Studies in the Flexibility of Macrocycle Ligands. Calculation of Macrocycle Cavity Size by Force-field Methods. Crystal and Molecular Structures of $[CoLCl][ClO_4]_2$ and $[CuL][PF_6]_2$ {L = 2,13-dimethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),14,16-triene}†

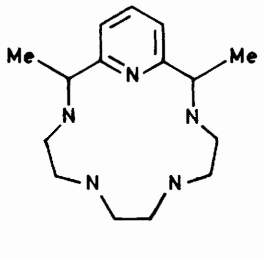
Michael G. B. Drew,* (the late) Stephen Hollis, and Paul C. Yates
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

The crystal structures of the compounds $[CoLCl][ClO_4]_2$ (**1**) and $[CuL][PF_6]_2$ (**2**) have been determined {L = 2,13-dimethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),14,16-triene}. Complex (**1**) is orthorhombic, space group $P2_12_12_1$, $Z = 4$, with $a = 12.931(8)$, $b = 16.604(12)$, and $c = 11.441(9)$ Å; (**2**) is monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 14.145(11)$, $b = 9.030(6)$, $c = 16.743(11)$ Å, and $\beta = 90.9(3)°$. 1 336 (1) and 1 608 (2) above background reflections have been measured on a diffractometer, and the structures refined to R 0.086 and 0.076 respectively. Both structures contain discrete cations and anions. In complex (**1**) the cobalt atom is six-co-ordinate being bonded to the five donor atoms of the macrocycle [Co–N 1.812(16)—2.001(12) Å] and to the chloride ion [Co–Cl 2.173(5)Å] in an octahedral environment. In (**2**) the copper atom is five-co-ordinate being bonded to all five donor atoms of the macrocycle L with a geometry intermediate between a square pyramid and a trigonal bipyramid: Cu–N 1.930(14)—2.145(25) Å. The macrocycle adopts three different conformations in complexes (**1**), (**2**), and the related structure of $[FeLCl_2][ClO_4]$ which is seven-co-ordinate. These conformations are investigated by force-field methods. In particular a general method is described to calculate a hole-size profile of macrocycles.

Molecular mechanics has been successfully applied to organic molecules for many years,[1] but recently there has been growing interest in its application to inorganic complexes.[2–5] The main difficulty is in estimating the parameters for the force field which include the metal atom. Good estimates of parameters in organic molecules have been obtained by several methods. One method is to choose parameters that optimise the fit between structures calculated from force-field methods and those obtained by *X*-ray crystallography. The situation is much more complicated in transition-metal complexes because of the intricacies of metal–ligand bonding and the different preferences of metals for particular geometries which have to be taken into account. These difficulties have not been overcome and at the present time the application of force-field methods to metal complexes is at a preliminary stage.

In this paper we present a method for calculating the 'hole' size profile for a macrocycle by using molecular mechanics. The particular method does not depend upon accurate parameters and can be applied to any macrocycle. The goodness of fit of a metal ion in the surrounding co-ordination sphere has a crucial influence upon the chemical properties of the resulting metal complex and it is therefore important to develop a suitable method for the calculation of macrocycle 'hole' size. Two methods have been published recently[4,6,7] and these are compared to our method below.

The macrocycle 2,13-dimethyl-3,6,9,12,18-penta-azabicyclo-[12.3.1]octadeca-1(18),14,16-triene, L, is used as a model for our calculations. It is particularly suitable for this purpose because it has been shown *via* crystal structure determinations that it can adopt three different conformations dependent upon the metal size, counter ions, and preferred geometry. With Cu^{2+}, Co^{3+}, and Fe^{3+} ions, complexes are formed of formulae $[CoLCl][ClO_4]_2$ (**1**), $[CuL][PF_6]_2$ (**2**), and $[FeLCl_2][ClO_4]$ (**3**) respectively. We report here the crystal structures of (**1**) and(**2**) for which a preliminary report has been published.[8] The structure of the iron complex (**3**) is also available.[9]



L

Results and Discussion

The structures of both complexes (**1**) and (**2**) consist of discrete cations and anions. The cations $[CoLCl]^{2+}$ and $[CuL]^{2+}$ are shown in Figures 1 and 2 respectively together with the common atomic numbering scheme.

