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(55) Although we find five coordination attractive, with three good donor ligands required for an $SnCl_3$ cation to coordinate CO, it is perfectly possible that **19** and the insertion intermediate in reaction 34 undergo substantial dissociation of Ph_3P to give analogous four-coordinate complexes. As we are past the rate-determining step in the kinetics, nothing definite can be said on this point. The rate is inhibited by extra Ph_3P, but that merely reflects inhibition of the weak substrate binding in eq 31. Loss of one Ph_3P from **20** would have the advantage that insertion (reaction 34) could proceed via a four-coordinate intermediate as preferred by Thorn and Hoffmann,[44] whereas **20** as written would appear to require insertion from a trigonal bipyramidal structure with trans diaxial phosphines—a process which Thorn and Hoffman view unfavorably.[44]

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(57) It is difficult to say how general such regioselectivity is, as palladium hydrides are almost never stable enough to be observable, and their platinum analogues generally undergo reactions other than insertion with terminal acetylenes. On purely electronic grounds, studies with asymmetrically disubstituted acetylenes suggest that the opposite result may sometimes be preferred.[58] However, a strong steric preference for the direction of addition shown in reaction 37 is generally expected: Heck has assumed such regioselectivity in writing a mechanism for the Pd-catalyzed dimerization of phenylacetylene,[59] hydride complexes of early transition metals display such regioselectivity in adding to terminal acetylenes,[60] and $[HPt(acetone)(PR_3)_2]^+PF_6^-$ shows analogous regioselectivity in reacting with terminal olefins, giving exclusively primary alkyl complexes.[61]

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Enthalpies of Formation and Solution of Macrocyclic and Noncyclic Tetraaza Ligands. Origins of the Enthalpy Term in the Macrocyclic Effect

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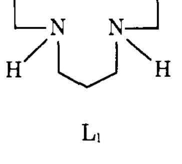
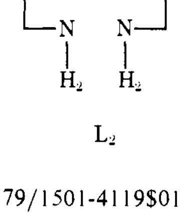
Abstract: The heats of combustion of 1,4,8,11-tetraazacyclotetradecane and 1,4,8,11-tetraazaundecane have been determined by bomb calorimetry and the standard enthalpies of formation derived (−27.7 ± 0.5 and −23.9 ± 0.5 kcal mol^{-1}, respectively). The enthalpies of solution of the same two compounds have been determined (−2.5 and −15.8 kcal mol^{-1}, respectively) in 0.5 M NaOH. The gas-phase $\Delta H_f°$ values of the ligands have been estimated and the macrocyclic enthalpy term, which has been determined previously for both Cu(II) (−4.7 kcal mol^{-1}) and Ni(II) (−4.9 kcal mol^{-1}) with these ligands, has been compared with the estimated difference in solvation energies of the two ligands (4.6 kcal mol^{-1}). A general discussion on the terms contributing to the macrocyclic enthalpy is presented.

Introduction

The macrocyclic effect, in which the stability of metal complexes is enhanced by coordination to macrocyclic as opposed to analogous noncyclic ligands, was first reported in 1969.[3] Since then, a great deal of interest has been shown in the thermodynamic origins of this extra stability, particularly with tetraaza ligands. Early conflicting studies assigned the extra stability to wholly entropy[4] or wholly enthalpy[5] terms based on enthalpy values obtained from temperature-dependent stability constant studies. More recently,[6-9] direct calorimetric determinations of enthalpy values have shown that the entropy term is always favorable and that the enthalpy term is dependent on the matching of the size of the macrocyclic ligand aperture to that of the metal ion. For octahedral complexes of copper(II) and nickel(II) with the title ligands L_1 and L_2, ΔH values for the metathetical reaction


L_1


L_2

$$ML_2(aq)^{2+} + L_1(aq) \rightarrow ML_1(aq)^{2+} + L_2(aq) \qquad (1)$$

which represents the macrocyclic effect are −4.7[8] and −4.9[9] kcal mol^{-1}, respectively.

Calorimetrically one determines the enthalpy change associated with the formation reaction

$$M^{2+}(aq) + L(aq) \rightarrow ML^{2+}(aq) \qquad (2)$$

and the difference between these enthalpy values for different ligands (L_1 and L_2) gives the macrocyclic enthalpy associated with reaction 1. It can therefore be seen that this macrocyclic enthalpy contains terms associated with *both* the metal complexes *and* the free ligands in solution.

