered to be mostly C–N and C–C bonding. We therefore have confined our attention to the two highest filled orbitals. Each nitrogen atom makes a contribution of 40–45% to each of these orbitals with the remainder of the orbital being composed of small coefficients from the other atoms. Since the molecule possesses a C_2 axis, we would expect that the two molecular orbitals which correspond to the nitrogen lone pairs would appear as a symmetric and antisymmetric set,[22] and this expectation is fulfilled by the calculation. As we change the value of θ_{ax} from 65 to 120°, the energy of the symmetric orbital rises from −11.77 to −11.66 eV, while the energy of the antisymmetric orbital falls from −11.49 to −11.70 eV. Therefore the two orbitals cross as a function of ring pucker with the symmetric orbital being the most stable at $\theta = 65°$ and the antisymmetric orbital being most stable at $\theta = 120°$. Hoffman has discussed the criteria for the ordering of symmetric and antisymmetric energy levels of this type but has not reported a change in their ordering as a function of the backbone conformation.[22] Although the two nitrogen lone-pair orbitals are not quite at the same energy, we have calculated the coupling constants on the assumption that equal amounts of unpaired electron are delocalized in both the symmetric and antisymmetric orbital.

In the case of N-methylethylenediamine the C_2 axis has been destroyed and the nitrogen lone-pair orbitals can no longer be identified as symmetric and antisymmetric. Instead they are easily recognized as being localized on either the primary or secondary amine. The secondary amine lone pair has an energy of −11.05 eV and is 88% localized on the secondary amino nitrogen with a contribution of only 1% from the primary amine. The primary amine lone pair has an energy of −11.65 eV, which is very similar to that of ethylenediamine, and is 90% localized on the primary amine with a contribution of less than 1% from the secondary amine. The difference in energy of these two lone pairs ($\Delta E = 0.60$ eV) is in good agreement with the difference in ionization potentials ($\Delta IP = 0.73$ eV) of ethylenediamine and N,N'-dimethylethylenediamine estimated by Yokoi and Isobe.[23]

If we consider the methyl group to be located at position 1 of Figure 2 we can then consider the contribution of each lone pair to the coupling constants at positions a, b and c, d. If we do so, we find that the highest filled MO, *i.e.*, the secondary amine lone pair, makes only a negligible contribution at d and c and is solely responsible for the coupling at a and b. For the other lone pair the situation is reversed so that the only significant coupling is with d and c. Further the coupling constants calculated for d and c from the primary amine lone pair are the same as the total coupling constants obtained from both lone pairs of ethylenediamine at the same value of θ_{ax}. Therefore, in the case of N-methylethylenediamine, protons d and c should have contact shifts identical with those of ethylenediamine, while protons a and b should have

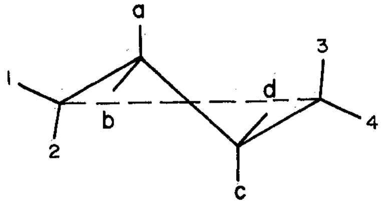

Figure 2.

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[16] D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1865 (1970).

[17] D. L. Cullen and E. C. Lingafelter, *ibid.*, **9**, 1858 (1970).

[18] The projection of 93° into a plane perpendicular to the C–N bond gives a value of 100° as indicated in Figure 1.

[19] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[20] J. R. Gollogy and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

[21] J. R. Gollogy and C. J. Hawkins, *ibid.*, **9**, 576 (1970).

[22] R. Hoffman, F. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

[23] H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jap.*, **42**, 2187 (1969).

contact shifts identical with those of *N,N'*-dimethylethylenediamine.

The ratio A_{eq}/A_{ax} as obtained from our calculations on ethylenediamine is plotted in Figure 3 as a function of θ_{ax}. Since the A_{eq}/A_{ax} ratio for protons a and b of *N*-methylethylenediamine does not fall on the same plot, we have also included our results for these protons.