In $[CoLCl]^{2+}$ (**1**) the metal atom is six-co-ordinate being bonded to all five donor atoms of the macrocycle [Co–N 1.812(16)—2.001(12) Å] and a chlorine atom [2.173(5) Å]. The geometry is approximately octahedral but with necessary distortions arising from steric constraints in the macrocycle. In $[CuL]^{2+}$ (**2**) the metal atom is five-co-ordinate, being bonded just to the five donor nitrogen atoms of the macrocycle [Cu–N 1.930(14)—2.145(25) Å]. The geometry of the co-ordination sphere is a trigonal bipyramid severely distorted towards a square pyramid.

In $[FeLCl_2]^+$ (**3**) the metal atom is seven-co-ordinate with a distorted pentagonal-bipyramidal structure.[9] The five donor

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† *Supplementary data available* (No. SUP 56260, 17 pp.): thermal parameters, H-atom co-ordinates, remaining bond parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: dyn = 10^{-5} N; cal = 4.184 J.

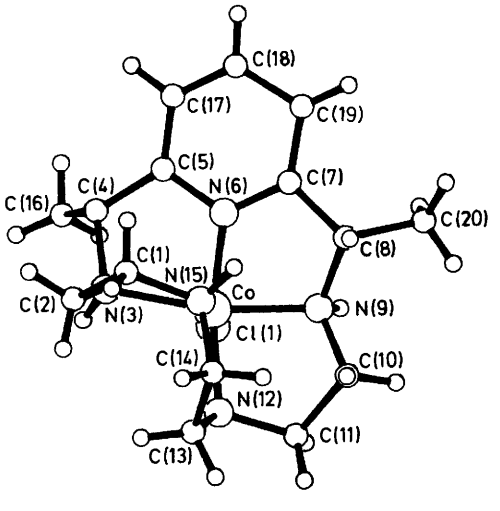

Figure 1. The structure of $[CoLCl]^{2+}$

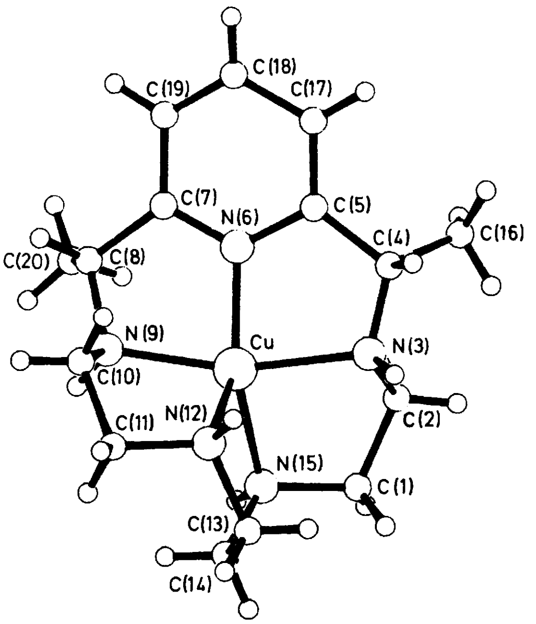

Figure 2. The structure of $[CuL]^{2+}$

atoms in the macrocycle form the equatorial girdle with Fe–N distances ranging from 2.203(20) to 2.323(17) Å. The FeN_5 moiety is planar to within 0.23 Å. These three structures, (**1**)—(**3**), indicate that macrocycle L can easily adapt to provide different environments of donor atoms for a particular metal; a square-pyramidal arrangement of donor atoms for Co^{3+}, a trigonal-bipyramidal set for Cu^{2+}, and a pentagonal planar set for Fe^{3+}. In addition each conformation has a particular 'hole' size profile to which the metal must conform to and this causes some unexpected M–N bond lengths. Thus Co^{3+} and Fe^{3+} have very similar ionic radii (0.61, 0.65 Å) but the mean M–N bond lengths in (**1**) and (**3**) differ by 0.35 Å. Clearly the most important factor in fixing the macrocycle conformation in these compounds is the required metal geometry. The match of metal size with macrocycle hole size is secondary.

We attempt to quantify the steric energy of these conformations by force-field calculations in the next section. Here details of the crystal structures of complexes (**1**) and (**2**) are discussed. However, it should be noted that the strain energy of a molecule is the sum of a large number of terms and emphasising just one or two unusual dimensions from a crystal structure is not always indicative of an excess of strain in the structure.

