Empirical Force-field Calculations of Strain-energy Contributions to the Thermodynamics of Complex Formation. Part 1. The Difference in Stability between Complexes containing Five- and Six-membered Chelate Rings

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The technique of conformational potential-energy minimisation has been applied to the ligands ethylenediamine (en) and propane-1,3-diamine (pd), and to four complexes of Ni^{II} with en, pd, 3-azapentane-1,5-diamine, and 4-azaheptane-1,7-diamine. The method of Boyd, as modified by Snow, using a general force field including contributions from non-bonded interactions, bond-stretching, and valence-angle deformations and torsional strain, has been used. The difference in the enthalpy of complex formation between five- and six-membered chelate rings is due mainly to steric-strain considerations. Valence-angle deformations, together with non-bonded interactions, represent the major contributions to this difference. Predicted differences in the total strain energy between complexes containing five- and six-membered chelate rings have been found to be in good agreement with experimentally determined values.

A LARGE number of phenomena in co-ordination chemistry have been interpreted in terms of steric effects. Thus, for example, the lower stability of complexes having six-membered rings as compared with their analogues with five-membered rings has been attributed [1-3] to steric strain. Several workers have used empirical force-field calculations to analyse the conformations of chelate rings,[4-7] and also the difference in stability between complexes of several closely related chelating ligands. In most of these studies, however, the stability differences were small, so that the significance of any agreement obtained with thermodynamic results was uncertain, or else the strain energies calculated could not be compared with thermodynamic data in the literature because none were available. This latter problem is related partly to the fact that most of these calculations have been carried out on complexes of Co^{III}, which, because of their kinetic inertness, are not amenable to thermodynamic studies.

The nickel(II) complexes of the pair of ligands 3-azapentane-1.5-diamine (3NH-ptd) and 4-azaheptane-

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[1] P. Paoletti, S. Biagini, and M. Cannas, *Chem. Comm.*, 1969, 513.

[2] S. Biagini and M. Cannas, *J. Chem. Soc.* (*A*), 1970, 2398.

[3] R. J. P. Williams, *J. Phys. Chem.*, 1954, **58**, 121.

[4] M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3610.

[5] D. A. Buckingham, I. E. Maxwell, A. M. Sargenson, and M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3617.

[6] G. R. Brubaker and R. A. Euler, *Inorg. Chem.*, 1972, **11**, 2357.

[7] S. R. Niketic, K. Rasmussen, F. Woldbye, and S. Lifson, *Acta Chem. Scand.*, 1976, **A30**, 485.

1,7-diamine (4NH-hd) provide an excellent check of the reliability of the calculated strain energies. For both $[Ni(3NH\text{-}ptd)_2]^{2+}$ and $[Ni(4NH\text{-}hd)_2]^{2+}$ the free-energy and enthalpy changes on complex formation have been determined,[8,9] and the difference in stability is quite large, 7.64 kcal mol^{-1} in ΔH and 7.84 kcal mol^{-1} in ΔG, compared with the small differences of only 1—2 kcal mol^{-1} examined by previous workers.* At the same time the crystal structures of both the $[Ni(3NH)\text{-}ptd)_2]^{2+}$ and $[Ni(4NH\text{-}hd)_2]^{2+}$ complexes have been determined,[2] and show considerable distortion of the ligands, in keeping with the idea that the stability difference is due to steric strain. The added advantage of having the crystal structures is that the co-ordinates of an actual molecule are used as trial co-ordinates, thus reducing the possibility of the program finding a false energy minimum, as compared with calculations starting from postulated structures with ideal geometry. The thermodynamics of complex formation [10] as well as the crystal structures [11,12] of the $[NiL_3]^{2+}$ complexes [L = ethylenediamine (en) or propane-1,3-diamine (pd)] have also been reported, providing a further suitable pair of complexes for examination of the difference in stability between five- and six-membered chelate rings.

Since the difference in enthalpy change on complex formation should also contain the difference in strain energy between the two free ligands, the strain energies (U) of the ligands en and pd were calculated from the reported crystal structures for en [13] and $[H_2pd]^{2+}$,[14] a proton from each nitrogen being disregarded in the latter case. The difference in U between two 3NH-ptd and two 4NH-hd molecules should be four times the difference in strain energy between en and pd.

