The N–M–N Bond Angle in the Chelate Ring of Ethylenediamine. The Crystal Structure of Tetra-aqua(ethylenediamine)nickel(II) Nitrate

By **Gloria J. McDougall** and **Robert D. Hancock**,* National Institute for Metallurgy, Private Bag X3015, Randburg 2125, South Africa

The crystal structure of $[Ni(en)(OH_2)_4][NO_3]_2$ is reported (en = ethylenediamine). The mean Ni–N bond length is 2.065 Å, and N–Ni–N bond angle 83.6°. N–M–N angles in en complexes, and O–M–O angles in acetylacetonates, are discussed in terms of their relation to M–N or M–O bond length. A conformational analysis of tris-en complexes is carried out so as to compare the predicted effect on the N–M–N angle of varying the M–N bond length with the observed relation between N–M–N angle and M–N length.

An interesting feature of chelate rings is that the angle formed by the two donor atoms and the metal atom to which they are co-ordinated is, more often than not, very different from that expected from the co-ordination geometry of the metal ion. For example, the O–M–O angle in octahedrally co-ordinated acetylacetonates can vary from 97 (Co^{III}) to 82° (Sc^{III}). Hon and Pfluger[1] noted in this instance that there was a correlation between bond length and 'bite size' (O–O distance in the chelate ring) and what appeared to be a contribution from the ionic nature of the M–O bond that decreased the bite size in a complex such as that of Al^{III}. From simple geometric considerations, one would expect that the ligand would tend to preserve a particular bite size, whereas this particular bite size can simultaneously accommodate only the required 90° O–M–O bond angle for octahedral co-ordination for a particular M–O bond length. At greater M–O bond lengths the angle must be less than 90°, and at shorter it must be more than 90°. In fact, bite size varies more strongly with the ionic nature of the bond within the group of octahedral acetylacetonates,[1] in exactly the opposite way from the requirements of a model based on an optimum bite size. This is particularly so for the rhodium(III) complex.[2]

However, there is still a relation between M–O bond length and O–M–O angle, as seen in Figure 1 which includes structural data for acetylacetonates of all co-ordination geometries. The solid line represents the relation expected for a fixed bite size of 2.8 Å, which is approximately the average bite size for acetylacetonates. The dotted lines represent the relation for bite sizes 0.1 Å smaller or larger than 2.8 Å. A change is expected in O–M–O angle as the co-ordination geometry changes, as indicated in Figure 1, from tetrahedral (109.5°) to Archimedean antiprismatic (75°). There appears from Figure 1 to be a very definite relation between O–M–O angle and M–O length. Within each group, however, the bond angle varies in such a way as to keep the bite size approximately constant. Superimposed on this is a variation such that bite size is larger for very 'soft'† metal ions, *e.g.* Pt^{IV}, Ru^{III}, and Rh^{III} in octahedral co-ordination and Rh^{I}, Pd^{II}, and Pt^{II} in square-planar co-ordination. The bite size is smaller for very 'hard' members, such as Sc^{III} and Al^{III}. One must assume that, in addition to the contributions from the preferred bite size, there must be a contribution from bonding effects. Thus, for example, the more covalent, 'soft' M–O bonds could result in a greater directional specificity in the interaction between the O and M atoms, resulting in a much stronger M–O–C force constant, leading to an opening of the O–M–O angle, as observed. A further important consideration in Figure 1 is that the O–M–O angles observed for $[Zr(acac)_4]$ are smaller than expected, which is not found to be so for the larger $[Ce(acac)_4]$. This must, almost certainly, be because Zr^{IV} is on the borderline in appropriate size for six- or eight-co-ordination, with strong ligand–ligand repulsion brought about by interaction between the co-ordinated oxygens. Thus, it is found that Zr^{IV} in $[Zr(acac)_2X_2]$ is octahedrally co-ordinated.[3] No structural determination appears to have been reported for these complexes, but one would speculate that the O–M–O angle would be as expected from the O–M–O length.

