electrochemically[40,41] suggests that the reaction system always contain nitrosyl species other than $[Fe(OEP)(NO)]^+$. The higher than expected magnetic moments are the evident result of small amounts of iron(III) impurities[42] and a low-spin iron(II) impurity. EPR spectra confirm the presence of low levels of a high-spin iron(III) contaminant ($g = 6$) and small amounts of a low-spin species as well.[43] $[Fe(TPP)(NO)(H_2O)]ClO_4$ is more susceptible to this decomposition,[44] and as noted previously, X-ray data collection was carried out at 96 K to retard this decomposition.

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Registry No. $[Fe(TPP)(NO)(H_2O)]ClO_4$, 89596-91-8; $[Fe(OEP)(NO)]ClO_4$, 89596-93-0.

Supplementary Material Available: Table IV, anisotropic temperature factors for $[Fe(TPP)(NO)(H_2O)]ClO_4$, Table VI, anisotropic temperature factors for $[Fe(OEP)(NO)]ClO_4$, and listings of observed and calculated structure amplitudes for both complexes (37 pages). Ordering information is given on any current masthead page.

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[40] Fujita, E.; Fajer, J. *J. Am. Chem. Soc.* **1983**, *105*, 6743–6745.

[41] Lancon, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1983**, *105*, 5610–5617.

[42] The moments correspond to impurity levels of between 3 and 8% of a high-spin iron(III) species of comparable molecular weight. The level of these high-spin impurities increases with time. Magnetic moments were measured at least 2 weeks after prepration owing to the necessity of sending samples from Nagoya to Notre Dame.

[43] This is possibly a nitrosyl iron(II) species. EPR parameters for this species contained in crystals of $[Fe(OEP)(NO)]ClO_4$ are $g_\perp = 2.052$, $g_\parallel = 2.010$, $A_{N\parallel} = 17.7$ G, and $A_{N\perp} = 19.1$ G.

[44] This is in accord with recently reported electrochemical results reported in ref 41.

Origin of the High Ligand Field Strength and Macrocyclic Enthalpy in Complexes of Nitrogen-Donor Macrocycles

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Abstract: The relationship between hole size in the cavities of tetraaza macrocycles, the strain-free M–N bond lengths for various metal ions, and the occurrence of the maximum value of the in-plane ligand field (LF) strength, $Dq_{(xy)}$, as a function of the size of the macrocyclic cavity, is discussed. It is shown that the maximum value of $Dq_{(xy)}$ occurs when the metal ion fits best into the cavity, rather than when the metal ion is compressed (Busch, 1971) by the macrocycle. It is shown by using empirical force-field calculations (EFF) that Co(III) is too small for an exact fit into most polyamine ligand systems, with a strain-free Co–N length of 1.925 Å. Nonbonded repulsions between adjacent ligands at such short M–N lengths prevent such short bond lengths being realized for virtually all complexes of Co(III) with polyamines, except for unusual circumstances, as found in complexes with macrocycles, such as 13-aneN_4 (1,4,7,11-tetraazacyclotridecane). The effect of steric strain on LF strength is investigated, and a simple model is developed which relates strain in the M–N bond to the LF strength. This model supports the idea that the high LF strength in complexes of macrocyclic ligands is due to a large number of secondary nitrogen donors in a situation of comparatively low strain in the M–N bond. EFF calculations are then used to calculate enthalpies of complex formation of complexes of polyamines with Ni(II) in aqueous solution, assuming that solvation effects can be neglected, and it is suggested on the basis of these calculations that the macrocyclic enthalpy is due to (1) the inductive effects of the extra secondary nitrogens in the macrocycle and (2) the high state of steric strain in the macrocyclic ligand, brought about by dipole–dipole repulsion in the gas phase, and a contribution from steric hindrance to solvation in aqueous solution.

The extra stability of the complexes of macrocyclic ligands over that of their open-chain analogues has been termed the macrocyclic effect.[1] The extra thermodynamic stability is usually, but not always, in the nitrogen-donor macrocycles, accompanied by a stronger ligand field.[2,3] It is generally agreed that the entropy contribution to the macrocyclic effect is due to the smaller configurational entropy of the macrocycle as compared with the open-chain ligand. Our interest in this paper is the origin of the enthalpy contribution, and, perhaps even more interesting, the stronger ligand field, in complexes of N-donor macrocycles.

Busch et al.[2-4] have suggested that the above stronger ligand field is produced by compression of the metal ion by the encircling macrocycle. They have carried out empirical force-field (EFF) calculations on the free macrocyclic ligands and determined the M–N bond lengths of coordinated metal ions which produce the least strain in the resulting complex. These best-fit metal–nitrogen bond lengths are shown in Table I. Busch et al. have further noted[3] that the ligand field strength of a metal ion such as Co(III) in a series of analogous complexes with the series of macrocycles 13-aneN_4 through 16-aneN_4 varies with the ring size of the macrocycle such that the ligand field (LF) is at a maximum for a particular ring size. Thus, for Co(III) this occurs in 13-aneN_4,

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Table I. In-Plane Ligand Field Splitting Parameters, $Dq_{(xy)}$, or d-d Band Energies, for Complexes of Tetraaza Macrocycles, with Ligand Coordinated in a Planar Fashion[a]

ligand[b]	ideal M-N length[c]	Co(III)[c]	Ni(II)[d] (low-spin)	Ni(II)[e] (high-spin)	Cu(II)[f]	Cr(III)[g]	Rh(III)[h]
12-aneN_4	1.83	[i]	2115	[i]	16 810[i]	[i]	[i]
13-aneN_4	1.92	*2750*	*2140*	[i]	18 310[i]	[i]	[i]
14-aneN_4	2.07	2562	2043	*1460*	*19 900*	*2450*	*25 000*
15-aneN_4	2.22	2362	1955	1240	17 610	2123	23 800
16-aneN_4	2.38	2295	[j]	1100			22 730
en_2		2530	1961[k]	1150	18 180[l]	2200	24 630[m]
strain-free M-N for metal[n]		1.925	1.89	2.10	2.03	2.05	2.04

[a] Units are cm^{-1}. Italic values are for macrocycle into which metal ion fits best, as discussed in text. [b] For abbreviations, see Figure 1. [c] From ref 3. Ideal M-N lengths in Å. $Dq_{(xy)}$ for Co(III) is for the *trans*-[Co(12-16-aneN_4)Cl_2]$^+$ complexes. [d] From ref 5, for the square-planar [Ni(12-16-aneN_4)]$^{2+}$ complexes, calculated from $Dq_{(xy)} = \nu_{(d-d)}/11.0$: Chang, J. W.; Martin, R. B. *J. Chem. Phys.* 1969, *73*, 4277-4283. Bossu, F. P.; Margerum, D. W. *Inorg. Chem.* 1977, *16*, 1210-1214. [e] $Dq_{(xy)}$ from ref 4, for high-spin *trans*-[Ni(12-16-aneN_4)Cl_2] complexes. [f] From: Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* 1979, 1581-1584. The energies are those of the higher energy d-d band in aqueous solution for the [Cu(12-16-aneN_4)]$^{2+}$ complexes. [g] $Dq_{(xy)}$ for *trans*-Cr(12-16-aneN_4)Cl_2^+ series. From: Swisher, R. G.; Brown, G. A.; Smiercak, R. C.; Blinn, E. L. *Inorg. Chem.* 1981, *20*, 3947-3951. [h] From: Bhattacharya, P. K. *J. Chem. Soc., Dalton Trans.* 1980, 810-812. These are energies of the low-energy band, since there is insufficient information to calculate $Dq_{(xy)}$. [i] These complexes are known [Co(III), high-spin Ni(II), Cr(III), Rh(III)] to have the folded cis structure. [j] No low-spin form detectable[5] in solution. [k] From: Lever, A. B. P.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* 1963, 2552-2555. [l] From ref 31. [m] From: Watt, G. W.; Alexander. P. W. *J. Am. Chem. Soc.* 1967, *89*, 1814-1818. [n] Units are Å. The skeleton of these strain-free bond lengths is discussed in the text.

which has a best fit around metal ions with M–N lengths of 1.92 Å. This is shorter than commonly found Co–N bond lengths in complexes with polyamines, which are in the range 1.94–2.04 Å. It thus seems reasonable that the high ligand field strength in this complex, which is also very much higher than in open-chain analogues, such as the bis(en) (en = ethylenediamine) complex, is due to compression of the Co(III) by 13-aneN_4.

The first difficulty for the above idea was noted by Fabbrizzi.[5a] In the series of complexes of the macrocycles 12-aneN_4 through 16-aneN_4 with low-spin Ni(II), the maximum LF strength (Table I) is found in the 13-aneN_4 complex. The preferred M–N bond length for fitting into 13-aneN_4 is 1.92 Å, which is actually slightly larger than the observed Ni–N bond lengths of 1.89 Å found in low-spin complexes of Ni(II) with open-chain polyamines. Fabbrizzi[5a] thus noted that the maximum LF occurred in this series of complexes with the macrocycle which fit best around the metal ion, which was not consistent with the compression hypothesis. A similar observation was made[5b] for the analogous series of Cu(II) complexes.