CONFORMATIONAL ANALYSIS

The force-field calculations that are described here were carried out with the program described in the Appendix. It considers the conformational potential energy (U) of a molecule as equal to the summation over the relevant internal co-ordinates of the four energy terms in (1) where

$$U = \sum_{ij} U(r_{ij})_{\mathrm{B}} + \sum_{ij} U(r_{ij})_{\mathrm{NB}} + \sum_{ijk} U(\theta_{ijk}) + \sum_{ijkl} U(\phi_{ijkl}) \quad (1)$$

$U(r_{ij})_{\mathrm{B}}$ is the potential energy for bond deformation between bonded atoms i and j, $U(r_{ij})_{\mathrm{NB}}$ the non-bonded potential energy between two atoms i and j, $U(\theta_{ijk})$ the potential energy for angle deformation between bonded atoms i—k, and $U(\phi_{ijkl})$ the potential energy for torsional strain about the bonded atoms i—l. Because the method of minimising these four energy terms with respect to the total conformational potential energy of a molecule has been described adequately [4,5,15,16] it will not be discussed further. However, the general mathematical form of the potential functions used to describe the four energy terms are defined below.

Bond-stretching and Valence-angle Deformation Potential Functions.—For bond-stretching and valence-angle deformation the deformations are assumed to have harmonic restoring forces. Hooke's law is therefore obeyed and the potential functions are of the forms (2) and (3) where r_{ij}^0

$$U(r_{ij})_{\mathrm{B}} = \tfrac{1}{2}k_{r_{ij}}(r_{ij} - r_{ij}^0)^2 \quad (2)$$

$$U(\theta_{ijk}) = \tfrac{1}{2}k_{\theta_{ijk}}(\theta_{ijk} - \theta_{ijk}^0)^2 \quad (3)$$

and θ_{ijk}^0 represent strain-free lengths and angles respectively. The stretching and bending force constant $k_{r_{ij}}$ and $k_{\theta_{ijk}}$ are listed in Table 1. Some of the constants are those of Schachtschneider and Snyder [17] as used by Buckingham *et al.*,[5] whereas others have been fitted by Buckingham *et al.*[5] or the present workers to give the best agreement with

TABLE 1

Force-field potential-function constants

(*a*) Non-bonded potential-function constants

Non-bonded atoms	$10^{11}\,a_{ij}$ / erg molecule^{-1}	b_{ij} / Å^{-1}	$10^{11}\,c_{ij}$ / erg Å^6 molecule^{-1}	Ref.
H · · · H	45.8	4.08	0.341	18 [a]
C · · · H	218.0	4.20	0.840	18 [a]
N · · · H	195.0	4.32	0.690	19 [a]
C · · · C	1 640.0	4.32	2.070	18 [a]
C · · · N	1 472.0	4.44	1.695	19 [a]
N · · · N	1 295.0	4.55	1.390	19 [a]

(*b*) Bond-angle force constants

Bond-angle type	$10^{-5}k_{\theta ijk}$ / dyn cm^{-1}	θ^0_{ijk} / rad	Ref.
H–C–H	0.52	1.911	17 [a]
H–N–H	0.53	1.911	*a*, *b*
N–C–H	0.65	1.911	*a*
C–N–H	0.56	1.911	*a*
C–C–H	0.65	1.911	17 [c]
C–C–N	0.90	1.911	*c*
N–Ni–N	0.30	1.571	*c*
Ni–N–H	0.10	1.911	*c*
Ni–N–C	0.20	1.911	*c*
C–N–C	0.90	1.911	*c*
C–C–C	1.00	1.911	17 [a]

(c) Bond-length force constants

Bond type	$10^{-5}k_{r_{ij}}$ / dyn cm^{-1}	r_{ij}^0 / Å	Ref.
N–H	6.16	0.99 [d]	*b*
C–H	5.00	1.08 [d]	17 [a]
C–C	5.00	1.50	17 [a]
C–N	6.00	1.49	*a*
Ni–N	0.68	2.10 [b]	*b*

(d) Torsional force constants

Bond type	$10^{11}V$ / erg molecule^{-1}
C–N	0.0057
C–C	0.0057

[a] As taken from Buckingham *et al.*[5] [b] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1966, **22**, 759, 1707. [c] Fitted to give the best agreement for $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$. [d] 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1968, vol. 3.

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* Throughout this paper: 1 cal = 4.184 J; 1 dyn = 10^{-5} N.

[8] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1961, 2994.

[9] P. Paoletti, F. Nuzzi, and A. Vacca, *J. Chem. Soc.* (*A*), 1966, 1385.

[10] I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 1407.

[11] L. N. Swink and M. Atoji, *Acta Cryst.*, 1960, **B13**, 639.

[12] G. D. Andreetti, L. Cavalca, and P. Sgarabotto, *Gazzetta*, 1971, **101**, 494.

[13] P. S. Jamet-Delcroix, *Acta Cryst.*, 1973, **B29**, 977.

[14] S. Hirokawa, M. Masakuni, M. Seki, and T. Noguchi, 'Memoirs of the Defense Academy, Japan,' 1968, vol. 8, no. 1, p. 485.