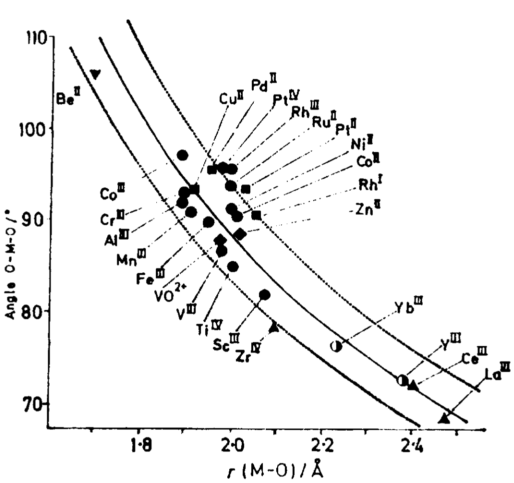

FIGURE 1 Relation between the O–M–O angle in the acetylacetonate ring and M–O bond length for various acetylacetonate complexes. Co-ordination geometries are: tetrahedral (▼), square-planar (■), square-pyramidal (♦), octahedral (●), pentagonal-bipyramidal (◑), and Archimedean antiprism (▲)

Unfortunately, electronic delocalisation over the chelate ring makes conformational analysis of the steric features of acetylacetonate (acac) rings rather difficult. No such problem is found for the ethylenediamine (en) ring, and many conformational analyses of en-type rings

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† For a quantitative discussion of the terms 'hard' and 'soft' see R. D. Hancock and F. Marsicano, *Inorg. Chem.*, 1978, **17**, 560.

have been carried out.[4-7] In trying to understand the factors governing bite size and the angle within the chelate ring formed by the metal atom and the two donor atoms, the en complexes would appear to be more promising than the acetylacetonates analysed in the work of Hon and Pfluger.[1] In Figure 2, the relation of M–N length to N–M–N angle is illustrated for en complexes. Although a relation exists, it does not follow the line (dotted) for a fixed bite of 2.83 Å. This bite size was calculated by assuming ideal geometry for the free en ligand, *i.e.* the N–C–C–N dihedral angle (ω) being 60° so as to minimise torsional and non-bonded repulsion effects.

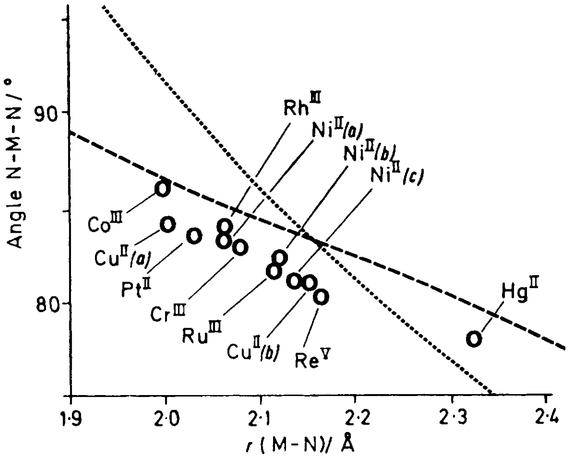

FIGURE 2 Relation between the N–M–N angle in the chelate ring and M–N bond length in various ethylenediamine complexes. For Cu^{II}, (*a*) = $[Cu(en)_2]^{2+}$ (square-planar) and (*b*) = $[Cu(en)_3]^{2+}$ ($\Lambda\delta\delta\delta$-octahedral); for Ni^{II}, (*a*) = $[Ni(en)(OH_2)_4]^{2+}$ and (*b*) and (*c*) are the $\Lambda\delta\delta\delta$ and $\Lambda\delta\delta\lambda$ isomers of $[Ni(en)_3]^{2+}$

In this paper we report a conformational analysis of the relation shown in Figure 2 using the empirical force-field program developed by Boyd[8] and modified by Snow.[6] Since a large component of the effects on the O–M–O angle, at least for Zr^{IV}, appeared to be due to ligand–ligand repulsion, the structure of the compound $[Ni(en)(OH_2)_4][NO_3]_2$ was determined by *X*-ray analysis. Previous calculations[9] had shown that the water molecules in this complex interacted far less strongly than co-ordinated polyamines, being able to rotate more freely away from strong steric interactions. For this reason, it was hoped that, in this compound, ligand–ligand repulsions would be minimised.

EXPERIMENTAL

Crystals of $[Ni(en)(OH_2)_4][NO_3]_2$ were prepared by allowing a 1 : 1 mixture of nickel(II) nitrate and en to evaporate slowly, and were recrystallised from water. The blue cylindrically shaped crystals were stable in the atmosphere, and the composition was confirmed by microanalysis (Found: C, 7.55; H, 5.05; N, 17.65; O, 50.0. $C_2H_{16}N_4NiO_{10}$ requires C, 7.65; H, 5.10; N, 17.8; O, 50.85%).