A further difficulty was noted[6] for the series of high-spin complexes of Ni(II), also shown in Table I. The maximum LF strength for this series is observed in the 14-aneN_4 complex, which has a best-fit size of 2.07 Å. It was suggested[4] that the "ideal" M–N bond length for high-spin Ni(II) was close to the 2.22-Å best-fit size of the 15-aneN_4 complex, which showed no enhanced ligand field as compared with open-chain analogues, and that the high LF here was also due to compression of the high-spin Ni(II) by the 14-aneN_4. The ideal M–N bond length for a metal ion is that which would be observed in the absence of any steric effects, such as the proposed compression effects. However, the observed M–N bond lengths for high-spin Ni(II) with polyamines are all very close to 2.10 Å, which suggests rather[6] that what we are seeing here is also an example of the "best-fit" hypothesis noted by Fabbrizzi[5] for low-spin Ni(II). An even more interesting effect was noted[6] for the complexes of smaller macrocycles such as 9-aneN_3 and 8-aneN_2. These have very much higher LF splitting parameters than their open-chain analogues, in spite of the fact that they do not encircle the metal ion and thus do not seem likely to exert any compressive forces on metal ions to which they are complexed.

We thus have the apparent paradox that the Co(III) series of complexes appears to fit the compression hypothesis, whereas the high- and low-spin series of Ni(II) complexes follow the best-fit hypothesis, and the occurrence of unusually high LF splitting in complexes of small macrocycles which do not encircle the metal ion is also inconsistent with the compression hypothesis. In a recent communication[6] it was suggested that the Co(III) series in Table I also supported the best-fit hypothesis. This was based on the observation that in EFF calculations[7-9] on polyamine complexes of Co(III), the observed Co–N bond lengths of about 2.00 Å were reproduced only if the ideal Co–N bond length used in the calculations was taken to be 1.925 Å. What is found in examining the cause of this bond lengthening from 1.925 out to 2.00 Å is that[9] the *van der Waals repulsions between the hydrogen atoms on adjacent ligands actually prevent closer approach to the metal ion.* This finding thus parallels the familiar idea of radius ratios in ionic solids, where anions ("ligands") above a certain size do not permit a close approach to a small cation. The implication of the EFF calculations is[9] that for some metal ions such as Co(III), the ideal M–N bond length may only be observable in unusual circumstances, such as found in macrocycles of appropriate size, in this case 13-aneN_4.

If, as we attempt to show here, the best-fit hypothesis is correct, it still does not explain the very high LF strengths, and, in particular, why the LF strengths should be higher than in the open-chain analogues. It was suggested[6] that the high LF was due to the presence of extra secondary nitrogens on the macrocycle, produced by cyclization of the open-chain analogue. This relates to what have been termed[10] "hidden" inductive effects. These can be observed, among other examples, in the complexes of C-substituted ethylenediamines.[10] The pK_a values of amine ligands have traditionally been regarded as indicative of inductive effects. The pK_a values of the ethylenediamines show no increase with increasing C-substitution, and yet, in a remarkable parallel to the behavior of macrocycles, the complexes show increased stability and LF strengths. Hidden inductive effects are "hidden" because the increasing basicity of the nitrogens is not evident in the pK_a values, the traditional measure of base strength. The contribution from the extra secondary nitrogens to the high LF strengths and stability of complexes of macrocycles is also, as we will show here, an example of a hidden inductive effect,[10] since the pK_a values of primary and secondary amines in water are hardly different. The nonresponse of the pK_a values of amines to inductive effects has been interpreted[10] as due to steric hindrance to solvation of the attached proton.

Compression of M–N bonds would produce a large unfavorable strain-energy contribution to the enthalpy of complex formation, so that the compression hypothesis does not accord with the greater

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(5) (a) Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1857-1861. (b) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Ibid.* **1978**, 577-583.

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thermodynamic stability of complexes of macrocycles. In this regard, Paoletti et al.[11] have measured log K_1 for Ni(II) with the macrocycles 14-aneN_4 through 16-aneN_4, and it is found that the complex with 14-aneN_4 is considerably more stable than that with 15-aneN_4. We would expect the latter complex to be the more stable if the ideal Ni–N length in high-spin complexes of Ni(II) were in the vicinity of 2.22 Å, the best-fit length for fitting into 15-aneN_4. The best-fit hypothesis is in agreement with the suggestion that the macrocyclic effect is produced by the macrocyclic ligand being "prestrained"[12] or "preoriented".[13] Normally, the free polyamine ligand exists[14] in much lower strain energy conformers in solution than it does once coordinated to a metal ion. Macrocycles are already in the right conformation for complexing the metal ion, and so should not[12,13] have this unfavorable increase in strain energy on complexation. This hypothesis can be tested by using EFF calculations. We have already demonstrated[12,14,15] that EFF calculations can be used to account for differences in enthalpies of complex formation in aqueous solution of a large number of polyamine complexes of high-spin Ni(II). An important provision here[14,15] is that satisfactory agreement can only be attained if it is postulated that the *enthalpy change on complex formation per Ni–N bond in a ligand where the nitrogen is secondary is 1.7 kcal mol^{-1} more favorable than where it is primary.*

In this paper, then, we use the EFF calculations in order to test further the "compression" and "best-fit" hypotheses and to evaluate the relative importance of the proposed hidden inductive effects and prestraining to the macrocyclic enthalpy and the high ligand field strength found in complexes of N-donor macrocycles. Recently, much work has been reported[16–18] on the free energies and enthalpies of complex formation of metal ions in the gas phase with a variety of amines and other organic ligands. Steric effects involving only one or two unidentate ligands coordinating to a bare ion in the gas phase are bound to be much smaller than those found for the hydrated metal ion in solution[10] and should thus allow us to evaluate confidently the relative base strengths of differently substituted amines.

Experimental Section

The EFF program, based on one developed by Boyd[19] and modified by Snow,[7] has already been described.[12] The force constants for Co(III) and for the organic part of the complexes are those reported by Snow.[7] For the Ni(II) ion, they are those found[12] to reproduce the structures of Ni(II) complexes most satisfactorily. Wherever possible, the initial coordinates for the EFF calculations are those from actual crystal structures and are referenced when each calculation is discussed. The idea here is that starting with the experimentally determined structure should minimize the probability of the program finding a false energy minimum. Another technique used frequently in this paper is to determine the strain energy of the complex as a function of the ideal M–N bond length.[9] All the force constants are kept constant at those for Ni(II) (high-spin), and the "ideal" M–N bond length is varied in small steps over a range from about 1.8 up to 2.4 Å. The minimum in the curve of strain energy vs. M–N bond length (see Figure 3) thus gives the best-fit size for metal ions into the particular ligand system. In addition, one is able to identify the steric interactions in the ligand system which are responsible for the effects observed. For example, the program lists all H–H nonbonded interactions according to the molecular numbering scheme used, and it is possible to pinpoint which of these are responsible for the van der Waals repulsions preventing close approach to the metal ion at short metal to nitrogen distances.

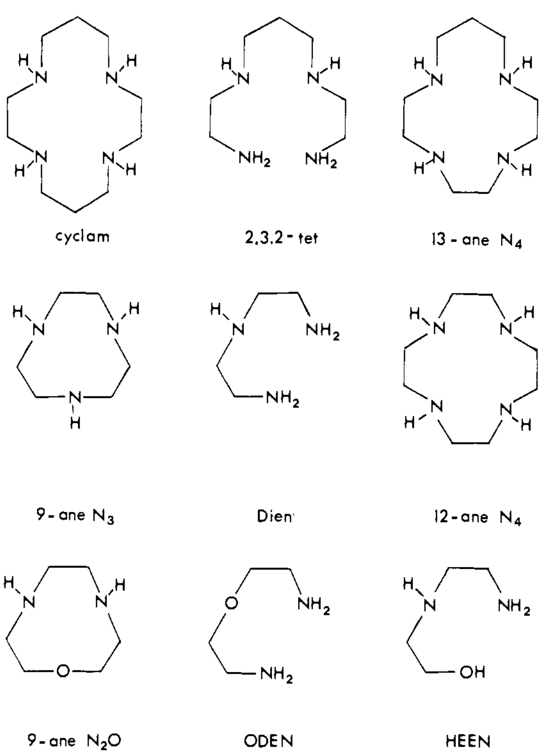

Figure 1. Ligands discussed in this paper.