In complex (**1**) the atoms Co, N(3), N(6), N(9), and N(12) are nearly planar (maximum deviation 0.06 Å) as is apparent from Figure 1. The fifth nitrogen atom in the macrocycle, N(15), is placed in an axial position relative to these four atoms. The N(3)–Co–N(12) angle is 105.1(6)° compared to 142.0(7)° in (**3**) where all five donor atoms are in the pentagonal plane. Clearly the dropping of N(15) from an equatorial to an axial site has been achieved without introduction of severe strain but there is still a small gap in the co-ordination sphere between N(3) and N(12). This ensures considerable distortion in the octahedron as the N(6)–Co–N(12) angle is 168.5(6)°. The N(3)–Co–N(9) angle at 167.8(6)° is equal to the sum of the N(3)–Co–N(6) and N(6)–Co–N(9) angles, and this consequence of the five-membered ring adds to the distortion from octahedral geometry. The chlorine atom is tilted away from N(6) [Cl–Co–N(6) 98.4(5)] presumably because of the influence of the methyl groups C(16) and C(20) which are on the same side of the metal as the chlorine atom.

The three saturated N–C–C–N torsion angles are all some way from the ideal 60°, being N(9)–C(10)–C(11)–C(12) −45.3, N(12)–C(13)–C(14)–N(15) 43.5, and N(15)–C(1)–C(2)–N(3) −48.6°. These values are some indication of the strain induced in the macrocycle in order to provide a square-pyramidal donor set for the Co^{3+} ion. Force-field methods show that this conformation has the highest strain energy of the three macrocycle conformations in structures (**1**)—(**3**). Cobalt(III)–nitrogen distances in *X*-ray structures are usually in the range 1.94—2.01 Å and the present bond lengths are at the short end of that range. In particular we note that the Co–N(6) (pyridine) bond length is only 1.812(16) Å, though the shortness of this bond relative to Co–N(3) and C–N(9) is shown below to be a steric effect.

Each of the four NH groups is involved in an intramolecular hydrogen bond to a perchlorate oxygen atom. Dimensions are: O(21)···N(9) $(x, y, 1 + z)$ 2.99 Å (O···H–N 153°, O···H 2.11 Å); O(23)···N(12) $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ 3.06 Å (131°, 2.35 Å), O(12)···N(3) $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ 2.93 Å (137°, 2.16 Å); and O(13)···N(15) $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ 2.84 Å (157°, 1.94 Å).

In the structure of $[CuL]^{2+}$ the Cu, N(3), N(6), and N(9) atoms form an approximate plane (the copper atom is 0.17 Å from the plane of the three nitrogen atoms). The Cu,N(6),N(12),N(15) plane intersects this plane at 76.6° so that the metal geometry resembles a distorted trigonal plane with N(3) and N(9) in axial positions. As in the cobalt structure, the N(3)–Cu–N(9) angle is distorted from linear because of the constraints of the two five-membered rings around the pyridine ring. In the equatorial plane the angles are N(6)–Cu–N(12) 123.6(6), N(6)–Cu–N(15) 151.1(6), and N(12)–Cu–N(15) 84.6(6)°. The reason for the difference between N(6)–Cu–N(12) and N(6)–Cu–N(15) is hard to establish as the two angles would be identical in an ideal trigonal bipyramid. In a force-field minimisation starting from the crystallographic co-ordinates, the two angles refined to 134 and 140° respectively. As molecular mechanics does not take electronic effects into account, these results strongly suggest that the angle difference is due to the Jahn–Teller effect rather than to steric repulsions.

The N–C–C–N torsion angles in complex (**2**) are much closer to ideal than in (**1**) being N(12)–C(13)–C(14)–N(15) 59.8, N(9)–C(10)–C(11)–N(12) 55.2, and N(15)–C(1)–C(2)–N(3) 46.8°. The Cu–N bond lengths are in the range 1.930(14)—

2.145(25) Å with the shortest bond as usual to the pyridine nitrogen. The distances are normal for five-co-ordinate copper(II).

There are a few close F···H–N interactions that might indicate some weak hydrogen bonding. Distances less than 3.2 Å with hydrogen atoms placed suitably in between are F(26)···N(12) $(\frac{1}{2} + x, -y, -\frac{1}{2} - z)$ 3.14 Å (F···H–N 144°, F···H 2.32 Å) and F(12)···N(3) $(\frac{1}{2} + x, -y, -\frac{1}{2} - z)$ 3.15 Å (145°, 2.32 Å).