[15] R. H. Boyd, *J. Chem. Phys.*, 1968, **49**, 2574.

[16] M. Dwyer, R. J. Geue, and M. R. Snow, *Inorg. Chem.*, 1973, **12**, 2057.

[17] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 1963, **19**, 117.

structural data. Bond-stretching and valence-angle deformation terms have been included for all the bonds and bond angles within the molecule.

Non-bonded Potential Functions.—The non-bonded potential function between a pair of atoms i and j has been based on a Buckingham-type potential, *viz.* (4) where the

$$U(r_{ij})_{\mathrm{NB}} = a_{ij}\exp(-b_{ij}r_{ij}) - (c_{ij}/r_{ij}^{6}) \qquad (4)$$

r_{ij}^{-6} term represents the attractive forces and the exponential term approximates the repulsive forces. The constants a_{ij}, b_{ij}, and c_{ij} are those of De Coen *et al.*[18] and Liquori *et al.*,[19] as used by Buckingham *et al.*,[5] and are listed in Table 1.

All the interactions between non-bonded atoms up to a distance of 1.20 times the sum of their respective van der Waals radii have been included in the calculations, except for 1,3 geminal interactions.

TABLE 2

Final energy terms (kcal mol^{-1}) from the minimisation, together with the differences in the total strain energies and enthalpy on complex formation

	en	pd	$[\mathrm{Ni(en)_3}]^{2+}$	$[\mathrm{Ni(pd)_3}]^{2+}$	$[\mathrm{Ni(3NH\text{-}ptd)_2}]^{2+}$	$[\mathrm{Ni(4NH\text{-}hd)_2}]^{2+}$
Bond-length deformations	0.043	0.074	0.18	1.02	0.74	2.15
Non-bonded interactions	0.648	0.824	0.32	4.96	1.49	8.00
Valence-angle deformations	0.189	0.248	1.87	5.16	5.42	7.38
Torsional strain	0.009	0.017	2.20	1.97	4.21	3.78
Total conformational energy	0.889	1.163	4.57	13.11	11.86	21.31
Difference in strain energy		0.274		8.54		9.45
Strain energy adjusted for additional methylene groups				7.72		8.35
Difference in enthalpy change on complex formation				6.6 [10]		7.6 [8,9]

TABLE 3

Comparison of selected bond angles and nickel–ligand bond lengths in the crystals with those predicted by the energy-minimisation calculations

$[\mathrm{Ni(en)_3}]^{2+}$

Bond angles (°)	Minimisation	Crystal [11]
N(1)–Ni–N(2)	84.3	82.3 (1.0) *
N(1)–Ni–N(3)	90.7	91.2 (1.0)
N(2)–Ni–N(3)	94.7	93.4 (1.0)
Ni–N(1)–C(1)	105.1	109.7 (1.2)
N(1)–C(1)–C(2)	108.5	111.1 (2.3)
Bond lengths (Å)		
Ni–N	2.117	2.120 (0.013)

$[\mathrm{Ni(pd)_3}]^{2+}$

Bond angles (°)	Minimisation	Crystal [12]
N(1)–Ni–N(2)	85.1	87.5 (0.1)
N(1)–Ni–N(3)	91.6	89.1 (0.1)
N(2)–Ni–N(3)	92.8	92.4 (0.1)
Ni–N(1)–C(1)	120.4	118.9 (0.3)
Ni–N(2)–C(3)	120.4	124.5 (0.1)
N(1)–C(1)–C(2)	112.6	113.4 (0.3)
C(1)–C(2)–C(3)	112.4	113.7 (0.3)
N(2)–C(3)–C(2)	112.7	110.0 (0.3)
Bond lengths (Å)		
Ni–N(1)	2.133	2.136 (0.005)
Ni–N(2)	2.162	2.182 (0.005)

$[\mathrm{Ni(3NH\text{-}ptd)_2}]^{2+}$

Bond angles (°)	Minimisation	Crystal [2]
N(1)–Ni–N(2)	82.9	81.6
N(2)–Ni–N(3)	83.2	81.9
N(1)–Ni–N(6)	90.2	90.3
Ni–N(1)–C(1)	106.0	109.1
Ni–N(2)–C(2)	105.8	108.4
N(1)–C(1)–C(2)	109.1	112.0
N(2)–C(2)–C(1)	106.4	103.6
C(2)–N(2)–C(3)	115.5	112.9
Bond lengths (Å)		
Ni–N(1)	2.164	2.14
Ni–N(2)	2.058	2.05

$[\mathrm{Ni(4NH\text{-}hd)_2}]^{2+}$

Bond angles (°)	Minimisation	Crystal [2]
N(1)–Ni–N(2)	89.4	92.5
N(2)–Ni–N(3)	91.2	92.4
N(3)–Ni–N(4)	91.7	90.2
Ni–N(2)–C(1)	119.3	121.3
Ni–N(3)–C(3)	117.3	117.4
N(2)–C(1)–C(2)	112.0	113.3
N(3)–C(3)–C(2)	115.0	114.2
C(3)–N(3)–C(4)	107.0	107.3
C(1)–C(2)–C(3)	112.6	113.6
Bond lengths (Å)		
Ni–N(2)	2.112	2.12
Ni–N(3)	2.195	2.22

* Standard deviations, where available, are in parentheses.