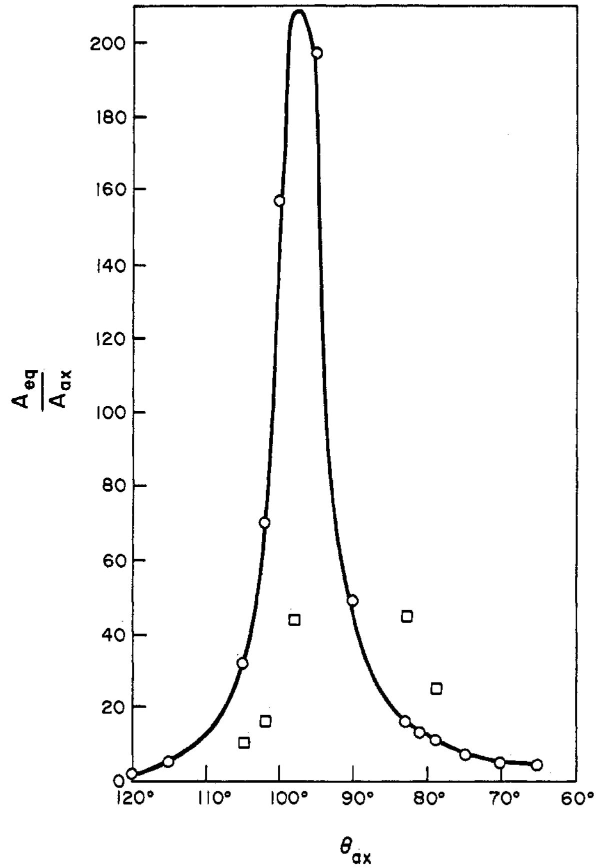

Figure 3.—Plot of the calculated ratio A_{eq}/A_{ax} against θ_{ax}: ○, ethylenediamine; □, protons a and b of *N*-methylethylenediamine.

We have also investigated the effect of the HCH angle on the plot in Figure 3. We find that increasing the HCH angle shifts the plot to smaller values of θ_{ax}. As a rough guide, an increase of 1° in the HCH angle shifts the maximum in Figure 3 about 1° toward smaller θ_{ax}.

Discussion

If we use our calculated values of A_{ax} and A_{eq} at $\theta_{ax} = 90°$, we can solve for the values β_0 and β_2 in eq 2. In that case we find $\beta_0 = 0.47$ G and $\beta_2 = 22.2$ G. The plot obtained from the molecular orbital calculation differs from that obtained from eq 3 in several details. The most important difference is that the MO plot peaks at 97° while eq 3 reaches a maximum at 90°. Similar deviations from eq 2 have recently been reported for alkyl radicals which have been distorted from tetrahedral geometry.[24] Since the chelated ethylenediamine molecule has considerable deviation from tetrahedral geometry, we have decided to rely on the curve obtained from the MO calculations rather than that obtained from eq 3.

For the complex $Ni(en)_3^{2+}$ Ho and Reilley[8] reported contact shifts of -162 ± 5 ppm for the equatorial protons and -10 ± 5 ppm for the axial protons in a "frozen" conformation. Thus the experimental ratio A_{eq}/A_{ax} falls between 33 and 11, using the assigned error limits. From Figure 3 we can see that this range of ratios cuts our calculated curve at two values of θ_{ax}, *i.e.*, $\theta_{ax} = 79–88°$ and $\theta_{ax} = 105–111°$.

Ho and Reilley have also reported "frozen" conformation contact shift values for the *N,N'*-dimethylethylenediamine complex.[7] The values reported are $\Delta\nu_{eq} = -188 \pm 2$ ppm and $\Delta\nu_{ax} = 6 \pm 2$ ppm and so the range of experimental ratios $\Delta\nu_{eq}/\Delta\nu_{ax}$ is 23–47. Using the plot for *N*-methylethylenediamine in Figure 3 we find that this experimental ratio arises when θ_{ax} lies in the region 78–84° and also when θ_{ax} is 97–100°. Thus the amount of ring pucker is either the same for both chelate rings or differs by a small amount, depending on which of the two solutions above is the correct one. We can determine which of these two solutions is the correct one by comparing the calculated ratios A_{eq}/A_{me} and A_{me}/A_{ax} with the observed contact shift ratios for the *N,N'*-dimethylethylenediamine complex. In order to do this we must have a value for the contact shift of the methyl groups of *N,N'*-dimethylethylenediamine in a frozen conformation.