Force-field Calculations.—There are several problems that need to be solved before force-field methods can be routinely applied to metal complexes. In particular accurate parameters are required for terms in the force field involving the metal atom such as M–X bond lengths (X = donor atom), X–M–X angles, X–M–X–C and M–X–C–C torsion angles, X···Y (Y = any atom) coulombic terms, and X···Y van der Waals terms. In addition some force fields require cross terms. For organic molecules, force constants and ideal dimensions have become well established. In the main these have been obtained by empirical methods; by adjusting parameters so that as many molecules as possible refined to the correct experimental dimensions. This parametisation has taken many years because there are many different combinations of parameters that can be varied which have a similar effect on molecular shape and indeed several different force fields have been developed with varying parameters.

In a subsequent paper, estimates of the parameters that provide a suitable force field for metal complexes will be presented. In this work we describe a method for obtaining a macrocycle hole-size profile that is not dependent upon accurate force-field parameters and is therefore transferable to all types of system. In the first stage of the calculation the crystallographic co-ordinates for $[CoLCl]^{2+}$, $[CuL]^{2+}$, and $[FeLCl_2]^{2+}$ were used. Parameters for non-metal terms were taken from the MM2 program[10,11] which was used throughout the calculations. Values for the initial M–N stretching force constant, *k*(s), were taken as Cu–N 0.89 mdyn Å^{-1}, Co–N 2.25 mdyn Å^{-1} (both from ref. 2), and Fe–N 2.50 mdyn Å^{-1} (our estimate). The cubic stretch term, *c*(s), required by the MM2 program, was set at −2.00 Å^{-1}. Due to the periodicity of the torsional barrier around the M–N bonds, the force constants for the barriers were assumed to be zero. The M–X–C–C barriers were fixed at values equivalent to those for C–X–C–C given in ref. 10.

An ideal metal-atom geometry was assumed for each complex, *i.e.* trigonal bipyramidal or square pyramidal for $[CuL]^{2+}$, octahedral for $[CoLCl]^{2+}$, and pentagonal bipyramidal for $[FeLCl_2]^{+}$. Angle-deformation terms included in the force field were N–Cu–N 0.030 mdyn Å rad^{-2} (ideal bond angle θ_0 = 90, 120, or 180° where appropriate), N–Co–N 0.400 mdyn Å rad^{-2}, N–Co–Cl 0.278 mdyn Å rad^{-2} (θ_0 = 90, 180°), N–Fe–N, N–Fe–Cl, and Cl–Fe–Cl 0.500 mdyn Å rad^{-2} (θ_0 = 72, 90, 144, and 180°). Values for copper and cobalt were taken from ref. 2. Values for iron were estimated. Copper(II) is usually assigned a small value so that its co-ordination sphere can easily be distorted. This is an attempt to allow for the Jahn–Teller effect which so often distorts the ideal co-ordination sphere. Non-bonded interaction constants involving the metal atom were estimated from ref. 12.

However, it was observed that varying these parameters had a negligible effect on the final conformations. The non-bonded interaction parameters were estimated[12] for Cu as ε 0.165 kcal mol^{-1} and r^* 2.35 Å, for Co as ε 0.150 kcal mol^{-1} and r^* 2.40 Å, and for Fe as ε 0.130 kcal mol^{-1} and r^* 2.45 Å; terms as defined in ref. 10.

Calculation of Macrocycle Hole Size.—The M–N stretching force constant was increased to a value of 25 mdyn Å^{-1}. The stretching of this bond becomes the dominant term in the strain energy. Hence the bond length will be optimised to the ideal length at the expense of other quantities. Indeed all the bond lengths refined to exactly this value. So the strain-energy contribution is due entirely to the macrocycle conformation which has adjusted to fit to the metal of a particular radius.

The ideal M–N bond length, l_o, can then be varied and the refinement repeated. A plot of M–N against strain energy can then be obtained. Graphs for the three different conformations of the macrocycle are shown in Figures 3 and 4. The results show different hole-size profiles for the macrocycle in the three conformations. The curve for the planar conformation is quite sharp indicating that this conformation (and the resulting