Torsional Potential Energy.—It is usual to estimate the energy required to twist a bond from the experimentally observed barrier to rotation about the bond.[4] According to Scott and Scheraga [20] the torsional strain in a molecule

$$U(\phi_{ijkl}) = U_{\mathrm{NB}} + (V/2)(1 + \cos 3\phi_{ijkl}) \qquad (5)$$

can be computed from an equation that considers, separately, contributions from non-bonded and quantum-mechanical components, *viz.* (5) where V is that part of the experimental barrier not accounted for in the non-bonded term U_{NB}, and ϕ_{ijkl} is the torsion angle generated by bond twisting about the bonded atoms j and k. Only torsional interactions having one-parameter potentials obeying the criterion $0 \leqslant \phi \leqslant 60°$ are included in the calculations.

The torsional barriers about C–C and C–N bonds are 2.4 and 1.54 kcal mol^{-1} respectively.[5,21] These values were obtained by subtraction of the non-bonded contributions from the observed rotational barriers in ethane and methyl-

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[18] J. L. De Coen, G. Elefante, A. M. Liquori, and A. Diamiani, *Nature*, 1967, **216**, 910.

[19] A. M. Liquori, A. Diamiani, and G. Elefante, *J. Mol. Biol.*, 1968, **33**, 439.

[20] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, 1965, **42**, 2209.

[21] D. J. Millen, *Progr. Stereochem.*, 1962, **3**, 138.

amine respectively. Buckingham *et al.*,[5] using the Gollogly and Hawkins[22] form of the torsional barrier to rotation about a co-ordinate bond, have shown that the barrier to rotation about the Co–N bond alone makes a negligible contribution to the torsional term (contributions from non-bonded interactions being included separately). Hence, in the present calculations, torsional contributions for rotation about the Ni–N bond have been neglected. All interactions arising from bond twisting about the skeletal ligand atoms, including nickel and hydrogen as peripheral atoms, are included, and the contribution per interaction is taken as 0.80 kcal mol^{-1}.

RESULTS AND DISCUSSION

Because of the large forces required to distort C–C, C–N, N–H, and C–H bond lengths the energy-minimised values for these bond lengths are in excellent agreement with the unstrained values ($\pm$0.01 Å). Furthermore, all the bond angles involving hydrogen atoms were found to be within 3° of the ideal value, the hydrogen-atom positions being generated on the assumption that the hydrogen atoms form tetrahedral bonds with C and N atoms. Hence no comparisons are drawn between the energy-minimised and ideal values for C–C, C–N, N–H, and C–H bond lengths or bond angles that involve hydrogen atoms in Table 3.

Since the barrier to rotation about the Ni–N co-ordinate bond has been assumed to be small and consequently neglected in these calculations, the chelating ligand is free to adopt any conformation about the metal ion. This has no effect on the internal potential energy of the complex, and hence any comparison of the computed torsional angles with those in the crystal structure would be meaningless.

Ethylenediamine and Propane-1,3-*diamine*.—According to Wertz and Allinger[23] the C–C–C bond angle in the n-alkanes is 113°. Consequently, in the calculations involving en and pd this value has been used as a reference value for the unstrained C–C–C and N–C–C bond angles. In the en crystal[13] the N–C–C bond angle was found to be 114.3 ± 0.1°, which is in good agreement with the minimised value of 113.5°. For pd the C–C–C and N–C–C bond angles were found[14] to be 109.3 ± 1.3 and 109.2 ± 1.2° respectively, compared with values of 113.5 and 113.4° generated by the minimisation, respectively. The poor agreement is probably due to the fact that the pd crystal structure is not accurately known, the R index for the structure determination being 0.196.

The total conformational potential energy for the two ligands en and pd included the summation of 68 and 96 interaction terms respectively, and the various contributions to the total strain energy are given in Table 2. It is interesting to note that the same strain energy was calculated for en using the hydrogen-atom co-ordinates determined in the crystal structure as starting co-ordinates. In both ligands the major contribution to the total strain energy is in the form of H ··· H non-bonded interactions between hydrogen atoms on adjacent C and N atoms, and, in the case of pd, also H ··· H repulsions on adjacent C atoms (see Table 2). The major interactions are: C–H ··· H–N, at a non-bonded distance of 2.40 Å, contributing 0.11 kcal mol^{-1} per interaction; and C–H ··· H–C, at a non-bonded distance of 2.45 Å, contributing 0.07 kcal mol^{-1} per interaction.

