TABLE I.

NiL_n,	L = *en*	*pn*	en_3	*dien*	$dien_2$	*tetren*	*2,3,2-tet*	*cyclam*
ΔU	0.61	2.14	0.80	4.04	6.70	11.06	3.33	1.33
$-\Delta H$, calc:	8.99	7.46	28.00	12.06	2.55	18.04	19.27	24.67
$-\Delta H$, obs:	9.0	7.8	28.0	11.9	2.53	18.3	19.2	24.1

in the order R = Me < Et < *i*-propyl < *t*-butyl, although the pK_a's are almost invariant. This effect is attributable to greater steric hindrance to solvation for the proton. For 1° *versus* 2° nitrogens, it is found in the gas phase, for example, that $(CH_3)_2NH$ is a much stronger base than CH_3NH_2, although their pK_a's in water are identical. This effect is partly attributable to quenching of polarizability effects [2], and also steric hindrance to solvation. The E and C equation of Drago and Wayland [3] is used to show that in the absence of steric effects, the Cu–N bond in $[\mathrm{Cu}(\mathrm{H}\mathit{fac})_2\mathrm{NRR}'_2]$ is stronger by 3.3 kcal mol^{-1} when NRR'_2 is $(CH_3)_2NH$. This qualitative suggestion that the M–N bond is stronger when N is 2° is supported [4] by empirical force field calculations of the increase in conformational potential energy, *U*, on complex-formation of Ni(II) with a variety of polyamine complexes. In each case, *U* has been calculated for each of the species in the reaction below, allowing calculation of ΔU.

$$\begin{array}{ccccc} \mathrm{M} & + & \mathrm{L} & \overset{\Delta U}{\rightleftharpoons} & \mathrm{ML} \\ U_{\mathrm{M}} & & U_{\mathrm{L}} & & U_{\mathrm{ML}} \end{array}$$

It was found that consistency could only be obtained by making the 2° Ni–N bond 1.7 kcal mol^{-1} more exothermic than the 1°. If a value of 4.8 kcal mol^{-1} is accorded to the ideal Ni–N bond to a nitrogen in the absence of steric strain, summation of the appropriate number of contributions from 1° and 2° nitrogens followed by subtraction of ΔU allows one to calculate $-\Delta H$ as shown in the Table. All calculations are for the high-spin complexes. From these results, one may assign the macrocyclic enthalpy to, firstly the presence of more 2° nitrogens in *cyclam*, followed by a smaller ΔU than is found for *2,3,2-tet.* An important point in favour of these ideas which suggests stronger Ni–N bonds, is that 10 Dq for the Ni(II) *cyclam* complex is higher than for *2,3,2-tet.* Contributions of solvation and entropy effects to the macrocyclic effect are discussed. Results below are in kcal mol^{-1}.

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Some Properties of Macrocyclic Complexes in Solution which are Related to the Ligand Ring Size

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The relation between the structural features of ligands and the properties of their metal complexes, which has been generally observed in coordination chemistry, is demonstrated dramatically in the case of tetra-aza macrocycles. In particular, solution properties of macrocyclic complexes (thermodynamic and kinetic stabilities, redox behaviour, spin-state equilibria) are strongly dependent on the size of the ligand cavity. For instance, in the formation of Ni(II) and Cu(II) complexes with a series of 12- to 16-membered cyclic tetramines, the most exothermic reactions occur with the 14-membered ring; expansion or contraction of the ligand cavity results in a substantial decrease of the enthalpy of formation, up to 60%. Likewise, the electrode potential values for the Ni(II)/Ni(III) couple, for the same macrocyclic systems, show a completely analogous ring size dependence: the attainment of the +3 state is easiest for the symmetric 14-membered ligand and becomes progressively more difficult by either an increase or decrease in size of the ligand cavity (up to 0.4 V). This behaviour seems to be related to the strength of the in-plane metal–macrocycle interactions, which in turn derive from the relative compatibility between the geometrical features of the ligand and the electronic requirements of the transition metal ion, in the appropriate oxidation state.