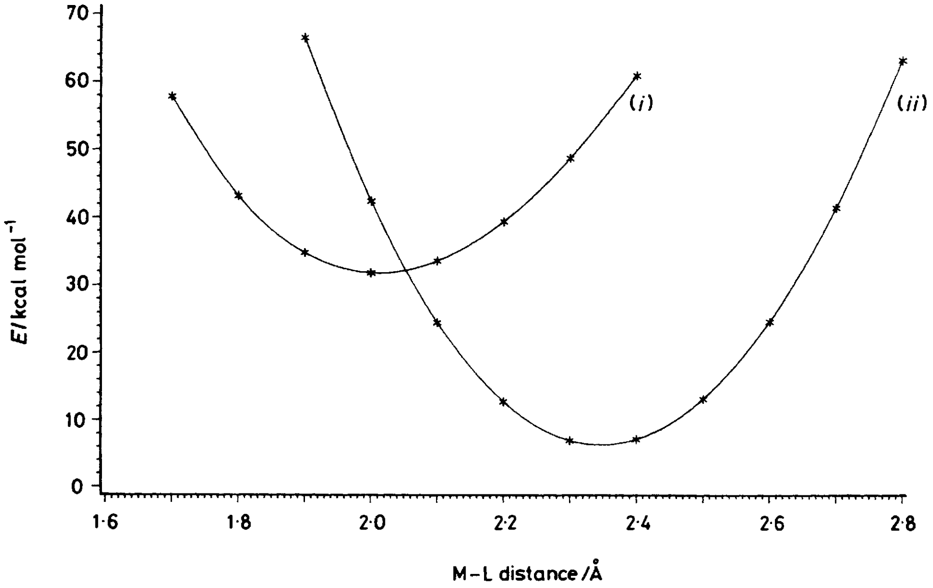

Figure 3. Plot of steric energy against M–N distance for conformation of L with (*i*) a square-pyramidal donor set which combines with a chlorine atom to provide an octahedral environment and (*ii*) a pentagonal-planar donor set of nitrogen atoms which combines with two chlorine atoms to provide a pentagonal-bipyramidal metal environment

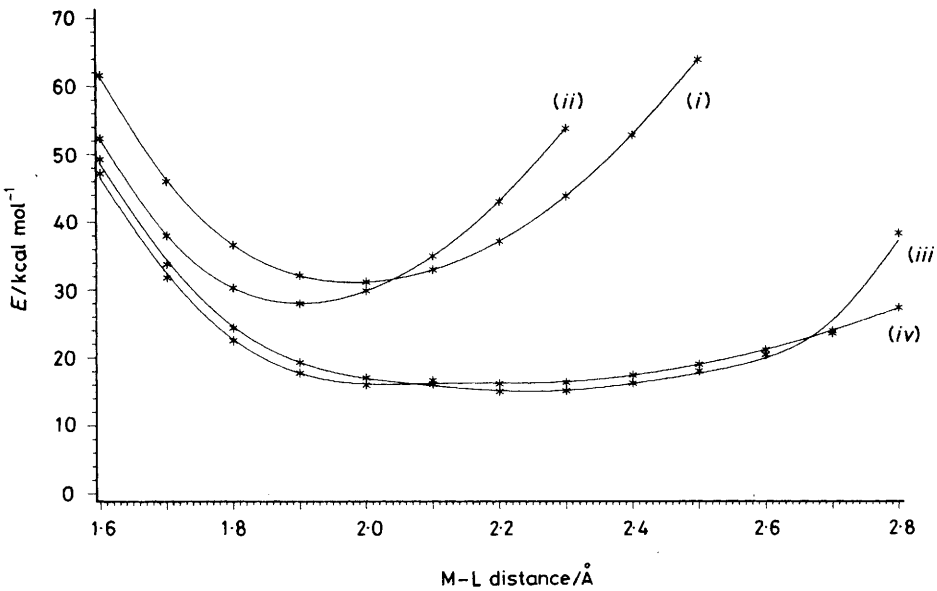

Figure 4. Plot of steric energy against M–N distance for conformation of L with two different geometries for the donor set: (*i*) square-pyramidal geometry with a force constant for N–Cu–N of 0.30 mdyn Å rad^{-2}; (*ii*) trigonal-bipyramidal geometry with a force constant as in (*i*); (*iii*) square-pyramidal geometry with a force constant for N–Cu–N of 0.03 mdyn Å rad^{-2}; and (*iv*) trigonal-bipyramidal geometry with a force constant as in (*iii*)

seven-co-ordinate structure) is best suited to a M–N distance of 2.30—2.40 Å. In fact the mean Fe–N distance in complex (**3**), is 2.39 Å. The curve for the square-pyramidal conformation shows a minimum energy at 2.05 Å which is well above the normal Co^{III}–N bond length. The mean Co–N distance in complex (**1**) is only 1.90 Å and clearly the metal does not fit well into the macrocycle hole. However the preference of cobalt(III) for the octahedron more than compensates for the misfit.