The difference in strain energy between en and pd is 0.27 kcal mol^{-1} and this value will be taken to represent the additional strain energy introduced into a molecule on addition of an extra methylene group. A further assumption is that this extra strain energy is additive, *i.e.* the addition of N methylene groups will result in an overall increase in the total strain energy of N(0.27) kcal mol^{-1}.

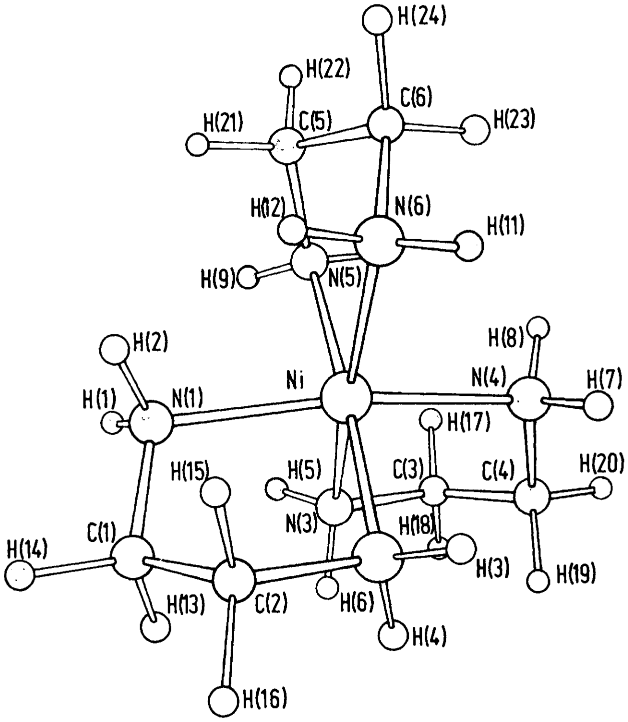

FIGURE 1 ORTEP[24] energy-minimised conformation of the [Ni(en)]$_3$$^{2+}$ complex. The energy (kcal mol^{-1}) associated with H ··· H interactions is as follows: 0.16 for H(1) ··· H(13), H(2) ··· H(14), H(3) ··· H(15), H(5) ··· H(17), H(6) ··· H(18), H(7) ··· H(19), H(8) ··· H(10), H(9) ··· H(21), H(10) ··· H(22), H(11) ··· H(23), and H(12) ··· H(24); 0.17 for H(2) ··· H(12), H(4) ··· H(16), and H(8) ··· H(20)

Tris(ethylenediamine)nickel(II) *and Tris(propane*-1,3-*diamine)nickel*(II).—The summation of the total conformational potential energy for $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$ included 408 and 501 interaction terms respectively. The agreement between the bond angles and nickel–ligand bond length found in the crystal and those derived from the minimisation is good, as is apparent from Table 3.

Comparison of the various contributions to the total strain energy for $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$ (see Table 2) shows that, in going from a five- to a six-membered

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[22] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1163.

[23] D. H. Wertz and N. L. Allinger, *Tetrahedron*, 1974, **30**, 1579.

[24] C. Nave and M. R. Truter, *J.C.S. Dalton*, 1974, 2351.

chelate ring there is an increase in the total strain energy of 8.54 kcal mol^{-1}, corresponding to increased contributions from bond-length distortions, non-bonded interactions, and valence-angle deformations, although the torsional strain in $[Ni(pd)_3]^{2+}$ is slightly less than in $[Ni(en)_3]^{2+}$. This is probably associated with greater flexibility of the larger pd when compared with the en ligand.