Ho and Reilley[7] have published the observed contact shifts for the complex in question, but these shifts are the result of a rapid equilibrium which averages the shifts of the frozen conformations. We have calculated the coupling constant of the methyl group in both axial and equatorial positions at values of $\theta_{ax} = 80$ and 110° and we find that the methyl coupling constant is not very sensitive with respect to the orientation of the methyl group to the ring, with all values falling in the range 6.5–7.0 G. The experimental results of Ho and Reilley[7] lend support to this conclusion in that the *dl* and meso forms of the ligand show methyl resonances at -136 and -131 ppm, respectively. Since the meso form has one axial and one equatorial methyl group, it has no preference for either ring conformation and therefore the observed signal represents an average of the axial and equatorial shifts. The *dl* form has 4 times as many equatorial as axial groups on the time average, and hence its shift represents an average which is greatly weighted toward the "frozen" conformation in which the methyl group is equatorial. Therefore the contact shift for the "frozen" equatorial methyl group must be about -136 ± 3 ppm.

The experimental ratio $\Delta\nu_{eq}/\Delta\nu_{me}$ thus spans the range 1.34–1.43 while the ratio $\Delta\nu_{me}/\Delta\nu_{ax}$ covers the range 16–35. From our calculations of *N*-methylethylenediamine with $\theta_{ax} = 98°$ we find $A_{eq}/A_{me} = 12.8/6.8 = 1.9$ and $A_{me}/A_{ax} = 6.8/0.32 = 21$ which is reasonable agreement. On the other hand when $\theta_{ax} = 79°$ we find $A_{eq}/A_{me} = 17.0/6.8 = 2.5$ and $A_{me}/A_{ax} = 6.8/1.6 = 4$, which is much worse agreement. We are thus led to the conclusion that the correct value of θ_{ax} for *N,N'*-dimethylethylenediamine is 97–100°, which is not the crystal structure result for ethylenediamine. We can explain these results by postulating a less puckered ring for *N,N'*-dimethylethylenediamine than for ethylenediamine or by postulating a less puckered

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[24] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

ring for ethylenediamine in solution than in the solid state. We favor the latter explanation.

We have considered the possibility that the above conclusion could be dependent upon our choice of semiempirical molecular orbital calculations. In order to check this possibility, we have carried out INDO calculations on N-methylethylenediamine using the same structural parameters as we used in the extended Hückel calculations. The results are quite similar to the extended Hückel results and lead to the same conclusion regarding θ_{ax}. For example the INDO results at $\theta_{ax} = 98°$ are $A_{eq}/A_{me} = 2.0$ and $A_{me}/A_{ax} = 10.5$ while at $\theta_{ax} = 79°$ $A_{eq}/A_{me} = 2.6$ and $A_{me}/A_{ax} = 6.0$.

We have also examined the effect of our choice of the HCH angle upon the various ratios used to determine the value of θ_{ax} in solution. We have carried out calculations with HCH angles of 102 and 109.5° and in both cases the ratios for the large angle ($\sim$100°) are in closer agreement with the experimental ratios than are those for the small angle ($\sim$80°). Therefore the conclusion regarding the value of θ_{ax} in solution holds independently of the choice of HCH angle.

The value of θ_{ax} in the solid state can be determined from the crystal structure by calculating the appropriate dihedral angle. From the crystal structure of $Ni(en)_3SO_4$,[15] in which the hydrogen atoms are observed, we find $\theta_{ax} = 83°$. The value of θ_{ax} in $Ni(en)_3(NO_3)_2$[25,26] has been widely quoted as 64°,[5,7-9] but unfortunately this value is in error. The angle θ_{ax} is the dihedral angle formed between the planes defined by NiNC and by NCH_{ax}. Swink and Atoji did not report this angle since they did not locate the H atoms, but they did report the angle between the planes defined by NiNC and NCC; they reported this latter angle as 56°. If we assume tetrahedral angles about the carbon, we are led to the incorrect value of 64° for θ_{ax}. In order to carry out our molecular orbital calculations, it was necessary for us to determine a set of atomic coordinates in a cartesian coordinate system. This is easily done using standard crystallographic programs. When we used these cartesian coordinates to calculate the dihedral angle quoted above as 56°, we found a value of 35°. Therefore the correct value of θ_{ax} is 85° in $Ni(en)_3(NO_3)_2$, not 64°, if we assume tetrahedral HCH angles. However, if we assume the 93° HCH angle, then θ_{ax} is 95° in $Ni(en)_3(NO_3)_2$.