Crystal Data.—$C_2H_{16}N_4NiO_{10}$, Monoclinic, space group $P2_1/c$, $a = 12.079$, $b = 12.803$, $c = 7.604$ Å, $\beta = 90.914°$, $U = 1\,175.79$ Å^3, $F(000) = 383.95$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 17.07$ cm^{-1}, $\lambda = 0.710\,69$ Å.

Diffraction data were collected on a Philips PW 1100 four-circle diffractometer equipped with an incident-beam graphite-crystal monochromator using Mo-K_α radiation. An ω—2θ mode was used to scan each peak in the range $3 < \theta < 20°$, at a rate of 0.03° s^{-1}, covering a peak width of 0.9°. Background counts were obtained on both sides of the peak over periods of 15 s. Data reduction included correction for background and Lorentz polarisation, the merging of equivalent reflections, and a $3\sigma(F)$ cut-off.

The structure was solved and refined using the program SHELX 76.[10] A Patterson map was calculated from the 1 088 observed reflections, and the nickel atoms were located in the four-fold general Wyckoff positions $d(x,y,z)$. The other non-hydrogen atoms were located on subsequent Fourier maps. Some hydrogens were found on a difference map, but those belonging to the water molecules labelled O(1) and O(3) (see Figure 3 for numbering scheme) had to be placed in geometrically calculated positions. All O–H bond lengths were constrained to 0.9 ± 0.2 Å in the final refinement. The thermal parameters of all the non-hydrogen atoms were refined anisotropically while a common isotopic temperature factor was refined for the hydrogen atoms. Atomic scattering factors were taken from ref. 11.

TABLE 1

Final least-squares fractional co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) $[Ni(en)(OH_2)_4]^{2+}$ cation			
Ni	0.750 8(1)	0.532 2(1)	0.454 6(1)
N(1)	0.640 3(4)	0.426 8(5)	0.556 2(7)
N(2)	0.868 0(4)	0.427 6(5)	0.550 6(7)
O(1)	0.748 4(4)	0.456 5(4)	0.210 5(6)
O(2)	0.623 8(4)	0.629 4(4)	0.361 5(6)
O(3)	0.753 8(4)	0.625 5(4)	0.679 8(6)
O(4)	0.873 1(4)	0.632 8(4)	0.366 4(6)
C(1)	0.705 2(7)	0.351 8(7)	0.667 5(11)
C(2)	0.812 2(6)	0.328 8(6)	0.588 7(11)
(*b*) NO_3^- anions			
N(3)	0.481 2(5)	0.371 6(5)	0.079 3(8)
O(5)	0.562 3(5)	0.393 5(5)	−0.008 2(7)
O(6)	0.393 6(4)	0.341 0(5)	0.003 7(7)
O(7)	0.484 6(5)	0.379 8(5)	0.241 1(7)
N(4)	1.006 2(5)	0.375 1(5)	0.062 1(8)
O(8)	1.089 8(5)	0.338 5(4)	−0.009 6(7)
O(9)	0.924 4(4)	0.404 8(4)	−0.026 1(7)
O(10)	0.008 1(4)	0.380 5(5)	0.224 1(7)
(*c*) Proposed hydrogen co-ordinates			
N(1)H(1)	0.600(4)	0.396(4)	0.461(5)
N(1)H(2)	0.593(4)	0.452(4)	0.602(5)
N(2)H(3)	0.903(4)	0.450(4)	0.649(5)
N(2)H(4)	0.912(4)	0.413(4)	0.457(5)
C(1)H(5)	0.669(4)	0.286(4)	0.685(5)
C(1)H(6)	0.725(4)	0.384(4)	0.788(5)
C(2)H(7)	0.793(4)	0.291(4)	0.471(5)
C(2)H(8)	0.855(4)	0.280(4)	0.673(5)
O(1)H(9)	0.692(1)	0.403(1)	0.183(1)
O(1)H(10)	0.766(1)	0.497(1)	0.103(1)
O(2)H(11)	0.611(4)	0.642(4)	0.255(5)
O(2)H(12)	0.637(4)	0.678(4)	0.434(5)
O(3)H(13)	0.719(1)	0.601(1)	0.789(1)
O(3)H(14)	0.821(1)	0.666(1)	0.710(1)
O(4)H(15)	0.879(4)	0.642(4)	0.268(5)
O(4)H(16)	0.875(4)	0.690(4)	0.418(5)

At the termination of refinement, the conventional *R* factor, using unit weights, was 0.04. However, unexplained electron density of 0.8 e Å^{-3} was observed. The final positional co-ordinates of the atoms are given in Table 1, bond lengths and angles in Table 2. Thermal parameters and observed and calculated structure factors are available as Supplementary Publication No. SUP 22699 (11 pp.).* The numbering scheme is as shown in the ORTEP [12] diagram of the molecule in Figure 3.