Results and Discussion

The EFF approach has been shown[7-9] to work well for several complexes of Co(III) and Ni(II). We report here the results of such calculations on several more complexes of these metal ions, which are aimed at showing how increasing the bulk of the ligands so as to increase the packing density around the metal ion affects the geometry of the complex, and in particular the M–N bond lengths. At the same time, comparison of the predicted and observed structural parameters will allow the reader to be satisfied as to the predictive power of the EFF approach. The results of these calculations are shown in Table II. It should be noted that *all the long M–N bonds observed are reproduced by the EFF using the ideal bond lengths of 1.925 Å for Co(III) and 2.10 Å for Ni(II).*

What the calculations show is that as we increase the bulk of the groups in passing from the tris(en) to tris(pn) complex (en = ethylenediamine, pn = 1,3-propanediamine), in order to relieve steric strain, the M–N bond lengths are increased, particularly for Ni(II), and the M–N–C angles are opened up to over 120° instead of the 109.5° for a regular tetrahedron. The same effect is found in the sterically crowded chloropentamethylamine complex of Co(III), as seen in Table II. The bond stretching and opening up of the Co–N–C angle has the effect of straightening out the Co–NH_2–CH_2 group, which thus diminishes the packing density around the Co. The pattern is thus reasonably clear. High-bulk ligands such as pn or methylamine produce longer M–N bonds and larger M–N–C angles. If we introduce a ligand such as carbonate which, because of its O–Co–O angle of 70°, packs efficiently around the metal ion, we see a drop in Co–N lengths in $[Co(pn)_2CO_3]^+$. Ligands such as 9-aneN_3 pack well around a larger metal ion such as Ni(II), and here we see the strain-free bond lengths realized, but repulsion between the two rings at shorter M–N bond lengths means that for Co(III) this is not possible. We have reproduced in Figure 2 a diagram of the $[Co(9\text{-ane}N_3)_2]^{3+}$ complex, showing which H–H nonbonded repulsions are responsible for the Co–N bond lengthening.

A ligand such as 1,2,3-tn has a low packing density, and we see in Table II that this ligand comes closer than the others to realizing the ideal Co–N bond lengths. The ligand 12-aneN_4 also

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Table II. Some Structural Parameters for Complexes of Co(III) and Ni(II), Calculated by Using the EFF, and Observed in Crystal Structures[a]

	$[Co(NH_3)_6]^{3+}$[b]	$[Co(en)_3]^{2+}$[c]	$[Co(pn)_3]^{2+}$[d]	$[Co(pn)_2CO_3]^{+}$[e]	$[Co(12\text{-}aneN_4)(NO_2)_2]^{+}$[f]	$[Co(9\text{-}aneN_3)_2]^{3+}$[g]	$[Co(CH_3NH_2)_5Cl]^{2+}$[h]	$[Co(1,2,3\text{-}pn)_2]^{2+}$[i]
Co–N[j] calcd	1.96	1.96	1.98, 2.00	1.94, 1.96	1.98, 1.94	1.96	2.00	1.95, 1.93
obsd	1.96	1.96	1.97, 1.99	1.94, 1.97	1.97, 1.94	1.97	1.99	1.96, 1.94
N–Co–N[k] calcd	(90)	88.0	94.7	91.6, 92.9, 90.0, 88.7	86.0	87.3	93.5, 94.0, 90.7, 89.4, 87.2	88.2, 92.6
obsd	(90)	85.6	91.0	91.9, 93.5, 91.4, 89.7	85.1	85.0	94.8, 96.6, 87.9, 91.7, 86.2	84.9, 94.1
Co–N–C[l] calcd		107.5	120.9	120.0, 117.7, 115.6, 114.7	107.4, 110.4	110.4, 106.5	120.3	109.0, 100.5
obsd		108.7	122.0	121.2, 120.2, 117.5, 115.8	108.3, 111.1	113.3, 104.6	122.7	109.4, 100.6

	$[Ni(NH_3)_6{}^{2+}$[m]	$[Ni(en)_3]^{2+}$[n]	$[Ni(pn)_3]^{2+}$[p]	$[Ni(dien)_2]^{2+}$[q]	$[Ni(dptn)_2]^{2+}$[r]	$[Ni(9\text{-}aneN_3)_2]^{2+}$[s]	$[Ni(en)_2]^{2+}$[t]	$[Ni(daco)_2]^{2+}$[u]
Ni–N[v] calcd	2.12	2.12	2.13, 2.16	2.06, 2.16	2.11, 2.20	2.09	1.91	1.94
obsd	(2.11)	2.12	2.14, 2.18	2.05, 2.14	2.12, 2.22	2.10		1.94
Ni–Ni–N[w] calcd	(90)	84.3	85.1	82.9	91.2, 91.7	84.5		90.0
obsd	(90)	82.3	87.5	81.6	92.4, 90.2	82.6		90.0
Ni–N–C[x] calcd		105.1	120.4	105.9	119.3, 117.3	109.8, 103.7		
obsd		109.7	121.7	108.7	121.3, 117.4	110.0, 104.8		

[a] Are the averaged parameters where these are not significantly different in the reported crystal structure. EFF calculations carried out by using ideal M–N bond lengths of 1.925 Å for Co(III) and 2.10 Å for Ni(II) (high spin). [b] The observed bond length is the mean of the range from 1.94 to 1.98 Å reported in the literature. [c] The $\Lambda[Co(en)_3\delta\delta\delta]^{3+}$ isomer. The structural parameters observed are from: Duesler, E. N.; Raymond, K. N. *Inorg. Chem.* 1971, *10*, 1486–1492. Witiak, D.; Clardy, J. C.; Martin, D. S. *Acta Crystallogr., Sect. B* 1972, *B28*, 2694–2699. Iwata, M.; Nakatzu, K.; Saito, Y. *Acta Crystallogr., Sect. B* 1969, *B25*, 2562–2571. Earlier references such as Nakatsu [Nakatsu, K. *Bull. Chem. Soc. Jpn.* 1962, *35*, 832–839 were rejected because of high *R* factors, in this case 12.8%. [d] Nagao, R.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B* 1973, *B29*, 2438–2447. [e] Geue, R. J.; Snow, M. R. *J. Chem. Soc. A* 1971, 2981–2987. [f] The *cis*-dinitro folded form from: Iitaka, Y.; Shina, M.; Kimura, E. *Inorg. Chem.* 1974, *13*, 2886–2891. The long Co–N bond lengths are to the nitrogens on the fold line of the macrocycle. Force constants for the nitro groups are from: Shimanouchi, T. *Pure Appl. Chem.* 1963, *7*, 131–145. The Co–N force constants to the nitro groups were the same as those used for polyamines. [g] From: Mikami, M.; Kuroda, R.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B* 1977, *B33*, 1485–1489. The ligand is actually (*R*)-2-methyl-1,4,7-triazacyclononane, but the presence of the methyl group should not much affect the structural parameters involving the Co(III). [h] Foxman, B. M. *Inorg. Chem.* 1978, *17*, 1932–1938. [i] Henrick, K.; McPartlin, M.; Munjoma, S.; Owston, P. G.; Sangokoya, S. A.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* 1982, 225–227. The short Co–N length is to the central nitrogen on the ligand. [j] Units are Å. [k] Angles in deg. Are the N–Co–N angles in the chelate ring, except where additional angles are reported. These can be identified by consulting the original papers. [l] Angles in deg. Comments otherwise as for N–Co–N angles. [m] Quite unbelievably, we were not able to locate a structure containing the $[Ni(NH_3)_6]^{2+}$ ion, and the reported M–N length is for the Co(II) complex, from Kime and Ibers [Kime, N. E.; Ibers, J. A. *Acta Crystallogr., Sect. B* 1969, *B25*, 168–169]. [n] Reference 38, the $\Lambda\delta\delta\delta$ isomer. [p] Andreetti, G. D.; Cavalca, L.; Sgarabotto, P. *Gazz. Chim. Ital.* 1971, *101*, 494-496. The two different bond lengths result from a skewing of the ligand so as to relieve steric packing problems. [q] From: Biagini, S.; Cannas, M. *J. Chem. Soc. A* 1970, 2398–2408. dien = 1,4,7-triazaheptane. The short Ni–N bond is to the central nitrogen of the ligand. [r] dptn = 1,5,9-triazanonane, structure from same ref as preceding complex. The long Ni-N bond is to the central nitrogen of ligand. It is of interest to note that the structure of the Co(III) bis(dptn) complex has been reported: Hambley, T. W.; Searle, G. H.; Snow, M. R. *Aust. J. Chem.* 1982, *35*, 1285–1295. The Co-N bond to the central nitrogen of the ligand is, as found for the Ni(II) complex, lengthened to 2.04 Å, with the outer Co–N lengths being 1.97 Å. EFF calculations by the latter authors predict these bond lengths fairly closely, the predicted lengths being, respectively, 2.03 and 1.97 Å, based on a strain-free Co–N of 1.925 Å for the EFF calculations. [s] From ref 39. [t] This calculation is included to show that for square-planar Ni(II) in a low-strain environment, very close to the strain-free Ni–N bond length of 1.89 Å for square planar Ni(II) will be realized. [u] From: Boeyens, J. C. A.; Fox, C, submitted for publication, for the complex of square-planar low-spin Ni(II) with daco, where daco is 1,5-diazacyclooctane. [v] Bond lengths in Å. [w] Bond angles in deg. Refer to the bond angles in the chelate ring. [x] Bond angles in deg.