If there is no enthalpy difference between the free ligands in solution, the macrocyclic enthalpy is only a measure of the energy difference between the macrocyclic and the noncyclic

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Table I. Auxiliary Data (atm = 101.325 kPa)

compd	M, g mol^{-1}	ρ, g cm^{-3}	$(\delta e/\delta p)_T$,[a] J atm^{-1} g^{-1}	C_p, J K^{-1} g^{-1}
polythene	13.344	0.90	0.0293	1.94
filter paper	27.198	1.50	negligible	1.68
L_1	200.326	0.73	(0.0209)	1.87
L_2	160.262	0.97	(0.0209)	3.42

[a] Values in parentheses are estimates.

complex. The purpose of this work is to investigate the magnitude of the enthalpy difference between the ligands in solution, thereby gaining further insight into the thermodynamic origins of the macrocyclic effect.

Experimental Section

A. Reagents. L_1, 1,4,8,11-tetraazacyclotetradecane (Strem Chemicals), was purified by double recrystallization from acetonitrile and finally zone refined (50 passes) in a sealed tube under dry nitrogen. The melting temperature against time curve obtained by differential scanning calorimetry (Perkin-Elmer DSC2) indicated a purity of better than 99.98 mol % and a fusion temperature of 464.5 K. A scanning rate of 2.5 K min^{-1} was used in the determination of the purity and the melting curve was evaluated using a computer program similar to that described by Marti.[10]

L_2, 1,4,8,11-tetraazaundecane (Eastman-Kodak), was purified by distillation in vacuo and collecting the fraction distilling at 185 °C and 35 mmHg. This material was stored in a sealed ampule prior to combustion. GLC analysis of the sample just before the series of combustions using two different columns failed to show any impurity peaks. Under similar conditions it was possible to determine impurity levels of 0.03 mol % of water which is, of course, the least desired impurity.

B. Bomb Calorimetry. The calorimeter (internal volume 0.200 dm^3), its calibration, and the auxiliary equipment have been described previously.[11] It was used with 1.00 cm^3 of water initially in the bomb and an initial oxygen pressure of 30 atm at 298.15 K. The oxygen was purified by passage over heated cupric oxide to remove combustible material. The samples of L_2 for combustion were enclosed in polythene,[12] care being taken to work only under dry nitrogen during sample transfer.

The standard specific energies of combustion of the polythene and filter paper fuse were −46.350 and −17.225 kJ g^{-1}, respectively. The polythene and filter paper fuse analyzed as $C_{0.943}H_{2.00}$ and $CH_{1.686}O_{0.843}$, respectively. The experimental results are based on 1975 atomic weights.[13]

The quantities in Table I were used to reduce weighings to masses, convert the energy of the actual bomb process to that of the isothermal process, and reduce to standard states.[14] The specific heat capacities were determined on the DSC using sapphire as a standard.[15]

After combustion the bomb solution and several washings were combined and diluted to 0.100 dm^3. The solution was then analyzed for nitric acid by both the UV spectroscopic method[11,16] and potentiometric titration with standard sodium hydroxide. Both methods yielded, within the limits of experimental error (±0.2%), the same concentration of nitric acid as in the case of the triphenylamine combustions.[17] The combustion products were checked for CO and other products of incomplete combustion, but none was detected. No nitrous acid was formed during the series of combustions.

C. Solution Calorimetry. The enthalpies of solution of ligands L_1 and L_2 were determined by an LKB reaction and solution calorimeter (8700-1) using an ampule technique. A few milligrams of the component of the reaction being studied was sealed in a glass ampule (1 cm^3). The sealed ampule was now placed in the ampule holder and immersed in the reaction vessel containing 80 cm^3 of 0.5 M NaOH solution.

The system was left to stand until thermal equilibrium had been attained, and the reaction started by breaking the ampule.

Electrical calibration was made after each run. Four runs were carried out for each of L_1 and L_2, and the average enthalpies of solution are reported in Table V.

The solid L_1 dissolved completely within less than 1 min, giving an absolutely clear solution.