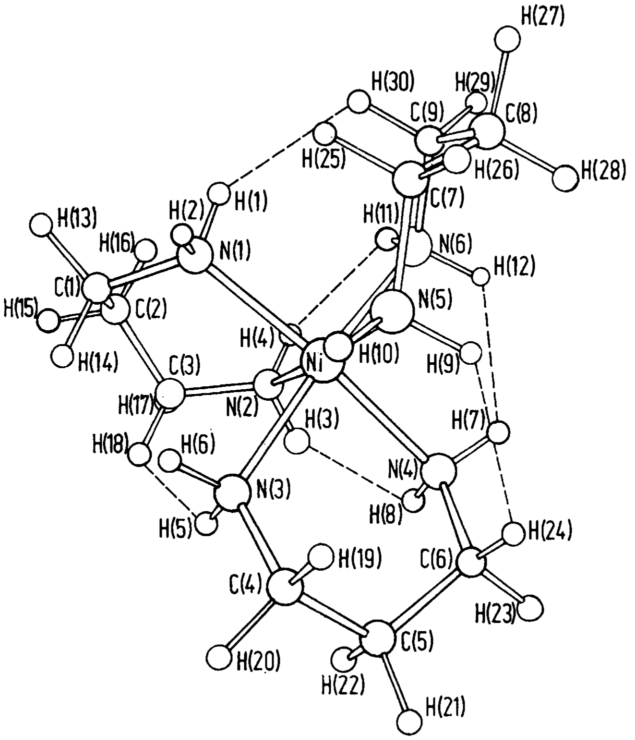

FIGURE 2 ORTEP [24] energy-minimised conformation of the $[Ni(pd)_3]^{2+}$ complex. Broken lines indicate H · · · H non-bonded interactions of energy ⩾0.62 kcal mol^{-1}. Other energies (kcal mol^{-1}) as follows: H(1) · · · H(30), 0.38, H(2) · · · H(13) 0.16, H(2) · · · H(25) 0.29, H(3) · · · H(8) 0.50, H(3) · · · H(17) 0.16, H(4) · · · H(11) 0.50, H(4) · · · H(17) 0.17, H(5) · · · H(18) 0.38, H(6) · · · H(14) 0.29, H(6) · · · H(20) 0.16, H(7) · · · H(12) 0.50, H(7) · · · H(13) 0.16, H(8) · · · H(23) 0.17, H(9) · · · H(24) 0.38, H(10) · · · H(19) 0.29, H(10) · · · H(26) 0.16, H(11) · · · H(29) 0.16, H(12) · · · H(29) 0.17

In an analysis of Table 2 it should be borne in mind that, in general, the order of magnitude of the force constants for bond-length deformation is very much greater than that for the force constants for valence-angle deformation, which in turn is greater than that for the force constants for torsional deformation. Any applied stress must therefore appear first as torsional strain. On complexation of en with Ni^{II} the largest contribution to the total strain energy is in the form of a torsional contribution. However, introduction of an extra methylene group increases the flexibility of the ligand and introduces an extra degree of freedom for the relief of torsional strain. This explains the lower torsional-strain contribution to the total strain energy observed for the $[Ni(pd)_3]^{2+}$ complex.

The energy-minimised conformations of the $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$ complexes are shown in Figures 1 and 2, which are ORTEP [25] drawings. The most significant H • • • H non-bonded interactions, together with the energy associated with each interaction, are also listed. In Figure 2 the broken lines indicate non-bonded interactions of energy >0.62 kcal mol^{-1}. The difference in total strain energy between $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$ (see Table 2) is 8.54 kcal mol^{-1}, which, after the presence of three additional methylene groups has been taken into account, reduces to 7.72 kcal mol^{-1}. On the other hand, the reported enthalpies of formation,[10] $\Delta H(\beta_3)$ of $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$, are -27.9 ± 0.1 and -21.3 ± 0.4 kcal mol^{-1} respectively.* This gives a difference in $\Delta H(\beta_3)$ of 6.6 kcal mol^{-1}, in good agreement with the value of 7.72 kcal mol^{-1} which corresponds to the difference in the total strain energy between the two complexes as calculated in the minimisations.

Bis(3-*azapentane*-1,5-*diamine*)*nickel*(II) *and Bis*(4-*azaheptane*-1,7-*diamine*)*nickel*(II).—As a further example of the fact that the difference in the enthalpy of formation between five- and six-membered chelates is