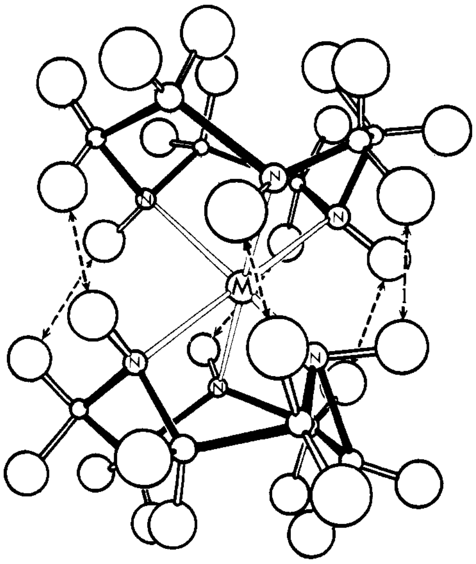

Figure 2. ORTEP[45] drawing of the $[M(9\text{-aneN}_3)_2]^{n+}$ ion, showing the strong interligand H–H nonbonded repulsions (– – –), and intraligand repulsions (···) which result in the Co–N bond being stretched from its strain-free length of 1.925 Å to a final value of 1.97 Å in the Co(III) complex. The skeletal atoms of the 9-aneN$_3$ ring are joined by the black-filled bonds, while the hydrogen atoms are shown as large open circles. The H–H nonbonded repulsions shown are all in excess of 0.5 kcal mol^{-1} in energy.

packs efficiently, and with CO_3^{2-} present, we find average Co–N bond lengths[20] of 1.95 Å. Square-planar coordination around low-spin Ni(II) provides an excellent low packing density situation, and we find here that the strain-free M–N length is realized quite often. Even when longer Ni–N lengths are found, as seen for daco in Table II, these are accurately reproduced by the EFF. Daco with its six methylene groups provides a sufficiently high packing density around the Ni(II) that Ni–N bond lengthening occurs.

Many different EFF parameter sets exist,[21] and strain-free Co–N bond lengths of 2.00 Å have been used in EFF calculations.[22,23] One must thus ask whether different parameterization of the EFF without postulating short Co–N strain-free bond lengths might not reproduce the observed structural parameters in Table II. Further, how sensitive is the ideal Co–N length of 1.92 Å to the choice of other parameters, such as the H–H nonbonded repulsion parameters.

In an attempt to answer this, we have repeated the EFF calculations on the $[Co(9\text{-aneN}_3)_2]^{3+}$ complex using reported[23] EFF parameters with an ideal Co–N length of 2.00 Å. This predicts a Co–N bond length of 2.03 Å, as was predicted[22,23] for all of the other polyamine complexes of Co(III) analyzed. In order to obtain the observed Co–N of 1.97 Å, we found that an ideal Co–N length of 1.925 Å had to be used. Thus, even though the H–H repulsion parameters are rather different than those used by us, in order to predict Co–N lengths accurately, the same ideal Co–N length must be used.

What emerges here is that the calculations show that M–N bond lengths are dominated by the exponential repulsion term in r, the separation between nonbonded atoms, in expression 1 for

$$U(r_{ij})\text{NB} = a_{ij}\exp(-b_{ij}r_{ij}) - c_{ij}/(r_{ij})^6 \qquad (1)$$

nonbonded interactions, where the interacting nonbonded atoms are hydrogens. $U(r_{ij})$NB is the nonbonded potential energy, between atoms i and j, and a_{ij}, b_{ij}, and c_{ij} are constants specific to the type of atoms interacting. r_{ij} is the internuclear separation between the two nonbonded atoms. The exponential nature of this term means that the H–H approach is effectively prohibited beyond limits which have been established by calculation on a large number of organic compounds.[21] It thus seems highly probable that the strain-free M–N lengths reported in Table I are correct. The strain-free M–N lengths for Co–N and Ni–N are those used to reproduce the structures in Table II. Those for Cr(III) and Rh(III) were derived by using the EFF field and are the strain-free M–N lengths which reproduce the observed M–N bond lengths[24] in the $[M(NH_3)_6]^{3+}$ complexes. These, like the strain-free M–N for Ni(II), are slightly shorter than the M–N lengths found in observed structures, by about 0.02 Å. Cu(II) is somewhat problematic, as reported Cu–N bond lengths range from 1.99 (in-plane) to 2.15 Å (regular octahedron) depending on the degree of tetragonal distortion. The value selected is that found[25] in several structures where four in-plane nitrogens were present, with elongated bonds to axial oxygens (water, sulfate, etc.). The electronic spectral data in Table I for Cu(II) were recorded in water, where we must presume weakly coordinated waters to be present on the axial positions. For truly square-planar copper(II), slightly shorter Cu–N bond lengths of 2.00 Å are found.[26] *Table I suggests very strongly that the best-fit hypothesis is correct.*

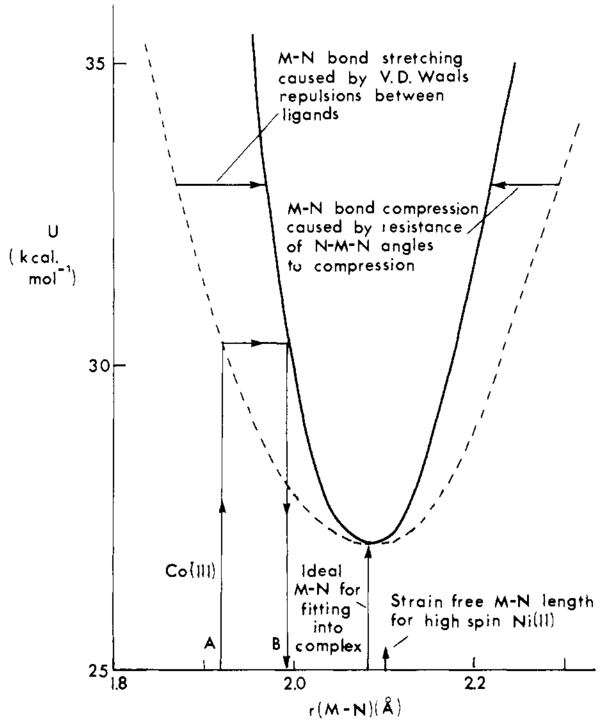

Figure 3. Final energy-minimized strain energy, U, plotted as a function of both ideal (···) and final energy minimized (—) metal to nitrogen bond length, r(M–N), for the $[M(9\text{-aneN}_3)_2]^{n+}$ ion. Inclusion of U as a function of ideal M–N length allows us to read the final energy-minimized bond length for a metal ion such as Co(III) off the diagram. Thus, the ideal Co–N length of 1.925 Å at point A leads to a final energy-minimized Co–N length at point B of 1.98 Å. The diagram shows similarly that Ni(II) fits almost exactly into the bis(9-aneN$_3$) system.

A point of special interest in Table I in relation to the value of Dq_{xy} is the fact that for both high- and low-spin Ni(II), not only is the LF in the best-fit tetraaza macrocycle but also in the macrocycle one size up much larger than that for the open-chain analogue. We thus find that Dq_{xy} is also much larger than that found in the open-chain analogue for low-spin Ni(II) with 14-aneN$_4$, best-fit size 2.07 Å, and for high-spin Ni(II) with 15-aneN$_4$, best-fit size 2.22 Å. For the compression hypothesis to remain tenable, we would have to postulate that low-spin Ni(II)

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was being compressed by 14-aneN_4, when all reported Ni–N bond lengths for low-spin Ni(II) are much shorter than 2.07 Å. Similarly, for high-spin Ni(II), we would have to postulate that the strain-free Ni–N bond length was well in excess of 2.22 Å, when the only structures where such long bond lengths occur are special cases, such as the bis(dptn) complex in Table II, where the long Ni–N bond length to the central nitrogen donor is a result of steric crowding. *We are thus seeing stronger ligand fields than found in the open-chain analogues, in the complexes of macrocycles which are far too large to be compressing the metal ion.*

In Figure 3 is shown the strain energy of the $[M(9\text{-ane}N_3)_2]^{n+}$ ion as a function of M–N length. In calculating the strain energies all the EFF parameters involving the metal ion were kept constant at those for high-spin Ni(II), while the value of the strain-free M–N length was varied at intervals of 0.05 Å from 1.8 to 2.4 Å. As stated above, the calculations at short M–N length are dominated by van der Waals repulsions, and the fact that we are using constant values of the M–N force constants makes very little difference. For example, the Co–N force constants are 3 times as large as those for Ni–N, but the difference in predicted bond length for the 9-aneN_3 complex is only 0.015 Å if we use Ni–N force constants with an ideal Co–N of 1.925 Å, instead of the correct Co–N force constants. What Figure 3 shows is that metal ions with an M–N length of 2.08 Å fit best into the bis(9-aneN_3) system. At bond lengths less than this value, as seen in Figure 2, the M–N bonds are stretched out from the ideal value (broken line) to the final energy minimized value (solid line). This is caused by the van der Waals repulsions shown in Figure 2, which result in the M–N bond length being stretched out from 1.925 to 1.98 Å. At M–N length greater than 2.08 Å, the metal–nitrogen bonds are compressed. This is caused by a combination of attractive van der Waals forces and the resistance of the N–M–N bond angle to compression. If we consider that ligands will have a preferred bite size (N–N distance), then simple geometric considerations show that as the M–N length increases, so the N–M–N angle must be compressed. This bond angle compression is relieved as the M–N bonds become compressed. The ability of the ligand to compress the metal ion will thus depend to a certain extent on the size of the N–M–N angle bending force constants. For very ionic M–N bonding one might find small N–M–N bending constants and only a small tendency for the M–N bonds to be compressed.