Table II. Summary of Typical Calorimetric Experiments at 298.15 K[c]

	L_1	L_2
m(compd)/g	0.417 221	0.395 326
m(polythene)/g		0.035 300
m(filter paper)/g	0.008 424	
$n_i(H_2O)$/mol	0.055 34	0.055 34
$\Delta R/\Omega$	1.1232	1.1259
$-\Delta R\epsilon$(calor)/cal[a]	−3630.00	−3638.73
$-\Delta R\epsilon$(cont)/cal	−10.50	−10.58
$\Delta E(HNO_3)$/cal	1.17	11.25
ΔE(ign)/cal[b]	0.25	0.30
ΔE_w/cal	1.12	1.25
$-\Delta e_c°$(compd)/kcal g^{-1}	8.6364	8.2096

[a] ϵ(calor) denotes the energy equivalent of the calorimeter, (3.23184 ± 0.0012) kcal Ω^{-1}. [b] Items 81–85, 87–90, 93, and 94 of the computation form of ref 14, correction to standard states. [c] The symbols and abbreviations are those of ref 18 except as noted (cal = 4.184 J).

Table III. Summary of Experimental Results at 298.15 K

	$-\Delta e_c°$(compd)/kcal g^{-1} (cal = 4.184 J)	
	L_1	L_2
	8.6364	8.2096
	8.6369	8.2103
	8.6385	8.2136
	8.6343	8.2081
	8.6375	8.2109
mean	8.6367	8.2105
std dev	0.0007	0.0009

Table IV. Derived Molar Values for Condensed State at 298.15 K (cal = 4.184 J)

compd	$-\Delta E_c°$/kcal mol^{-1}	$-\Delta H_c°$/kcal mol^{-1}	$-\Delta H_f°$/kcal mol^{-1}
L_1	1730.2 ± 0.5	1732.6 ± 0.5	27.7 ± 0.5
L_2	1315.8 ± 0.5	1317.6 ± 0.5	23.9 ± 0.5

Results

A. Standard Enthalpies of Formation from Combustion Calorimetry. Results for typical combustion experiments for both compounds are summarized in Table II. The symbols and equations used are as defined in ref 18 with $\Delta E(HNO_3)$ denoting the energy of decomposition of the nitric acid formed in the combustion. Values of $\Delta E_c°/M$, the specific energy of the idealized combustion reaction, for all experiments are given in Table III. The generalized combustion reaction is represented by the equation

$$C_aH_bN_c(\mathrm{l\ or\ c}) + (a + b/4)O_2(g) = aCO_2(g) + b/2H_2O(l) + c/2N_2(g) \quad (1)$$

Derived values of the standard molar energy of combustion $\Delta E_c°$, the standard molar enthalpy of combustion $\Delta H_c°$, and the standard molar enthalpy of formation $\Delta H_f°$ of the compounds in the condensed state are given in Table IV. Values of $\Delta E_c°$ and $\Delta H_c°$ refer to eq 1 and values of $\Delta H_f°$ refer to the equation

$$aC(\mathrm{c,\ graphite}) + b/2H_2(g) + c/2N_2(g) = C_aH_bN_c\ (\mathrm{l\ or\ c}) \quad (2)$$

The uncertainties in Table IV are twice the standard deviation of the mean and include the uncertainties in the calibrations and energies due to polythene and filter paper fuse.[12] The

Scheme I

$$\begin{tikzcd}
 & \text{elements} \arrow[dl, "-23.9"'] \arrow[dr, "-27.7"] & & \\
C_7H_{20}N_4(l) + 3C(c, \text{graphite}) + 2H_2(g) \arrow[rr, "\Delta H_3 = -3.8"'] \arrow[d] \arrow[dd, bend right=60, "-15.8"'] & & C_{10}H_{24}N_4(c) \arrow[d] \arrow[dd, bend left=60, "-2.5"] & (3) \\
C_7H_{20}N_4(g) + 3C(c, \text{graphite}) + 2H_2(g) \arrow[rr, "\Delta H_4"'] \arrow[d] & & C_{10}H_{24}N_4(g) \arrow[d] & (4) \\
C_7H_{20}N_4(aq) + 3C(c, \text{graphite}) + 2H_2(g) \arrow[rr, "\Delta H_5 = +9.5"'] & & C_{10}H_{24}N_4(aq) & (5) \\
L_2 & & L_1 &
\end{tikzcd}$$

Table V. Enthalpies of Solution in 0.5 M NaOH

compd	$-\Delta H_s°$, kcal mol^{-1}
L_1	2.51 (8)[a]
L_2	15.82 (4)

[a] The values in parentheses are the standard deviations on the last significant figure.

values[19] $\Delta H_f°(CO_2, g) = -94.051$ kcal mol^{-1} and $\Delta H_f°(H_2O, l) = -68.315$ kcal mol^{-1} were used to derive the values of $\Delta H_f°(C_aH_bN_c, l \text{ or } c)$.