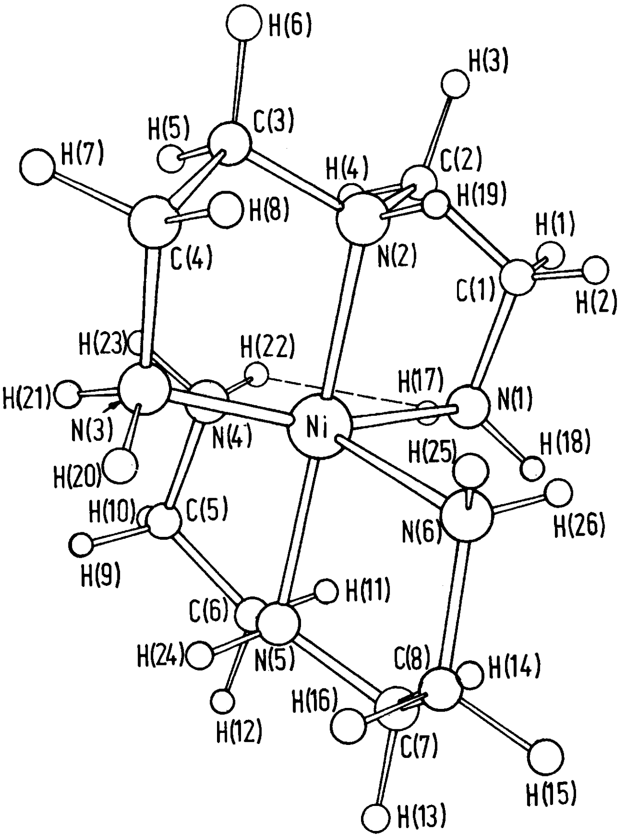

FIGURE 3 ORTEP [24] energy-minimised conformation of the $[Ni(3NH(ptd)_2]^{2+}$ complex. Broken lines as in Figure 2. Other interaction energies (kcal mol^{-1}) as follows: 0.22 for H(1) · · · H(17), H(9) · · · H(23), and H(10) · · · H(22); 0.62 for H(17) · · · H(22)

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* Throughout this paper, $\Delta H(\beta_n)$ refers to the enthalpy change on formation of the complex $[ML_n]$.

[25] C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, 1965.

largely due to strain considerations, conformational potential-energy calculations were made for $[Ni(3NH\text{-}ptd)_2]^{2+}$ and $[Ni(4NH\text{-}hd)_2]^{2+}$. These calculations included the summation of 471 and 589 interaction terms respectively. From Table 3 it can be seen that the agreement between the bond angles and nickel–ligand bond lengths in the crystals [2] {no standard deviations were specified, but *R* for $[Ni(3NH\text{-}ptd)_2]^{2+}$ was 0.092 and for $[Ni(4NH\text{-}hd)_2]^{2+}$ was 0.089} and those predicted by the minimisation calculations is reasonably good.

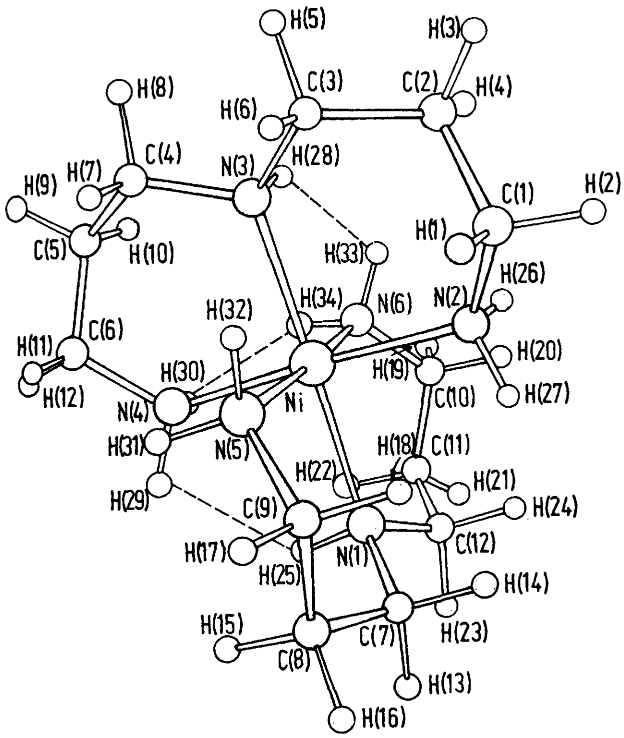

FIGURE 4 ORTEP [24] energy-minimised conformation of $[Ni(4NH\text{-}hd)_2]^{2+}$ complex. Broken lines as in Figure 2. Other interaction energies (kcal mol^{-1}) as follows: H(5) · · · H(8) 0.27, H(6) · · · H(32) 0.33, H(8) · · · H(9) 0.24, H(11) · · · H(31) 0.25, H(12) · · · H(30) 0.24, H(13) · · · H(23) 0.27, H(14) · · · H(27) 0.33, H(19) · · · H(34) 0.24, H(20) · · · H(26) 0.25, H(21) · · · H(23) 0.24, H(25) · · · H(29) 0.62, H(28) · · · H(33) 0.62, and H(30) · · · H(34) 0.74

Analysis of the various contributions to the total strain energy (see Table 2) indicates the presence of a trend similar to that observed for the previous two complexes, *viz* that increased contributions from bond-length deformations, non-bonded interactions, and valence-angle deformations account for the higher strain in the six-membered complex when compared with the analogous five-membered complex.

Figures 3 and 4 show ORTEP [25] drawings of the energy-minimised conformations of $[Ni(3NH\text{-}ptd)_2]^{2+}$ and $[Ni(4NH\text{-}hd)_2]^{2+}$, all H · · · H non-bonded interactions of energy >0.62 kcal mol^{-1} being indicated by broken lines. Other significant H · · · H non-bonded interactions together with the energy associated with each interaction are also listed.