Bonding to Secondary Nitrogens in Nonmacrocyclic Ligands. If we create secondary nitrogens by adding extra chelate rings, as happens in passing from en to dien, it has already been demonstrated[14] that the cumulative ring strain created is sufficient to cancel out the extra stabilization expected from the presence of a secondary nitrogen. If we interpose alternating five- and six-membered rings in the polyamine complex, this strain is alleviated sufficiently for us to see an enhanced stability,[27] as has been shown quantitatively by using EFF calculations[15] for ligands such as 2,3,2-tet. Another instance[14] where the extra stability induced by the secondary nitrogen becomes apparent is in ligand pairs such as HEEN and ODEN (Figure 1). The ligands are very similar, except that HEEN has a secondary nitrogen plus alcoholic oxygen where ODEN has an ethereal oxygen plus primary nitrogen. We thus find[28] that the difference in stability for the Ni(II) complexes is such that its complex with HEEN is 1.6 kcal mol^{-1} more stable than that with ODEN. This finds a ready explanation in the fact that here we have managed to turn a primary into a secondary nitrogen, without, presumably, increasing the strain in the resulting complex. As will be discussed below, transition-metal ions do not respond to oxygens being transformed from "primary" (alcoholic) to "secondary" (ethereal) as they do for the same change with nitrogen. In keeping with our interpretation of the difference in bonding strength between HEEN and ODEN in terms of primary and secondary nitrogens, it is found[29] that $10Dq$ in the HEEN complexes is much higher than in those of ODEN.

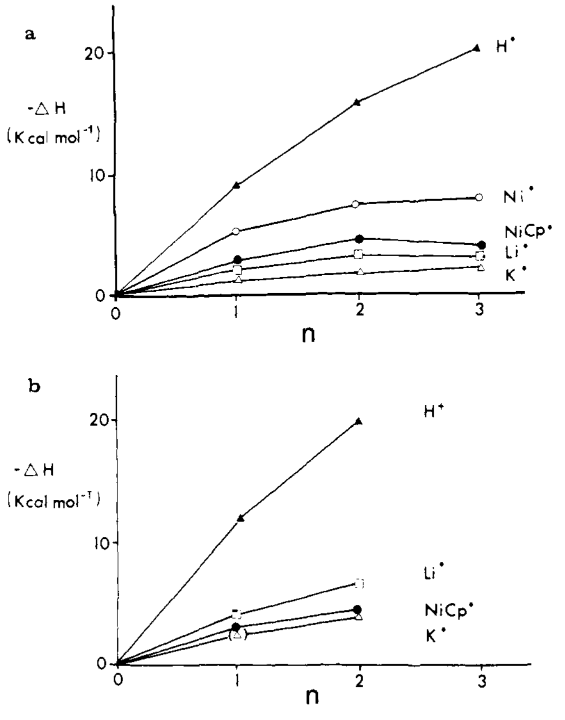

Figure 4. (a) Increase in ΔH of complex formation of methyl-substituted amines, $(CH_3)_nH_{(3-n)}N$, in the gas phase, relative to that for the ammonia complex ($n = 0$), as a function of n ($n = 1$ = methylamine, $n = 2$ = dimethylamine, $n = 3$ = trimethylamine). Data from ref 16–18. (b) Increase in ΔH of complex formation in the gas phase relative to the complex with water ($n = 0$) in the series H_2O, CH_3OH ($n = 1$), and $(CH_3)_2O$ ($n = 2$) as a function of n, for a variety of Lewis acids. Data from ref 16–18.

A large number of crystallographic studies on Cu(II) complexes of *N*-methyl- and *N*-ethyl-substituted ethylenediamines by Pajunen et al.[30] have demonstrated that the M–N bond lengths are increased by such *N*-alkyl substitution. Our EFF calculations on the bis complex of *N,N'*-diethylethylenediamine with Cu(II) predict, using an ideal Cu–N bond length of 2.00 Å for a square-planar complex, a long Cu–N bond length of 2.09 Å to the tertiary nitrogen and 2.03 Å to the primary nitrogen. This can be compared with the observed[30] values of 2.08 and 2.02 Å. The bond lengthening to the tertiary nitrogen is produced by van der Waals repulsions between the hydrogens on the ethyl groups and those on the rest of the complex. Once again what we are seeing here is basically a problem of packing all these groups around the metal ion.

Lever[31] has demonstrated the effect of packing density with bis(*N,N'*-dimethylethylenediamine) complexes of Cu(II). With ligands such as water present, which coordinate to the axial sites on the Cu(II) complex, the ligand field is much weaker than in the analogous complexes with en itself. When counterions such as perchlorate are used, which do not occupy the axial sites in the solid state, the ligand field is now found to be much stronger in the *N,N'*-dimethylethylenediamine than in the analogous en complexes. We thus see that for these complexes when the coordination number drops from 6 in the presence of water to 4 with the more weakly coordinating perchlorate, the lower packing density around the Cu(II) allows the greater basicity of the secondary nitrogens to become manifest.

Bonding to Primary and Secondary Amines in the Gas Phase. The pK_a values of primary and secondary amines in water are very similar. For example, the pK_a for methylamine is 10.6 and for

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Table III. Values of 10*Dq* Corrected for Strain-Energy Effects for Ni(II) Complexes with Six Nitrogen Donor Atoms[a]

complex[b]	U_{M-N}	U_{NMN}	$\Sigma U_{MNC(H)}$	ΣU_M	U_{ML}	10*Dq*	10*Dq*(cor)[d]
$[Ni(NH_3)_6]^{2+}$	0	0	0	0	0	10750	10750
$[Ni(en)_3]^{2+}$	0.06	0.96	0.64	1.66	4.57	11500	12000
$[Ni(pn)_3]^{2+}$				4.28	13.12	10900	12150
$[Ni(dien)_2]^{2+}$	0.50	2.81	0.61	3.92	11.87	11700	12900
$[Ni(dptn)_2]^{2+}$	1.57	0.29	3.08	4.93	21.32	11000	12400
$[Ni(penten)]^{2+}$	0.26	5.50	1.36	7.12	27.98	10600	12700
$[Ni(9\text{-ane}N_3)_2]^{2+}$	0.02	2.92	0.88	3.82	27.05	12350	13500

[a] Units are kcal mol^{-1} for strain energy, U. U_{M-N} is for Ni-N bond length deformation, U_{NMN} is for N-Ni-N bond angle deformation, and $U_{MNC(H)}$ is for deformation of the Ni-N-C and Ni-N-H bond angles. ΣU_M is the total strain energy in the complex, involving the metal ion, and equals $U_{M-N} + U_{NMN} + U_{MNC(H)}$. ΣU_{ML} is the total strain energy in the complex. [b] Abbreviations: en = ethylenediamine, pn = 1,3-propanediamine, dien = 1,4,7-triazaheptane, dptn = 1,5,9-triazanonane, penten = *N,N,N',N'*-tetrakis(2-aminoethyl)ethylenediamine, 9-aneN_3 = 1,4,7-triazacyclononane. [c] Units are cm^{-1}. Mostly from ref 35, or cited in text. [d] 10*Dq*(cor) is 10*Dq* + $\Sigma U_M/1.2$, expressed in cm^{-1}, and is 10*Dq* corrected for steric strain, as discussed in the text.

dimethylamine is 10.8.[28] This further example of a "hidden" inductive effect[10] has lead to a strong intuitive feeling among many chemists that the basicities of the primary and secondary nitrogens are not intrinsically very different. This is evidenced, for example, in the rejection[32] of the idea that greater basicity of the secondary nitrogens contributed to the macrocyclic effect. The early work of Munson[33] on gas-phase basicities of amines demonstrated the very much greater proton basicity of the secondary nitrogen, but it was not clear that this extended to metal ions. Data on the binding of amines to metal ions in the gas phase have recently become available,[16-18] which clarify this situation.

In Figure 4a is shown the increase in the enthalpy change on complex formation in the gas phase as hydrogen is replaced by methyl in the series from ammonia to trimethylamine and from water to dimethyl ether as in Figure 4b. Woodin and Beauchamp have shown[16] using electrostatic calculations that the curvature in the relation for Li^+ in Figure 4 is due to steric repulsion between the Li^+ and the added methyl groups, and *were it not for the steric repulsion, there would be a steady increase in* $-\Delta H$ *per methyl group added.* The increase in $-\Delta H$ for each metal ion as we pass from the ammonia to the methylamine complex should thus be the best indicator of inductive effects, since steric effects should here be at a minimum. This increase in $-\Delta H$ of complex formation in the gas phase in passing from ammonia to methylamine for the proton is 9.0 kcal mol^{-1}, for $NiCp^+$ it is 2.9 kcal mol^{-1}, and for Li^+ it is 2.0 kcal mol^{-1}. For the bis(amine) complexes formed by other metal ions it is 8.55 kcal mol^{-1} for $FeBr^+$ and for Ni^+ it is 5.31 kcal mol^{-1}.[17,18] There is thus evidence that in the gas phase all metal ions respond favorably to a change from primary to secondary amines. This supports strongly our contention[14] that metal–nitrogen bonds to secondary nitrogens are intrinsically stronger than those to primary nitrogens and also makes our estimate of this difference as 1.7 kcal mol^{-1} for the Ni^{II}–N bond in aqueous solution seem most reasonable.