B. Solution Enthalpies. Results for enthalpies of solution for both ligands are reported in Table V.

These quantities were measured in 0.5 M NaOH instead of pure water in order to avoid the protonation of the amines, which are both strong bases.

Discussion

The origins of the enthalpy term contributing to the macrocyclic effect, can be considered by use of the thermochemical cycle shown in Scheme I. ΔH_5 is the interesting quantity, being the difference in the standard enthalpies of formation of L_1 and L_2 in solution (here 0.5 M NaOH). As can be seen, the macrocyclic ligand L_1 is 9.5 kcal mol^{-1} less stable in solution than the noncyclic ligand L_2. This term is made up of two parts: (a) the difference due to the replacement of two N-H bonds with a $NCH_2CH_2CH_2N$ group, i.e., cyclizing the ring (ΔH_4); (b) the difference in the solvation energies from the gas phase. Unfortunately both these ligands are extremely involatile making the determination of ΔH_{vap} or ΔH_{sub} impossible without recourse to sophisticated equipment allowing for the measurement of very low vapor pressures. Thus an experimental value for ΔH_4 is not available at present. However, using the group additivity bond energy scheme first observed by Benson and Buss[20] and the group values tabulated by Cox and Pilcher[21] it is possible to calculate values for the standard gas-phase enthalpies of formation of both ligands. It must be remembered that such calculations do not allow for the nitrogen lone pair/lone pair interactions and any strain energy within the ring system in the cyclic ligand. Both these contributions would lead to a positive increase in ΔH_4. The strain energy should, however, be small since previous studies[8,22] have demonstrated that an alternating 5, 6, 5, . . . chelate ring sequence possessed by complexes of both L_1 and L_2 provides the most favorable ligand conformations resulting in minimum strain. Both ligands, having alternate ethylene and propylene bridges between the nitrogen donors, can adopt a more or less strain-free conformation when the four donor nitrogen atoms are confined to the same plane. The following values are therefore calculated.

$$\Delta H_f°(L_1, g) = +2.6 \text{ kcal mol}^{-1}$$

$$\Delta H_f°(L_2, g) = -2.3 \text{ kcal mol}^{-1}$$

leading to a calculated value for ΔH_4 of +4.9 kcal mol^{-1}.

This corresponds to a standard enthalpy of sublimation of L_1 of 30.3 kcal mol^{-1} and a standard enthalpy of vaporization of L_2 of 21.6 kcal mol^{-1}. Both values appear reasonable; assuming the value for L_2, since it is not affected by ring strain or lone-pair interactions, a direct molar mass ratio would give approximately 27 kcal mol^{-1} for the standard enthalpy of vaporization of L_1. Thus the enthalpy of fusion of L_1 should now be about 3 kcal mol^{-1} at 298 K, provided that ring strain and lone-pair interactions are ignored. We have obtained $\Delta H_{fusion}(L_1) = 6.4$ kcal mol^{-1} at its melting point (464.5 K) from the DSC purity determinations. Correcting the latter value to 298 K gives $\Delta H°_{fus}(298 \text{ K}) = 4.7$ kcal mol^{-1} and suggests that the contribution from ring strain and lone-pair interactions will be small. However, in the absence of experimental values for $\Delta H_{sub}(L_1)$ and $\Delta H_{vap}(L_2)$ the best we can conclude is that 4.9 kcal mol^{-1} is a lower limit for ΔH_4 and further contributions from ring strain or lone-pair terms in the cyclic ligand will make ΔH_4 more endothermic.

Using these calculated gas-phase standard enthalpies of formation, $\Delta H_4 = +4.9$ kcal mol^{-1}, we now obtain a value of +4.6 kcal mol^{-1} for the corresponding difference in solvation energies from the gas phase. This means that the reaction $L_1(g) \rightarrow L_1(aq)$ is 4.6 kcal mol^{-1} less exothermic than the corresponding reaction with the noncyclic ligand L_2, presumably due to a greater interaction with the solvent in the latter case. In view of the uncertainty expressed above about ΔH_4 this value must be regarded as a lower limit which would increase in the event of significant contributions from ring strain or lone-pair effects, although it is unlikely that it could ever approach the 14 kcal mol^{-1} associated with this effect by Margerum's group.[5]