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in the least significant digits in parentheses

(*a*) $[Ni(en)(OH_2)_4]^{2+}$			
Ni–N(1)	2.058(6)	Ni–N(1)–C(1)	107.2(4)
Ni–N(2)	2.073(6)	Ni–N(2)–C(2)	108.3(4)
Ni–O(1)	2.093(4)	N(1)–Ni–N(2)	83.6(2)
Ni–O(2)	2.091(5)	N(1)–Ni–O(1)	91.7(2)
Ni–O(3)	2.088(4)	N(1)–Ni–O(2)	92.3(2)
Ni–O(4)	2.079(5)	N(1)–Ni–O(3)	94.0(2)
N(1)–C(1)	1.494(10)	N(2)–Ni–O(1)	90.7(2)
N(2)–C(2)	1.465(10)	N(2)–Ni–O(3)	94.5(2)
C(1)–C(2)	1.463(11)	N(2)–Ni–O(4)	91.7(2)
		O(1)–Ni–O(2)	88.6(2)
		O(1)–Ni–O(4)	90.0(2)
		O(2)–Ni–O(3)	86.6(2)
		O(2)–Ni–O(4)	92.5(2)
		O(3)–Ni–O(4)	84.7(2)
		N(1)–C(1)–C(2)	110.9(6)
		N(2)–C(2)–C(1)	108.6(6)
(*b*) NO_3^-			
N(3)–O(5)	1.226(7)	O(5)–N(3)–O(6)	119.8(6)
N(3)–O(6)	1.259(7)	O(5)–N(3)–O(7)	120.5(6)
N(3)–O(7)	1.235(7)	O(6)–N(3)–O(7)	119.8(6)
N(4)–O(8)	1.246(7)	O(8)–N(4)–O(9)	121.4(6)
N(4)–O(9)	1.245(7)	O(8)–N(4)–O(10)	117.1(6)
N(4)–O(10)	1.234(7)	O(9)–N(4)–O(10)	121.5(6)

RESULTS AND DISCUSSION

The conformational analysis of the tris-en complexes is complicated by the *gauche* conformation of the en ring, in that this leads to δ and λ forms, and, with the chirality of the metal centre, to a total of eight possible isomers, four of which are mirror images of the other four. All four types represented by the pairs of optical isomers have been found. The available evidence [13] suggests that hydrogen bonding to the counter ion and solvate molecules plays an important part in determining which of these isomers is observed. Hydrogen bonding to other groups in the crystal is outside the scope of the present calculations, but it should be borne in mind that these effects might also be responsible for some of the observed effects. Thus, the average N–M–N bond angle in the Λδδλ form of $[Ni(en)_3]^{2+}$ is 80.8°,[13] while that in the Λδδδ form is 82.3°.[14] Interestingly, as found for the chromium(III) complexes, this decrease in N–M–N angle as the number of λ rings is increased in the Λ series of isomers is accompanied by a definite increase in bond length from 2.12 Å in the δδδ to 2.14 Å in the δδλ form. Inspection of models would suggest that the H–H repulsion is much larger in the δδλ than the δδδ form. For the sake of simplicity, the present calculations are confined to the Λδδδ form.

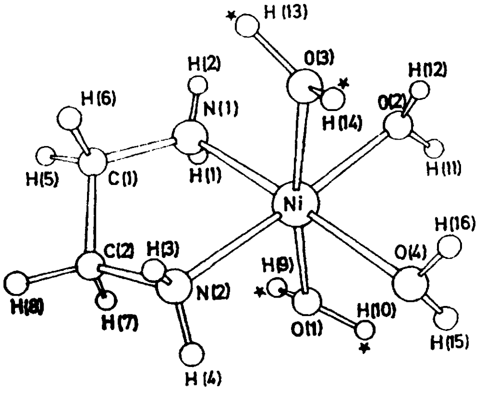

FIGURE 3 ORTEP [12] diagram of $[Ni(en)(OH_2)_4][NO_3]_2$. Hydrogen positions are those actually determined, except for those marked (★), which were generated using the program SHELX,[10] making use of an oxygen pivot to fit the protons to the region of maximum electron density