We have included Figure 4b because it shows up an interesting difference in the way transition-metal ions such as the $NiCp^+$ (Cp = cyclopentadienyl) ion and a non-transition-metal ion such as Li^+ with highly ionic metal-to-ligand bonding respond to oxygen or nitrogen as hydrogens are replaced by methyls. We see in Figure 4a that the response to replacing hydrogens by methyls on nitrogens is strongest for the $NiCp^+$ ion, whereas in Figure 4b, the same change produces a stronger response in Li^+. This suggests that one of the reasons for the preference of transition-metal ions for nitrogen donor macrocycles may be due to the lack of response of these metal ions to the potential change in inductive effect when oxygen donor macrocycles are formed by turning the alcoholic groups of the open-chain analogue into ether groups. This is evidenced, as mentioned above, in the lower stability of complexes of Ni(II) and Cu(II) with the ligand ODEN than with HEEN, accompanied by weaker ligand field strengths.

Steric Strain and 10*Dq*. If we strain the M–N bond, this leads to a diminishing of the overlap between the nitrogen and metal orbitals forming the bond, and hence to a decrease in 10*Dq*, if we consider the molecular orbital interpretation[34] of LF theory. Such effects are reasonably clear if we compare the complex of Ni(II) with penten (*N,N,N',N'*-tetrakis(2-aminoethyl)ethylenediamine) with its tris(en) complex: 10*Dq* in the former is[35] 10 600 cm^{-1}, while in the latter it is[36] 11 500 cm^{-1}, and $-\Delta H$ of complexation are respectively[28] 19.7 and 28.0 kcal mol^{-1}. When we examine the EFF-generated structure of $[Ni(penten)]^{2+}$ and compare it with that of $[Ni(en)_3]^{2+}$, we see that the former is severely sterically strained, with considerable N–M–N angle distortion, while that in the tris(en) structure is comparatively stain free. It is clear that the low 10*Dq* and $-\Delta H$ for the penten complex must relate to the high steric strain of U = 13.0 kcal mol^{-1}, compared with 4.57 kcal mol^{-1} in the tris(en) complex. What is needed is a simple means of relating strain to 10*Dq*. Our approach is to assume that strain-energy contributions involving the metal ion will lead to a decrease in LFSE (ligand field stabilization energy), while those involving the ligand only will not. Since for octahedral Ni(II), LFSE = $-12Dq$, we simply have to sum the contributions to U_{ML} which involve the metal atom, which we will call $\sum U_M$, divide by 1.2, and add this to the measured value of 10*Dq* to obtain 10*Dq*(cor), which is the hypothetical value of 10*Dq* which would be observed in the absence of steric strain. In Table III are seen the results of such calculations for a variety of complexes of Ni(II). We see now that 10*Dq*(cor) for $[Ni(penten)]^{2+}$ is 12 700 cm^{-1}, actually higher than for $[Ni(en)_3]^{2+}$, where it is 12 000 cm^{-1}. One would expect this on the grounds of inductive effects, since penten has four primary and two tertiary nitrogens, against the six primary nitrogens in the tris(en) complex.

Before proceeding further, we should consider the nature of the contributions to $\sum U_M$. Included in $\sum U_M$ are the N–M–N bending contributions, whose effects in decreasing overlap in the M–N bond are fairly obvious. Also included are the M–N bond length deformations. One might be presented with the problem that M–N bond length compression should actually increase 10*Dq*. There is no evidence in any of the structures examined here that such compression, beyond small values of about 0.01 Å, actually takes place. Finally, one has to include angle deformations of the Ni–N–C and Ni–N–H bonds. These contribute strongly to diminished orbital overlap in the M–N bond where Ni–N bond lengths may be fairly normal, but the orientation of the orbital from the nitrogen is poor for overlap with that from Ni(II). We have not included torsional contributions involving the Ni atom. These are set at zero,[12] except where the Ni is a terminal atom, as in the Ni–N–C–H contribution about the N–C bond. Since it is not clear how torsion around the N–C bond might influence 10*Dq*, these small contributions are omitted.

In Figure 5 is shown the relationship between 10*Dq*, or 10*Dq*(cor), and n, the number of alkyl groups attached to the nitrogens. We see that there is almost no relationship between 10*Dq* and n, whereas a reasonable linear relationship between

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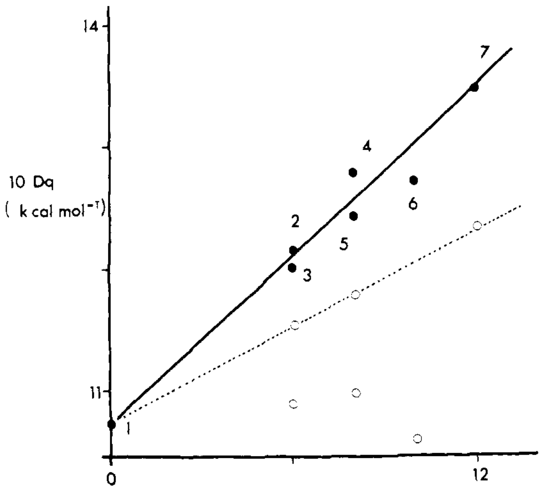

Figure 5. Relationship between $10Dq$(···○) or $10Dq$(cor) (—●) and n, the number of alkyl groups attached to the nitrogen, in complexes of Ni(II) with six nitrogens attached to them. $10Dq$(cor) is $10Dq$ corrected for steric distortion of the Ni–N bond, as described in the text. Complexes are (1) $[Ni(NH_3)_6]^{2+}$, (2) $[Ni(en)_3]^{2+}$, (3) $[Ni(pn)_3]^{2+}$, (4) $[Ni(dien)_2]^{2+}$, (5) $[Ni(dptn)_2]^{2+}$, (6) $[Ni(penten)]^{2+}$, and (7) $[Ni(9\text{-}aneN_3)_2]^{2+}$. Abbreviations: en = ethylenediamine, pn = 1,3-propanediamine, dien = 1,4,7-triazaheptane, dptn = 1,5,9-triazanonane, penten = N,N,N',N'-tetrakis(2-aminoethyl)ethylenediamine, and 9-aneN_3 = 1,4,7-triazacyclononane.

$10Dq$(cor) and n is found. Figure 5 thus provides a graphic illustration of how steric effects diminish $10Dq$ and mask inductive effects. Thus, just as we explain[37] the increase in $10Dq$ from 10750 to 11500 cm^{-1} in passing from $[Ni(NH_3)_6]^{2+}$ to $[Ni(en)_3]^{2+}$ in terms of the inductive effects of the ethylene bridges of the latter complex, so we explain the further increase to 12350 cm^{-1} in $[Ni(9\text{-}aneN_3)_2]^{2+}$ as a logical extrapolation in terms of the presence of secondary rather than primary nitrogens. What appears to be special about $[Ni(9\text{-}aneN_3)_2]^{23}$ is, as seen in Table III, that the strain in the M–N bonds is, unlike that in $[Ni(penten)]^{2+}$, relatively low, so that the inductive effects are not completely masked.

Alper and Zompa[38] have attempted to explain the high LF found in $[Ni(9\text{-}aneN_3)_2]^{2+}$ as being due to trigonal distortion of the complex. One might point out here that the amount of trigonal distortion in this complex is not especially large. For example, the trigonal twist distortion[39] in $[Ni(en)_3]^{2+}$ with its much lower $10Dq$, is 9.8°, while that in $[Ni(9\text{-}aneN_3)_2]^{2+}$ is only 3.4°.[40] The splitting of the $^3A_{2g} \rightarrow {}^3T_{2g}$ band, assigned as being due to trigonal distortion,[38] is much more convincingly assigned[36] as due to spin–orbit coupling of the $^3T_{2g}$ and ^1E_g levels, which is the generally accepted interpretation of this type of splitting.

Much more important for our discussion here is the preparation of low-spin $[Fe(9\text{-}aneN_3)_2]^{n+}$ complexes, where n is 2 and 3.[41] *The low-spin state here indicates that the Fe(II) and Fe(III) are in the presence of a strong ligand field, comparable at least to that found in the tris(bpy) complexes, which are also low spin.* If the strong ligand field in the bis(9-aneN_3) complexes was only apparent, we would not expect spin pairing, but rather high-spin complexes, as is actually found for $[Fe(en)_3]^{2+}$.