The stability constants [8,9] for the formation of $[Ni(3NH\text{-}ptd)]^{2+}$ and $[Ni(3NH\text{-}ptd)_2]^{2+}$ are $\log k_1 = 10.5$ and $\log k_2 = 8.0$ respectively, and for the formation of $[Ni(4NH\text{-}hd)]^{2+}$ and $[Ni(4NH\text{-}hd)_2]^{2+}$ are $\log k_1 = 9.2$ and $\log k_2 = 3.2$ respectively. Although the formation constants for the 1 : 1 complexes are very similar, addition of the second ligand results in a much lower log k_2 value in the case of $[Ni(4NH\text{-}hd)_2]^{2+}$. This can, to a great extent, be attributed to large interligand H · · · H non-bonded interactions introduced into the $[Ni(4NH\text{-}hd)_2]^{2+}$ complex on addition of the second ligand (see Figure 4 and Table 2), as suggested by Paoletti and his co-workers.[1]

The difference in the total strain energy between $[Ni(3NH\text{-}ptd)_2]^{2+}$ and $[Ni(4NH\text{-}hd)_2]^{2+}$ is 9.45 kcal mol^{-1}, which is reduced to 8.35 kcal mol^{-1} after accounting for the four additional methylene groups (see Table 2). This value agrees well with 7.64 kcal mol^{-1},[8,9] the difference in the $\Delta H(\beta_2)$ of formation of the two complexes.

Conclusions. By means of these calculations it has been possible to demonstrate quantitatively that the difference in the enthalpy of formation of five- and six-membered chelate rings is due mainly to strain considerations. As expected, valence-angle deformations play a more prominent role in absorbing strain energy than do bond-length deformations, and together with non-bonded interactions represent the major contributions to the difference in steric strain between five- and six-membered rings.

A possible criticism of this work is that individual solvent effects have been ignored. Since the two ligands in each pair of ligands studied are so similar, the only difference being the presence of an additional methylene group per ethylene unit, it is believed that the solvent medium will not affect the relative difference in the free-enthalpies of formation of the complexes involved. In support of this generalisation there is spectrophotometric evidence that the crystal-field absorption bands for $[Ni(pd)_3]^{2+}$ and $[Ni(en)_3]^{2+}$ in water and in acetonitrile occur in the same positions. Nevertheless, this hypothesis will be tested by measurement of the enthalpies of formation of $[Ni(en)_3]^{2+}$ and $[Ni(pd)_3]^{2+}$ in different solvent media.

Macrocyclic effect. The magnitude of the strain energies involved in attaching a large polyamine ligand to a metal ion has suggested to us a possible explanation for the extra stability of complexes of macrocyclic ligands relative to their open-chain analogues. Examinaton of the crystal structure of the free ligand cyclam [24] (1,4,8,11-tetra-azacyclotetradecane) shows that it has an almost identical conformation to that found in the structure of the nickel(II) complex,[26] so that the increase in strain energy on complex formation should be very small. This is in contrast to open-chain polyamines, where, as has been shown, the increase in strain energy is very considerable. We suggest that the macrocyclic effect could be due, at least in part, to the fact that macrocyclic ligands are *prestrained*, *i.e.* the strain

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[26] B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

energy of the final complex is already present in the free ligand. At present, strain-energy calculations are being carried out in a further investigation of this hypothesis.

APPENDIX

The Program.—The force-field calculations were carried out on a CDC 174 Cyber computer using a program derived from the original described by Boyd [15] and adapted for use on the CDC by Snow.[4] To ensure that molecules of different sizes are compared without bias it was necessary to modify the program in several ways. These changes mainly relate to the interaction count and the concomitant reduction of the non-bonded limit when the count reaches a programmed maximum.

The unmodified version accumulates an interaction count before discrimination by user's option. On reaching the critical count the threshold value that determines the maximum distance for the inclusion of non-bonded interactions is lowered until the total interaction count is less than the allowed maximum. However, many of the interactions counted in this way are ignored in the refinement step. By this procedure, the final non-bonded limit is too critically dependent on the number of interacting atoms for applications in which direct comparison of several molecules is required. A simple device to compensate for this effect is to increase the upper limit for the initial count and to operate a filter that eliminates interactions that are zero by virtue of the specified potential types and to apply the final test only to the number of remaining interactions. The interactions, often numerous, to be excluded at user's discretion before refinement therefore cannot affect the non-bonded limit.

Convergence was considered complete when all the root-mean-square shifts were less than 2×10^{-3} Å.

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[7/1688 *Received, 26th September*, 1977]