The relation between N–M–N angle and M–N length calculated by the program is represented by the broken line in Figure 2. This was calculated by keeping constant all of the parameters that were used previously [9,15] for calculating the conformational potential energy of $\Lambda[Ni(en)_3\delta\delta\delta]^{2+}$, except for the ideal bond length for Ni–N which was varied at intervals of 0.05 Å from 1.9 to 2.4 Å. The program does reproduce the essential features of the observed relation, in that at shorter bond lengths the N–M–N angle is still not able to rise up to 90°, as would be expected from the bite size of en, and at longer M–N it is not compressed as much as might be expected. The geometry of the en ring is such that the N–M–N and M–N–C angles cannot simultaneously be the required 90 and 109.5° respectively and still maintain anything like the ideal dihedral angle ω of 60°. Either one has a bond length of 2.5 Å which satisfies the C–N–M angle at 109.5°, but produces an N–M–N of 70°, or else a bond length of 2.0 Å, which would give an N–M–N of 90° but a M–N–C of 99°. It is the conflict between the requirements of these two angles which results in the smaller N–M–N angles at smaller M–N bond lengths, and larger N–M–N at larger M–N than would be expected from a bite of 2.83 Å.

In Figure 4 is shown the total conformational potential energy of the $[Ni(en)_3]^{2+}$ ion as a function of M–N bond length, broken up into its contributions from bond stretching (U_B), angle deformation (U_θ), non-bonded interaction (U_{NB}), and torsion (U_ϕ). The large increase in U_θ at long M–N is almost entirely due to compression of the N–M–N angle, so that the resistance to compression in en complexes with long M–N values has a fairly simple explanation. At shorter M–N there is no dramatic increase in contributions from U_θ. Instead, a greatly increased contribution from U_{NB} is found, as is also the case at longer M–N. The expected contributions from U_θ on the basis of an ideal value of ω of 60° are distributed amongst other terms, chiefly U_{NB}, by flattening the ring at shorter M–N and opening it up at long M–N. The spread of ω values indicated by the program as M–N was varied was as follows:

M–N length/Å	1.92	2.01	2.11	2.23	2.37
ω/°	50.6	54.8	59.3	64.3	67.7

This increase in ω as a function of M–N length may be discerned as a rough trend in practice, with a value of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

55° in the cobalt(III) (M–N 1.98 Å),[16] 56° in the nickel(II) (M–N 2.12 Å),[14] and a mean of 64° in mercury(II) complexes (M–N 2.32 Å).[17] At shorter M–N, *ca.* 50% of the U_{NB} contribution is from H–H non-bonded interactions between adjacent rings, so that an important further contribution to compression of the N–M–N angle as the M–N length is shortened is attributable to interligand repulsion. M–N bond shortening is in fact strongly resisted below M–N 2.0 Å, as seen from the fact that the program lengthened the ideal M–N from 1.90 to 1.98 Å in the final energy-minimised co-ordinates, accounting for the large bond-stretching contribution at short M–N in Figure 4. The principal H–H interactions at short M–N are shown in Figure 5.

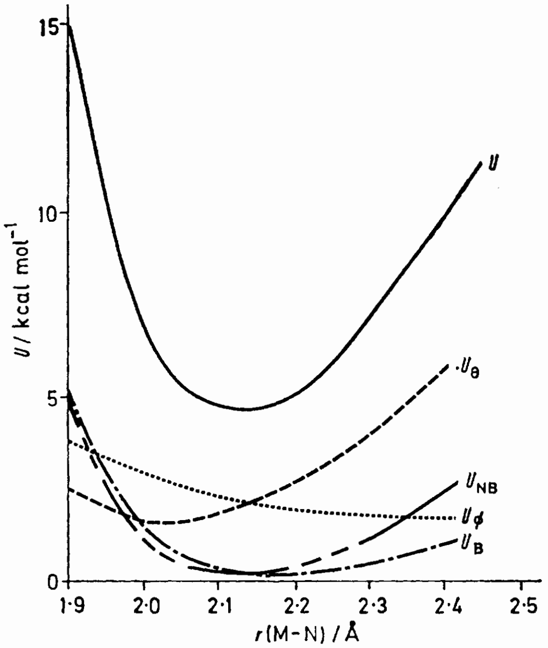

FIGURE 4 Total conformational potential energy of the $[M(en)_3]^{2-}$ ion as a function of M–N bond length. Also shown are the individual contributions from bond stretching (U_B), bond-angle deformation (U_θ), and non-bonded (U_{NB}) and torsional (U_ϕ) interactions