Four curves calculated from the macrocycle conformation found in complex (**2**) are shown in Figure 4. In the crystal structure the copper-atom geometry is distorted between the ideal square pyramid and trigonal bipyramid. Both ideal structures were fitted into the macrocycle hole with angle-bending force constants of (*a*) 0.03 and (*b*) 0.30 mdyn Å rad^{-2}. The curves calculated using the low force constants [type (*a*)] show a large range (2.0—2.7 Å) of Cu–N bond lengths for the minimum energy. For high bond lengths, this is only achieved by gross distortion of the co-ordination sphere giving rise to a lopsided and unrealistic arrangement of the Cu–N bonds around the metal. More realistic curves are obtained for force constants of 0.30 mdyn Å rad^{-2} with minima for both ideal geometries at *ca.* 1.85—2.05 Å, values which are obtained in the crystal structure.

These results for copper suggest that a force constant of 0.30 mdyn Å rad^{-2} is more realistic than the value of 0.03 mdyn Å rad^{-2} given in ref. 2, but force-field calculations on copper(II) will remain unsatisfactory because of the neglect of electronic effects.

The comparative steric energies at the minimum energy are 6.90 kcal mol^{-1} for (**3**), 31.77 kcal mol^{-1} for (**1**), and 14.84 (*a*), 31.00 kcal mol^{-1} (*b*) for (**2**) with a square-pyramidal geometry and 15.43 (*a*), 27.85 kcal mol^{-1} (*b*) for (**2**) with a trigonal-bipyramidal geometry.

This method for calculating hole-size profiles can be adapted to distinguish between the different types of M–N bond in a complex. The force constant for one of the M–N bonds is increased to 25 mdyn Å^{-1} and its ideal length is determined as described above. This value is then used in subsequent calculations where the ideal bond length for a second bond is found. This calculation is then carried out for the remaining M–N bonds. The whole process can then be repeated until a consistent set of ideal bond lengths is obtained.

However, in the present structures it seems clear that the shortness of the M–N (pyridine) bond compared to the others is a steric effect. We tried to find parameters for the Co–N bond lengths which would give as close a fit as possible to the crystal structure. Values for k(s) of 2.25 mdyn Å^{-1}, c(s) −2.00 Å^{-1}, and l_0 of 1.88 Å gave a good fit within 0.03 Å for all Co–N distances. The Co–N (pyridine) bond length decreased and the other Co–N distances increased to the observed values and it was not necessary to have two ideal bond lengths for the two types of Co–N bond.

There have previously been two attempts to calculate the hole size of macrocycles.[4,6] The method of Lindoy, Tasker, and co-workers [6,7] uses crystal structure data. The mean distance of the positions of the donor atoms from their centroid is calculated and this is taken as the 'hole' radius. This is too much of a simplification because no account is taken of the fact that the macrocycle conformation can often vary considerably (while keeping the same overall geometry) to encapsulate metals with different radius. Thus their calculation on the $[\text{CoLCl}]^{2+}$ crystal structure would have obtained a hole size for the macrocycle that was too small by 0.15 Å, our method having shown that the macrocycle fits best to M–N distances of 2.05 Å rather than the 1.98 Å found in the crystal structure. However the method of Lindoy and Tasker has the considerable virtue of being easy to use.

The method of Thom *et al.*[4] uses force-field methods. The M–N bond length is varied, the strain energy is calculated, and a plot of energy against distance is produced. The flaw in this method is that the force constants are not known accurately and therefore it is not known how much emphasis needs to be put on bond lengths, bond angles, coulombic forces, and non-bonded interactions. Therefore any such absolute calculation cannot be relied upon.

In our method, by increasing the M–N force constant, the macrocycle is forced to vary its conformation to accommodate the new bond length. This overcomes one of the major problems with force-field calculations which is that there is an abundance of false minima which are impossible to get out of without giving sufficient perturbation to the structure.

Experimental

Crystallographic Measurements.—The complexes [CoLCl][ClO_4]$_2$ (**1**) and [CuL][PF_6]$_2$ (**2**) were prepared following the published method[13] and recrystallised from ethanol and acetone respectively. Crystal data are given in Table 1.