It is of interest to compare these solid-state values with the value we have determined in solution and with the hydrogen bonding of the cation. It has been suggested that hydrogen bonding is important in the determination of the conformation[26] or degree of ring puckering[2,27] for this type of complex. Some recent crystal structures, as well as the results reported here, support this argument. In order to discuss this data let us introduce the angle ω, the dihedral angle between the planes defined by N_1–C–C and C–C–N_2, as a measure of ring pucker. In the salt $Ni(en)_3SO_4$, ω has a value of 56° and the shortest amino hydrogen–sulfate oxygen distance is 1.98 Å.[15] In the salt $Ni(en)_3(NO_3)_2$, ω has a value of 48° and the shortest amino hydrogen–nitrate oxygen distance is 2.25 Å.[25] This evidence suggests that as the hydrogen bonding becomes weaker, the ethylenediamine rings become less puckered. Our data indicate that in solution θ_{ax} is about 100°, which corresponds to an ω value of 40°. While it is not possible to evaluate the strength of the hydrogen bonds formed between the cation and the solvent, the ring-puckering data would indicate that these bonds may be weaker than they are in the solid state. This suggests that the degree of ring pucker should be solvent dependent, and as the solvent becomes less hydrogen bonding, the chelate rings should become less puckered. We are currently attempting to test this hypothesis experimentally.

It is also interesting to consider the amounts of spin which must be delocalized onto these ligands in order to produce the observed shifts. From eq 1 we can calculate the observed coupling constants for these complexes, which will be some fraction of the coupling constants which we have calculated for the free ligand. This fraction will then correspond to the amount of unpaired electron which has been delocalized onto the ligand. For ethylenediamine the experimental equatorial contact shift is −162 ppm for a "frozen" conformation, and this corresponds to coupling constant of 0.705 G. For the free ligand at $\theta_{ax} = 105°$ we calculate a total equatorial coupling constant of 16.4 G, or about 8.2 G from each lone pair, and from these numbers we conclude that 4.3×10^{-2} electron is delocalized into each of the nitrogen lone pairs. This number compares very favorably with the 4.2×10^{-2} electron which we found to be delocalized in the pyridine σ orbital in $[Ni(4\text{-}Mepy)_6{}^{2+}]$.[12] In the case of N,N'-dimethylethylenediamine the contact shift for the equatorial proton is −188 ppm or 0.816 G. At $\theta_{ax} = 98°$, our total calculated coupling constant is 12.6 G (*i.e.*, 6.3 G from each lone pair) so that 6.5×10^{-2} electron is delocalized into each lone-pair orbital. Thus we find more delocalization into the secondary amine lone pair, than into the primary amine lone pair. This is consistent with the energy of the secondary amine lone pair in N-methylethylenediamine occurring at a higher energy than the primary amine lone pair, since the higher energy would place it closer in energy to the half-filled metal orbitals, which would allow greater mixing. Our result is consistent with the epr results of Yokoi and Isobe,[23] who found that the amount of covalency in the metal–ligand bond increased with increasing methyl substitution for ethylenediamine complexes of Cu(II). Thus both nmr and epr results confirm the expected increase in metal–ligand bond strength due to the inductive effect of the methyl group. The fact that the formation constants do not follow this order has been pointed out and discussed by other workers.[7,23]

The results for the N,N'-dimethylethylenediamine complex, coupled with our finding that the lone pairs of N-methylethylenediamine are independent, would lead us to assign the most downfield peak in complexes of N-methylethylenediamine to proton b in Figure 2. Ho and Reilley have assigned this signal to proton d.[7] Our assignment gains strength from the following analysis. The observed resonance position for an

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(25) L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13**, 639 (1960). A reviewer has pointed out that several errors have been reported in this reference. Some of those errors are corrected in ref 26. The reviewer suggests that anyone who wishes to use molecular parameters from this reference must calculate them himself starting with the reported fractional coordinates, and we concur.

(26) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(27) J. K. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970).

equatorial proton undergoing rapid exchange between two sites is given by

$$\Delta\nu_{\text{obsd}} = X_\delta \Delta\nu_{\text{eq}} + X_\lambda \Delta\nu_{\text{ax}}$$