One should find, if inter-ring repulsion is an important factor in compressing the N–M–N angle, that this angle is larger in the complex $[Ni(en)(OH_2)_4]^{2+}$, which is found to be so at 83.6°, as compared with a value of 82.3° in the tris-en complex.[14] However, this opening of the N–M–N angle is accompanied by a shortening of the M–N bond length. The calculations indicate that we are not in the region where inter-ring repulsion is important, so that it seems that the opening up of the ring must be associated with the shorter M–N length with a mean value of 2.06 Å. In the cobalt(III) complex interligand repulsion appears to be considerable from Figure 4, with M–N 1.98 Å. It would be of considerable interest to see whether the N–M–N angle in the en ring in a cobalt(III) complex such as $[Co(en)(NH_3)_4]^{3+}$, where interligand repulsion should be lessened, is significantly larger than in the tris-en complex. The M–N bond length of 2.06 Å for Ni^{II} in its mono-en complex is extremely short. The M–N lengths in the nickel(II) complexes are longer than the 2.0 Å below which the program indicates that interligand repulsion causes lengthening. One must bear in mind that, because of the empirical nature of the force-field calculations, the latter indication could be in error. If, as seems likely, it is correct, then it must be concluded that the short M–N bond length does not represent a lessening of the forces which might cause bond stretching, but rather an intrinsically shorter bond. This short M–N bond would then be a result of the smaller structural *trans* influence of the water as opposed to other co-ordinated en ligands. A bond length of 2.09 Å has been reported [18] for M–N in $[Ni(en)_2(OH_2)_2]^{2+}$ which might be construed as a structural *cis* influence, since the two water molecules are axially co-ordinated. With an *R* factor of 0.16, perhaps not too much significance should be attached to this, but if correct it would lend support to the idea that ligand–ligand repulsion was important at M–N lengths well above 2.0 Å.

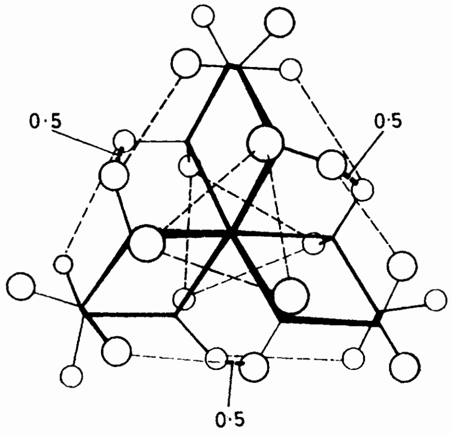

FIGURE 5 View down the three-fold axis of $\Lambda[M(en)_3\delta\delta\delta]^{n+}$, showing the major interligand non-bonded interactions (— — —) at short M–N bond length (1.92 Å) All have a value of *ca.* 0.2 kcal mol^{-1}, except for those indicated as 0.5 kcal mol^{-1} (1 cal = 4.184 J). Open circles are hydrogen atoms. Other atoms are not specifically indicated, but are situated at the meeting points of the bonds (solid lines)

In conclusion, the important factors in the geometry of the en ring are the N–M–N and M–N–C angles, which cannot simultaneously be their ideal values and still maintain ω = 60°. The ring attempts to accommodate the angles by flattening at short M–N, and opening up at long M–N, resulting in unfavourable non-bonded interactions at either extreme of the range of M–N lengths. It is interesting to note that the value of *U* is at a minimum at *ca.* 2.1 Å, which is where the majority of M–N bond lengths fall in en complexes. While the en complexes show a similar relation between M–N length and N–M–N angle to that observed between M–O and O–M–O in acetylacetonates, there does not seem to be a parallel dependence on the ionic or covalent nature of the M–L bond in the en complexes. This could simply be due to the more limited range of metal ions in Figure 2, since all those which form stable en complexes tend to be fairly soft, and one must await crystal-structure determinations on compounds such as the tetrakis(ethylenediamine)lanthanide(III) complexes. From this work it would appear that, for both the acetylacetonates and en complexes, interligand repulsion plays a very important part in determining O–M–O or N–M–N bond angles, and the bite size of the ligand.

The authors thank the National Institute for Metallurgy for permission to publish this work.

[9/254 *Received*, 19*th February*, 1979]

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