Intensity data were collected on a G.E.XRD5 diffractometer equipped with a manual goniostat, scintillation counter, and pulse height discriminator and employing zirconium-filtered radiation. The stationary-crystal–stationary-counter method was used for a 4° take-off angle and a counting time of 10 s. Backgrounds were taken from plots of background as a function of 2θ. Standard reflections measured during the course of the experiment showed no variation with time. The standard deviations $\sigma(I)$ of the reflections were taken to be $[I + 2E + (0.03I^2)]^{\frac{1}{2}}$, where E is the estimated background of the reflection. The data were not corrected for absorption or extinction.

Structure determination and refinement. The positions of the heavy atoms were determined from the Patterson functions. Successive Fourier syntheses gave the positions of the remaining atoms. The hydrogen atoms were fixed in trigonal or tetrahedral

Table 1. Crystal data and refinement details *

Compound	(**1**)	(**2**)
Formula	$C_{15}H_{27}Cl_3CoN_5O_8$	$C_{15}H_{27}CuF_{12}N_5P_2$
M	344.1	283.1
Crystal class	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Absences	$h00, h = 2n + 1$ $0k0, k = 2n + 1$ $00l, l = 2n + 1$	$0k0, k = 2n + 1$ $h0l, l = 2n + 1$
a/Å	12.931(8)	14.145(11)
b/Å	16.604(12)	9.030(6)
c/Å	11.441(9)	16.743(11)
β/°	(90)	90.9(3)
U/Å^3	2 456.3	2 138.3
F(000)	648	1 200
D_m/g cm^{-3}	1.80	1.72
D_c/g cm^{-3}	1.77	1.70
μ/cm^{-1}	12.64	11.68
Max. 2θ/°	50	50
No. of data measured	2 298	2 017
No. of data used in refinement	1 336	1 608
Final R value	0.086	0.076
R'	0.083	0.080

* Details common to both structures: $Z = 4$; $\lambda = 0.7107$ Å; criterion for data inclusion, $I > 2\sigma(I)$.

Table 2. Atomic co-ordinates (× 10^4) for complex (**1**) with estimated standard deviations in parentheses

Atom	x	y	z
Co	2 650(2)	2 418(3)	41(1)
Cl	3 776(3)	3 827(6)	−394(3)
N(3)	2 763(9)	3 377(16)	1 115(7)
N(6)	3 374(9)	955(19)	468(8)
N(9)	2 750(11)	1 217(20)	−911(9)
N(12)	1 804(10)	3 674(18)	−568(8)
N(15)	1 602(11)	1 393(18)	484(9)
C(1)	1 576(14)	1 657(23)	1 367(10)
C(2)	1 906(13)	3 196(21)	1 542(12)
C(4)	3 514(14)	2 636(24)	1 562(11)
C(5)	3 763(12)	1 207(23)	1 203(10)
C(7)	3 516(12)	−320(24)	87(12)
C(8)	2 980(13)	−329(24)	−681(10)
C(10)	1 974(15)	1 556(29)	−1 446(11)
C(11)	1 827(15)	3 169(24)	−1 404(12)
C(13)	894(12)	3 531(26)	−239(13)
C(14)	766(12)	1 942(23)	55(11)
C(16)	4 319(17)	3 755(33)	1 625(14)
C(17)	4 278(13)	110(29)	1 521(11)
C(18)	4 429(12)	−1 158(27)	1 138(14)
C(19)	4 059(13)	−1 415(26)	374(13)
C(20)	3 361(16)	−1 218(29)	−1 384(12)
Cl(1)	3 306(4)	2 320(6)	3 969(3)
Cl(2)	4 043(4)	2 166(7)	6 866(3)
O(21)	3 850(17)	2 160(34)	7 669(10)
O(22)	4 716(12)	1 159(21)	6 679(12)
O(23)	3 298(16)	1 632(27)	6 454(15)
O(24)	4 186(16)	3 581(22)	6 553(14)
O(11)	2 783(11)	3 269(20)	3 509(10)
O(12)	2 827(13)	1 313(18)	4 438(9)
O(13)	3 795(11)	3 313(21)	4 541(11)
O(14)	3 935(11)	1 573(19)	3 519(10)

Table 3. Atomic co-ordinates (× 10^4) for complex (**2**) with estimated standard deviations in parentheses