Here $\Delta\nu_{\text{eq}}$ and $\Delta\nu_{\text{ax}}$ are the contact shifts for a given proton in the "frozen" equatorial and axial environments and X_λ and X_δ are the mole fractions of the chelate rings in the λ and δ conformations.[28] The methylene protons in the Ni(II) complex of *N*-methylethylenediamine are observed at -112 and -127 ppm.[7] Our results suggest that the "frozen" contact shifts for the primary amine would be the same as for the ethylenediamine complex, namely, $\Delta\nu_{\text{eq}} = -162$ and $\Delta\nu_{\text{ax}} = -10$ ppm, and that the primary amine proton would be the one observed at $\Delta\nu_{\text{obsd}} = -112$ ppm. Making these substitutions and remembering $X_\lambda = 1 - X_\delta$, we can calculate $X_\delta = 0.66$ from eq 4. This means that twice as many methyl groups are in equatorial as axial positions. Ho and Reilley reported 4 times as many equatorial as axial methyl groups for *N,N'*-dimethylethylenediamine, which has twice as many methyl groups and hence greater preference for the δ conformation. Using this value of X_δ and assuming that the shift of the axial proton for the secondary amine is -6 ppm, as it is in *N,N'*-dimethylethylenediamine, we can write eq 4 for the signal at -127 ppm with only $\Delta\nu_{\text{eq}}$ as an unknown. We then find $\Delta\nu_{\text{eq}}$ for the secondary amine is -189 ppm which is in excellent agreement with the -188 ppm reported by Ho and Reilley[7] for *N,N'*-dimethylethylenediamine. Thus the assignment of the peak observed at -127 ppm to proton b is consistent with the reported shifts of ethylenediamine and *N,N'*-dimethylethylenediamine and our calculations.

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[28] When a ring changes from the δ to the λ conformation, a proton is moved from an equatorial to an axial position.

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Ligand Binding by Metalloporphyrins. III. Thermodynamic Functions for the Addition of Substituted Pyridines to Nickel(II) and Zinc(II) Porphyrins

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Free energy, enthalpy, and entropy changes for the addition of substituted pyridines to various nickel and zinc porphyrins have been determined in chloroform and benzene solutions. The stoichiometry of the reactions indicates formation of mono pyridinates with some nickel porphyrins and bis pyridinates with others, the latter requiring very high ligand concentrations. In contrast to the situation in iron porphyrin pyridinates, the π-acceptor ability of the ligands has little effect on the enthalpy of reaction of the nickel and zinc complexes. The dependence of the enthalpy of reaction on ligand basicity is strong for nickel porphyrin pyridinates in chloroform and for the corresponding zinc complexes in benzene but is less noticeable when these solvents are reversed. Specific solute–solvent interactions are suggested to explain this behavior. It is suggested that in nickel porphyrins hydrogen bonding between chloroform and the solvent-accessible side of the five-coordinate nickel porphyrins is very sensitive to changes in the metal–ligand bond strength on the opposite side of the porphyrin plane. In agreement with the expectation that zinc compounds will more readily accommodate the forced square-pyramidal structure than nickel, the changes attributed to hydrogen-bond effects in chloroform were found to be smaller in the zinc than the nickel compounds studied. In this respect the zinc porphyrins more closely resemble the iron(II) porphyrins which have been studied previously than do the nickel porphyrins and interactions between the aromatic porphyrin plane and benzene are thought to be more important.

Previous work[2,3] on the addition of substituted pyridines to iron(II) porphyrins has indicated that measurements of free energy, enthalpy, and entropy changes are necessary to an adequate understanding of the effect of substituent and reaction condition variations on the binding forces involved. Large and variable entropy changes accompany the formation of the complexes with iron(II) porphyrins, rendering conclusions based on stability constants alone invalid and in some cases misleading.

The iron(II) porphyrins are extremely sensitive to solvent change as well as to substitution on both the porphyrin and pyridine and it is important to determine whether this sensitivity is characteristic of the metalloporphyrin–pyridine system in general or whether it is confined to the Fe(II) complexes.

In addition to an investigation of the stoichiometry of nickel porphyrin addition reactions, this paper reports the thermodynamic parameters of the reactions between substituted pyridines and various nickel and zinc porphyrins in chloroform and benzene.

Experimental Methods

Methods for the preparation of most of the porphyrin esters used have been described previously.[2] α,β-Dinitrodeuteroporphyrin dimethyl ester was prepared by the method described by Caughey[4a] and mesotetraphenylporphine by the Rothemund procedure.[4b] The method of Caughey was used for the insertion

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[1] (a) University of Newcastle. (b) Avondale College. (c) CSIRO.

[2] S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **93**, 2153 (1971).

[3] S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *ibid.*, **92**, 2991 (1970).

[4] (a) W. S. Caughey, W. Y. Fujimoto, and B. P. Johnson, *Biochemistry*, **5**, 3830 (1966); (b) P. Rothemund and A. R. Menotti, *J. Amer. Chem. Soc.*, **63**, 267 (1941); P. Rothemund and A. R. Menotti, *ibid.*, **70**, 1808 (1948).