Prediction of Enthalpy of Complex Formation Using EFF Calculations. In the EFF approach one can predict enthalpies of formation of substances in the gas phase,[21] such as alkanes, by assuming an "ideal" strain-free bond energy for each type of bond. In essence, one sums the ideal bond energies for a molecule and then obtains a predicted enthalpy of formation by subtracting the strain energy from the sum of the ideal bond energies. For the complex-formation reactions which concern us here, no enthalpy data in the gas phase are available, since all the reactions have been studied in aqueous solution. Undoubtedly, solvation energies must make a large contribution to the observed enthalpies of complex formation, but this should be less important[12,14] if we compare differences between fairly similar complexes. Thus in our analysis of the difference in stability between similar complexes which have on the one hand five-membered rings and on the other hand six-membered rings,[12] it was assumed that the difference in solvation between, e.g., $[Ni(en)_3]^{2+}$ and $[Ni(pn)_3]^{2+}$ would be small and that the difference in enthalpy would be mainly ascribable to strain-energy differences. One also has to calculate the strain-energy differences between the free ligands, e.g., en and pn, and include them in the overall reaction

$$\underset{U_M}{M} + \underset{U_L}{nL} \xrightarrow{\Delta U} \underset{U_{ML}}{ML_n} \qquad (2)$$

and include nU_L as a favorable contribution to the overall change in strain energy on complex formation, ΔU.

Two approaches to eq 2 have been successful. One can say[12] that U_M is common to all reactions involving the same metal ion, in this case Ni(II), and neglect U_M in calculating ΔU. One then compares the difference in ΔU for the two complexes,[12] e.g., 6.7 kcal mol^{-1} between $[Ni(en)_3]^{2+}$ and $[Ni(pn)_3]^{2+}$, with the difference between their enthalpies[28] of complex formation, in this case 7.3 kcal mol^{-1}, showing excellent agreement. In the second approach,[14] one calculates ΔU including U_M for Ni(II) and then subtracts this ΔU from empirically derived ideal strain-free bond energies for forming the Ni–N bond in aqueous solution. These strain-free Ni–N energies are found empirically[14] to be −4.8 kcal mol^{-1} for forming Ni–N bonds to primary nitrogen, and at −1.7 kcal mol^{-1} more favorable, −6.5 kcal mol^{-1} for forming Ni–N bonds to secondary nitrogens in aqueous solution. In Table IV are shown the enthalpies of complex formation predicted for Ni(II) complexes with aliphatic amines by this approach, and it is seen that the level of agreement is excellent.

The suggestion that macrocyclic ligands were "prestrained"[12] or "preoriented" means that, in effect, we obtain a more favorable enthalpy of complex formation because the favorable U_L term in eq 2 is larger than usual. In Table IV we see that the predicted enthalpy for formation of the complex $[Ni(cyclam)(H_2O)_2]^{2+}$ is in excellent agreement with that observed.[13] This is not an indication, however, that in the simplest sense the idea that the macrocyclic effect results from "prestraining" or "preorienting" of the ligand[11,12] is correct. In the EFF approach, the dipoles on nitrogens are treated as small atoms.[21] If we leave out the dipoles on the nitrogens of polyamine ligands, the differences in strain energies of the open-chain polyamines are not much affected, and the accuracy of prediction of enthalpy changes on complex formation remains about the same. For the macrocycle, where the dipoles are forced into close proximity in the center of the ligand, the inclusion of dipoles is critical. If the dipoles are left out, then U_L for cyclam is smaller to the extent that ΔU is actually larger than for the open-chain analogue, and we would predict a more favorable enthalpy of complex formation for 2,3,2-tet than cyclam with Ni(II). The somewhat higher value of U_L calculated for cyclam than for 2,3,2-tet with dipoles left off is offset by a higher value of U_{ML}. The latter high U_{ML} is caused by the fact that the orientation of the nitrogens in the cavity of cyclam is poor for coordination in a planar fashion to a metal ion, even though the hole size is ideal for accepting a metal ion the size of Ni(II). Thus, the ligand cyclam is in a state of high strain in Table V because of dipole–dipole repulsion in the cavity of the macrocycle and is not due to the conformation of the ligand backbone. This would be expected, with hindsight, since the 14-membered cycloalkane ring is, like the cyclohexane ring, a system of low inherent strain,[21] having all of the hydrogens in the staggered position.

Our calculations show that a macrocyclic enthalpy will be produced by a high state of strain in the free macrocyclic ligand. This high U_{ML} is not, however, due to the conformation of the ligand itself, but relates to steric repulsions in the cavity of the macrocycle. In the gas phase this state of high strain could be

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Table IV. Enthalpy Changes on Complex Formation for Complexes of Ni(II), Observed, and Predicted by EFF Calculation as Described in the Text[a,b]

	$[Ni(en)(H_2O)_4]^{2+}$	$[Ni(en)_2(H_2O)_2]^{2+}$	$[Ni(en)_3]^{2+}$	$[Ni(pn)(H_2O)_4]^{2+}$	$[Ni(pn)_2(H_2O)_2]^{2+}$	$[Ni(pn)_3]^{2+}$
U_{ML}[c]	1.14	3.35	4.57	3.04	7.16	13.12
nU_L[d]	1.62	3.24	4.86	1.99	3.98	5.97
ΔU[e]	0.61	1.20	0.80	2.14	4.27	8.24
$\Delta H_{(ideal)}$[f]	−9.60	−19.20	−28.80	−9.60	−19.20	−28.80
$\Delta H_{(ideal)} + \Delta U$[g]	−8.99	−18.00	−28.80	−7.46	−14.93	−20.56
ΔH_{obsd}[h]	−9.00	−18.3	−28.00	−7.8	−15.0	−21.3

	$[Ni(dien)(H_2O)_3]^{2+}$	$[Ni(dien)_2]^{2+}$	$[Ni(dptn)(H_2O)_3]^{2+}$	$[Ni(dptn)_2]^{2+}$	$[Ni(trien)(H_2O)_2]^{2+}$	$[Ni(2,3,2\text{-tet})(H_2O)_2]^{2+}$	$[Ni(cyclam)(H_2O)_2]$
U_{ML}[c]	6.08	11.87	8.28	21.32	9.44	7.25	11.26
nU_L[d]	3.13	6.26	3.87	7.74	4.64	4.92	10.15
ΔU[e]	4.04	6.70	5.50	14.67	5.89	3.42	2.20
$\Delta H_{(ideal)}$[f]	−16.10	−32.20	−16.10	−32.20	−22.60	−22.60	−26.00
$\Delta U_{(ideal)} + \Delta U$[g]	−12.06	−25.50	−10.60	−17.53	−16.71	−19.18	−23.80
ΔH_{obsd}[h]	−11.9	−25.3	−10.60	−17.6	−14.00	−18.7	−23.6

[a] Units are kcal mol^{-1}. [b] For ligand abbreviations, see Figure 1. [c] The terms used to calculate ΔU, the change in strain energy, are from eq 2. U_{ML} is the strain energy of the complex. [d] U_L is the strain energy of the ligand, included n times for a complex with n polyamine ligands. [e] This is the total change in strain energy, and is given by $U_{ML} - nU_L - U_M$. U_M is the strain energy of the $[Ni(H_2O)_6]^{2+}$ ion, which is −1.09 kcal mol^{-1}. [f] $\Delta H_{(ideal)}$ is the sum of the strain-free Ni-N bonds formed in aqueous solution, being −4.8 kcal mol^{-1} per primary Ni-N, and −6.5 kcal mol^{-1} per secondary Ni-N, in the absence of steric strain. [g] The enthalpy of complex formation is predicted to be the sum of $\Delta H_{(ideal)}$ and ΔU. [h] The observed enthalpy change on complex formation, from ref 28. Note that these have been corrected to refer to the high-spin form only. Enthalpy for the high-spin cyclam complex from ref 13.

Table V. Final Energy Terms from the Force Field Calculations on Tetraaza Macrocyclic Ligands and Their Ni(II) Complexes[a]

	L = δ-cyclam[b]		L = 2,3,2-tet		L = 13-aneN$_4$		L = 2,2,2-tet	
	L	$[ML(H_2O)_2]^{2+}$	L	$[ML(H_2O)_2]^{2+}$	L	$[ML(H_2O)_2]^{2+}$	L	$[ML(H_2O)_2]^{2+}$
U_B[c]	0.77	0.94	0.33	0.50	0.87	2.98	0.28	0.46
U_{NB}	7.07	4.07	4.01	1.82	7.50	4.00	3.84	1.05
U_θ	1.67	4.41	0.54	3.31	2.20	7.46	0.49	3.54
U_ϕ	0.64	1.83	0.04	1.62	4.54	6.91	0.04	4.39
ΣU	10.15 (5.3)	11.26	4.92 (3.0)[d]	7.25	15.09	21.36	4.64	9.44
$U_L - U_{ML}$	−1.11		−2.33		−6.27		−4.80	
$\Delta U_{(cyclic)} - \Delta U_{(noncyclic)}$			1.22 (−1.7)[d]			−1.47		
add in 1.7 per extra 2° N[e]			4.62 (0.5)[d]			1.93		
obsd^2 difference in $\Delta H°$			4.9					
			(4.7)[g]			(1.5)[g]		