Atom	x	y	z
Cu	−963(2)	−759(1)	−76(3)
N(3)	−1 777(17)	199(16)	782(23)
N(6)	216(12)	−81(8)	244(11)
N(9)	103(13)	−1 395(10)	−1 020(13)
N(12)	−1 794(13)	−741(9)	−1 686(16)
N(15)	−2 137(13)	−1 543(10)	481(15)
C(1)	−2 747(28)	−1 098(18)	1 435(26)
C(2)	−2 178(26)	−328(12)	1 838(24)
C(4)	−1 058(17)	799(11)	1 140(17)
C(5)	29(16)	663(10)	743(14)
C(7)	1 136(12)	−316(10)	−142(15)
C(8)	1 170(17)	−1 160(12)	−621(21)
C(10)	−74(17)	−1 134(12)	−2 266(19)
C(11)	−1 210(21)	−1 227(15)	−2 615(25)
C(13)	−2 861(21)	−1 071(15)	−1 416(32)
C(14)	−2 721(20)	−1 780(11)	−691(27)
C(16)	−1 097(21)	1 101(12)	2 359(18)
C(17)	840(20)	1 182(11)	832(21)
C(18)	1 836(20)	966(10)	357(20)
C(19)	1 977(16)	223(13)	−10(21)
C(20)	1 537(22)	−1 770(14)	334(26)
P(1)	361(4)	−1 219(3)	4 049(5)
F(11)	379(14)	−1 932(7)	4 976(12)
F(12)	957(13)	−659(7)	4 973(13)
F(13)	−691(12)	−941(10)	4 484(22)
F(14)	1 508(14)	−1 473(11)	3 643(17)
F(15)	426(12)	−550(7)	3 098(13)
F(16)	−116(18)	−1 801(10)	3 105(12)
P(2)	3 900(4)	−1 548(3)	−2 568(5)
F(21)	3 083(12)	−2 149(7)	−2 079(17)
F(22)	4 697(14)	−906(8)	−3 107(15)
F(23)	4 754(15)	−1 937(10)	−1 839(21)
F(24)	4 250(22)	−2 170(11)	−3 433(25)
F(25)	3 570(19)	−903(10)	−1 656(18)
F(26)	3 122(21)	−1 146(16)	−3 494(28)

Table 4. Molecular dimensions (distances in Å, angles in °) in the co-ordination spheres

(*a*) Complex (**1**)

Co–Cl	2.173(5)	Cl–Co–N(15)	173.0(5)	N(12)–Co–N(6)	168.5(6)
Co–N(15)	1.908(15)	Cl–Co–N(12)	86.02(48)	N(9)–Co–N(6)	82.4(6)
Co–N(12)	1.929(15)	N(15)–Co–N(12)	90.6(6)	Cl–Co–N(3)	89.94(43)
Co–N(9)	1.934(16)	Cl–Co–N(9)	89.4(5)	N(15)–Co–N(3)	85.0(6)
Co–N(6)	1.812(16)	N(15)–Co–N(9)	96.6(6)	N(12)–Co–N(3)	105.1(6)
Co–N(3)	2.001(12)	N(12)–Co–N(9)	87.0(6)	N(9)–Co–N(3)	167.8(6)
		Cl–Co–N(6)	98.44(44)	N(6)–Co–N(3)	85.6(6)
		N(15)–Co–N(6)	86.0(6)		

(*b*) Complex (**2**)

Cu–N(3)	2.145(25)	N(3)–Cu–N(6)	82.4(7)	N(9)–Cu–N(12)	83.7(6)
Cu–N(6)	1.930(14)	N(3)–Cu–N(9)	162.8(8)	N(3)–Cu–N(15)	88.0(8)
Cu–N(9)	2.044(16)	N(6)–Cu–N(9)	82.5(6)	N(6)–Cu–N(15)	151.1(6)
Cu–N(12)	2.133(18)	N(3)–Cu–N(12)	97.9(8)	N(9)–Cu–N(15)	109.2(6)
Cu–N(15)	2.099(17)	N(6)–Cu–N(12)	123.6(6)	N(12)–Cu–N(15)	84.6(6)

positions. Those bonded to the same atom were given a common thermal parameter which was refined. The structures were refined using full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $(\sin\theta)/\lambda$ was $\sqrt{w} = 1$ for $F_o < F_c$ and $\sqrt{w} = F_c/F_o$ for $F_o > F_c$. In the two structures F_c was 90 and 70 respectively.

Calculations were made on the University of Reading Amdahl V7 using SHELX 76.[14] Atomic scattering factors were taken from ref. 15 together with corrections for anomalous dispersion. In the final cycle of refinement no shifts were $> 0.10\sigma$. Final positional parameters for complex (**1**) and (**2**) are given in Tables 2 and 3. The dimensions in the metal co-ordination spheres are compared in Table 4.

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