Turning to the macrocyclic effect and the origins of the extra stability of macrocyclic complexes the enthalpy change for the metathetical reaction 1 has been shown calorimetrically to be -4.7[8] and -4.9[9] kcal mol^{-1} for Cu(II) and Ni(II), respectively. Within experimental error, this is the difference in solvation energies between L_2 and L_1 and tempts one to conclude that the macrocyclic enthalpy can satisfactorily be explained in terms of ligand solvation. However, the situation is more complicated and the macrocyclic enthalpy ΔH_1 contains three contributing terms in relation to the thermochemical cycle shown in Scheme II. The third term in this equation is the difference in solvation energies of the ligands L_2 and L_1 and has been shown above to have a lower limit of -4.6 kcal mol^{-1}. It thus contributes favorably to the macrocyclic enthalpy.

The second term, the difference in hydration energies of the two complexes, is difficult to estimate precisely. The effective radius of the two complexes must be very similar and to this

Scheme II

$$\begin{tikzcd}
ML_2^{2+}(g) \arrow[d, "\Delta H^h(ML_2^{2+})"] & + & L_1(g) \arrow[r, "\Delta H_{gas}"] \arrow[d, "\Delta H^h(L_1)"] & ML_1^{2+}(g) \arrow[d, "\Delta H^h(ML_1^{2+})"] & + & L_2(g) \arrow[d, "\Delta H^h(L_2)"] \\
ML_2^{2+}(aq) & + & L_1(aq) \arrow[r, "\Delta H_1"] & ML_1^{2+}(aq) & + & L_2(aq)
\end{tikzcd}$$

$$\Delta H_1 = \Delta H_{gas} + \left\{\Delta H^h(ML_1^{2+}) - \Delta H^h(ML_2^{2+})\right\} + \left\{\Delta H^h(L_2) - \Delta H^h(L_1)\right\}$$

extent one would expect this term to be very small and since $r_{ML_1^{2+}}$ will be slightly smaller than $r_{ML_2^{2+}}$ it will have an unfavorable contribution to ΔH_1. The endothermic nature of this term will be enhanced if the solvent interacts with the two NH_2 groups on ML_2^{2+} more strongly than with the equivalent NH groups on the cyclic complex ML_1^{2+}. However, the extent of such an interaction is very difficult to quantify, but it should not exceed the difference in solvation energies of the free ligands (4.6 kcal mol^{-1}). This raises the interesting question of whether the traditional choice of L_2 as the reference ligand is a good one or whether a more appropriate reference ligand might not have been 2,5,9,12-tetraazatridecane, which is L_2 methylated on each terminal nitrogen. This latter choice would minimize any difference between the hydration energies of the cyclic and noncyclic complexes by equalizing the possibilities of solvent–complex interactions and making the radii of the two complexes almost identical.

The first term, ΔH_{gas}, is the difference in Cu–N bond energies in the two complexes in the gas phase. In the event of the estimate for the third term being good, and the second term being small and positive, then ΔH_{gas} must be small and negative. This might be reasonable when the two complexes are structurally very similar with identical geometries and similar Cu–N bond distances. This is the case of L_1 and L_2 since L_2 is almost exactly the right size for the exact matching of the size of the aperture in the ligand with the size of the metal ion,[23] keeping the four nitrogens planar. In cases where the macrocyclic ligand is replaced by one where the size of the ligand aperture is not matched by the metal ion and a distortion occurs from the MN_4 planar configuration then strain will be introduced into the system and this will be reflected in ΔH_{gas} and thus in ΔH_1. This happens with the smaller ligand 1,4,7,10-tetraazacyclododecane where the Cu(II) ion is too large to be accommodated in the ligand aperture[23] and the Cu(II) complex has recently been shown to be square pyramidal.[24,25] Here the macrocyclic enthalpy (using 1,4,7,10-tetraazadecane as reference ligand) is only 1.1 kcal mol^{-1}.[8] In reality, however, ΔH_{gas} for the system studied may well prove to be a small favorable term, confirming a macrocyclic effect in the gas phase.

In conclusion, despite the uncertainties surrounding some of the terms contributing to the macrocyclic enthalpy, we can say that the difference in hydration energies of the ligands plays an important part in the macrocyclic enthalpy. We will be continuing this study by determining the gas-phase thermochemical properties of the ligands on completion of a torsional effusion Knudsen cell which will allow the determination of very low vapor pressures and by the determination of the thermochemical properties of N-alkylated reference ligands and their metal complexes.

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