[a] The strain energy, ΣU, is calculated for each ligand and its high-spin Ni(II) complex. For each ligand, the increase in strain energy on complex formation is calculated, $U_L - U_{ML}$, and for the macrocyclic ligand and its open-chain analogue the difference in $U_L - U_{ML}$ is $\Delta U_{(cyclic)} - \Delta U_{(noncyclic)}$. In the absence of inductive effects, this quantity should be the macrocyclic enthalpy. Units are kcal mol^{-1}. [b] δ-cyclam is the most stable conformer. For ligand abbreviations see Figure 1, except for 2,2,2-tet, which is 1,4,7,10-tetraazadecane. [c] The contributions to the total strain energy, ΣU. U_B is the strain due to bond length deformation, U_{NB} is that due to nonbonded repulsions, U_θ is that due to bond angle deformation, and U_ϕ is the torsional contribution. [d] Strain energies calculated without dipoles on the nitrogens. It is seen that without this source of strain within the cavity of the macrocycle there would be only a very small macrocyclic enthalpy of 0.5 kcal mol^{-1} for the Ni(II) complex of cyclam. [e] This is the contribution to the macrocyclic effect from the "hidden" inductive effects of the secondary nitrogens, of which there are two extra on the macrocycles as compared with the open-chain analogues. [f] Reference 13, corrected to refer to high-spin forms of the Ni(II) complexes. [g] Actually refers to the macrocyclic enthalpy in the Cu(II) complexes, from: Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* 1979, 1581–1584. The macrocyclic enthalpy for Cu(II) with cyclam appears to be very similar to that for Ni(II), so that we offer the macrocyclic enthalpy for Cu(II) with 13-aneN$_4$ for comparison with the predicted value, since no macrocyclic enthalpy for Ni(II) with this ligand has been reported.

brought about by dipole–dipole repulsion. In addition to the parameters which treat the dipoles as small atoms, there is the problem of electrostatic repulsion between dipoles. Expressions which attempt to model these electrostatic repulsions have not proved satisfactory,[21] and so we have omitted these in our calculations. This seems justifiable on the grounds that in aqueous solutions the dipoles will be solvated and so such electrostatic repulsions should be diminished.

This raises, of course, the question of the effect of solvation. Margerum[42] originally proposed that steric hindrance to solvation was responsible for the occurrence of a macrocyclic enthalpy. Our calculations cannot model the effects of solvation, but inclusion of four hydrogen atoms on the nitrogens in place of the dipoles raises the strain energy of the ligand considerably. The resulting strain is, however, still less than if we include the electrostatic dipole–dipole repulsion terms. Our calculations thus suggest that we would still see a macrocyclic enthalpy in the gas phase which could be due to (1) relief of dipole–dipole repulsion within the macrocyclic cavity on complex formation and (2) the inductive effects of the greater number more basic secondary nitrogen in cyclam than in 2,3,2-tet.

Recent work[43] on the heats of solvation of cyclam and 2,3,2-tet from the gas phase into water have shown a heat of solvation for cyclam some 5.2 kcal mol^{-1} less favorable for cyclam than 2,3,2-tet. This has been interpreted tentatively[43] as indicating that the macrocyclic enthalpy is entirely due to the difference in the heats of hydration of the ligands. This conclusion must be approached with some caution, however. Although data on heats of solvation of amines from the gas phase are sparse, so that no trends can be identified, one cannot assume that adding three extra methylene groups in the place of two hydrogens on 2,3,2-tet to give cyclam would have no effect on the heats of solution and vaporization even in the absence of any steric hindrance to solvation. The

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conclusion[43] that there would be no macrocyclic enthalpy in the gas phase seems unlikely in the face of the fact that studies of several metal ions in the gas phase have shown[16-18] that there is a strong increase in enthalpy of complex formation as the nitrogen donor changes from primary to secondary, as shown in Figure 4. In addition, the relation between ΔH of complex formation and ligand field strength in polyamine complexes of Cu(II) and Ni(II) demonstrated by Fabbrizzi, Paoletti, and Lever[44] suggests that it is unlikely that a strong increase in LF strength as found for macrocyclic complexes compared with their open chain analogues would not be accompanied by a related increase in ΔH.

Conclusions

The data presented here appear to support the following conclusions.

(1) The increased ligand field strength found in complexes of macrocyclic ligands is at a maximum in the macrocycles which fit with the least steric strain around the metal ions.

(2) The increased LF strength is caused by the inductive effect of the increased number of secondary nitrogen donors present in a low-strain situation, which also contributes to the macrocyclic enthalpy.

(3) An important contribution to the macrocyclic enthalpy comes from strain in the cavity of the macrocycle, which in the gas phase would be caused by dipole–dipole repulsion and in aqueous solution would have a contribution from steric hindrance to solvation.

(4) van der Waals repulsions between ligands mean that for most metal ions the observed M–N bond lengths are somewhat longer than the strain-free lengths. This effect is of paramount importance for Co(III), which has a very short ideal Co–N length of 1.925 Å, which length is not realized in many of its complexes because of van der Waals repulsions. Only in complexes such as its complex with 13-aneN_4 can the ideal bond length be realized, and here we see a remarkably high LF.

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Registry No. $[Co(NH_3)_6]^{3+}$, 28219-81-0; $[Co(en)_3]^{2+}$, 23523-25-3; $[Co(pn)_3]^{2+}$, 46469-74-3; $[Co(pn)_2CO_3]^+$, 29826-35-5; [Co(12-aneN_4)$(NO_2)_2]^+$, 89707-71-1; [Co(9-ane$N_3)_2]^{3+}$, 89637-25-2; $[Co(CH_3NH_2)_5Cl]^{2+}$, 30051-70-8; $[Ni(NH_3)_6]^{2+}$, 15365-74-9; $[Ni(en)_3]^{2+}$, 15390-99-5; $[Ni(pn)_3]^{2+}$, 18347-71-2; $[Ni(dien)_2]^{2+}$, 19358-75-9; $[Ni(dptn)_2]^{2+}$, 46933-28-2; [Ni(9-ane$N_3)_2]^{2+}$, 59034-11-6; $[Ni(en)_2]^{2+}$, 15390-98-4; $[Ni(daco)_2]^{2+}$, 41685-78-3; $[Ni(penten)]^{2+}$, 31252-70-7; $[Ni(en)(H_2O)_4]^{2+}$, 15615-30-2; $[Ni(en)_2(H_2O)_2]^{2+}$, 15554-67-3; $[Ni(pn)(H_2O)_4]^{2+}$, 31082-54-9; $[Ni(pn)_2(H_2O)_2]^{2+}$, 46140-10-7; $[Ni(dien)(H_2O)_3]^{2+}$, 15662-52-9; $[Ni(dptn)(H_2O)_3]^{2+}$, 69622-25-9; $[Ni(trien)(H_2O)_2]^{2+}$, 15662-53-0; $[Ni(2,3,2\text{-tet})(H_2O)_2]^{2+}$, 36530-71-9; $[Ni(cyclam)(H_2O)_2]^{2+}$, 68317-92-0; [Ni(13-ane$N_4$)$(H_2O)_2]^{2+}$, 78088-44-5.

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Cofacial Assembly of Metallomacrocycles as an Approach to Controlling Lattice Architecture in Low-Dimensional Molecular Solids. Chemical, Structural, Oxidation-State, Transport, and Optical Properties of the Coordination Polymer [Fe(phthalocyaninato)(μ-pyrazine)]$_n$ and the Consequences of Halogen Doping

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Abstract: This contribution reports the first integrated chemical and physicochemical study of the consequences of iodine doping on the cofacially joined metallomacrocyclic coordination polymers $[Fe(Pc)(\mu\text{-pyz})]_n$ (Pc = phthalocyaninato, pyz = pyrazine). Polymers $\{[Fe(Pc)(\mu\text{-pyz})]I_y\}_n$, $y \lesssim 3$, were prepared via the reaction of either $[Fe(Pc)(\mu\text{-pyz})]_n$ or $Fe(Pc)(pyz)_2$ with iodine, and stoichiometry was established by elemental analysis and TGA/DTA (the latter measurements evidence stepwise loss of I_2, which is rather weakly bound, and then pyrazine). X-ray diffractometry indicates that the I_2-doped polymer is not highly crystalline, but that the undoped polymer is readily regenerated upon iodine removal. Resonance Raman spectroscopy indicates, by the reduced nature of the iodine species, that the polymer has been oxidized, while both ^{57}Fe Mössbauer (which supports the $\{[Fe(Pc)(\mu\text{-pyz})I_y\}_n$ structural formulation) and ESR spectroscopy argue that the oxidation is largely ligand centered. Reflectance spectroscopy indicates that any plasmalike edge in the infrared is extremely weak, in marked contrast to previously studied $\{[M(Pc)O]I_{1.1}\}_n$ polymers, M = Si, Ge. Four-probe charge-transport measurements on polycrystalline samples reveal large increases (up to 10^6) in electronic conductivity with increasing dopant level ($\sigma(\max) \approx 0.1\ \Omega^{-1}\ cm^{-1}$ at 300 K); the dependence of conductivity upon dopant level suggests the importance of percolation. The conductivity is thermally activated, with the apparent activation energies decreasing with increasing dopant level. A detailed analysis of the temperature dependence yields results in agreement with fluctuation-induced carrier tunneling through parabolic potential barriers separating the conducting regions.

The construction of multimolecular arrays in which conjugated metallomacrocycles are joined by covalent bridge in a cofacial manner (A) represents a powerful device for controlling lattice architecture and electronic delocalization in low-dimensional