

## Molecular graphics investigation of macrocyclic complexes

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**Abstract** - The techniques of molecular graphics and molecular mechanics have been used to investigate several different structural problems concerned with macrocycles. These include predictions of detailed molecular geometry; calculations of the "goodness of fit" of a metal ion inside a particular macrocycle in terms of defined geometric and energetic parameters; interactions between macrocyclic complexes and other molecules; and specifically the positioning of solvent guests within the macrocycle.

### INTRODUCTION

Molecular mechanics has been successfully applied to organic molecules for a number of years (ref. 1) but recently there has been increasing interest in using force-field methods to study inorganic structures in general and macrocyclic complexes in particular (refs. 2-5). There are two major problems in using molecular mechanics in this area; false minima and parameterisation of the force field.

The false minima problem is common to both inorganic and organic molecules and is a consequence of the energy minimisation method which is carried out by an iterative geometry optimisation. Thus, unless there is only one potential well for a molecule, the minimum energy geometry obtained will depend on the initial model. No known general method finds the global energy minima; what are found are local minima. So for complicated molecules, the minimum energy conformation found may well depend upon the intuition of the investigator. Attempts have been made to overcome this problem automatically through molecular dynamics, distance geometry, tree-searching (ref. 6), artificial intelligence (ref. 7) and a truth maintenance system (ref. 8) but none of these methods are as yet foolproof and it is often necessary for the individual chemist to play a part in the construction of suitable models. Molecular graphics is invaluable in this process. Molecules can be built up from their constituent parts, atoms can be added or removed, or changed from one atom type to another; individual sections can be translated, rotated and fitted together. The complete molecule can then be viewed from any direction, rotated, magnified and represented in different forms as required. This visualisation of the molecule is of enormous importance in the understanding of molecular shape. Models can be observed on the computer screen and quickly evaluated. In particular, unreasonable models can be rejected while others can be adjusted as required before energy optimisation.

The provision of parameters in the force-field for inorganic complexes has proved to be a difficult problem. For organic molecules, parameters have been evaluated over many years by comparing calculated and experimental data. Indeed force fields are so well established that the structures of most small molecules can be predicted almost exactly. However inorganic complexes are more complicated and less suitable for molecular mechanics, a technique which ignores electronic effects. Dimensions in organic molecules (e.g. C-C bond length, C-C-C angle) fall within quite small ranges and only minimal changes are observed even in strained molecules. In inorganic complexes metal-donor atom bonds and the angles subtended at metals vary considerably from one molecule to another being dependent on numerous factors including the electronic configuration of the metal and the nature and type of the ligands as well as the charge distribution in the molecule. This cannot just be catered for by just reducing the force constant for bonds and angles. One possible technique is to use 1,3 van der Waals interactions between donor atoms rather than angle terms at metal atoms thus removing the ideal angle dependence around metal atoms (ref. 9).

In all modelling of inorganic systems it is important to keep these two problems in mind and also to compare theoretical results with experimental values whenever possible. A number of successful studies have been carried out. In particular we have used molecular mechanics and molecular graphics to study a number of different structure problems associated with macrocyclic complexes.

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These include;

- (i) The encapsulation of a metal ion with particular stereochemical requirements, within a macrocycles of a particular shape and size (refs. 5,10,11,12).
- (ii) The calculation of steric energy for various conformations of macrocycles and macrocyclic complexes and the prediction of preferred conformations (ref. 11).
- (iii) The fitting of two metal ions, with or without bridging groups, within large macrocycles (ref. 5).
- (iv) The inclusion of solvent guests within macrocyclic complexes (ref. 13).
- (v) The design of bifacial macrocyclic complexes to facilitate the reactions of metal centres with molecules such as dioxygen (ref. 14).
- (vi) The interactions of macrocyclic complexes with surfaces and the investigation of possible mechanisms for catalytic activity (ref. 15).

These can be divided into two types; (i-iii) involve study of individual molecules while (iv-vi) involve intramolecular interactions. In this paper, we describe some of our recent work in these categories.

### COMPUTER MODELLING OF MOLECULAR GEOMETRY

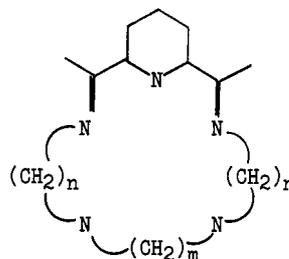
In the long term, it will be possible to model inorganic molecules as accurately as organic molecules but because of the difficulties involved in the parameterisation of the force field, it has proved necessary at present to have more limited objectives. In particular a number of workers have used molecular mechanics to calculate an ideal macrocycle hole size. This is a fundamental property of a macrocycle which specifies the size of the bonding cavity available to a metal ion. We have previously reported our method for the determination of ideal macrocycle hole sizes using molecular mechanics (refs. 10,11) which has been applied to a series of tetra-aza nickel complexes (ref. 10) and to penta-aza copper(II), cobalt(III) and iron(III) complexes (ref. 11). The method defines the nature of the central metal ion in terms of its size and geometric preferences. Here we calculate the ideal hole sizes of a series of macrocycles of the general form (L) and account for observed distortions of the coordination sphere observed in crystal structures.

Crystal structures of complexes with these macrocycles are listed in Table 1 together with observed M-N bond lengths. These can be divided into four structural types. In pentagonal bipyramidal complexes (1), the metal atom lies in the pentagonal plane of the macrocycle donor atoms and the axial positions are occupied by monodentate anions, as in  $[\text{FeL}^1(\text{NCS})_2]^+$  and  $[\text{FeL}^2(\text{NCS})_2]^+$  (ref. 16). In these structures with the smaller transition metals, the coordination sphere is relatively undistorted from the ideal geometry. As the metal size increases, this geometry becomes distorted; thus in  $[\text{MnL}^3(\text{NCS})_2]$ , type (2) (ref. 20) the macrocycle is folded such that the pyridine nitrogen considerably displaced (0.92Å) from the plane of the remaining four nitrogen donor atoms. As the metal size increases, this degree of fold increases so that in  $[\text{CdL}^3\text{Br}]^+$  (ref. 21) a pentagonal pyramid, type (3), is found with one sterically crowded axial site unoccupied. Finally, it is possible to obtain a distorted five-coordinate pentagonal planar complex (4) in which the macrocycle is not folded, as in  $[\text{AgL}^3]^+$  (ref. 19). But these distortions only occur with the 17-membered macrocycle  $\text{L}^3$ . Very few complexes with the larger cations can be prepared with the smaller and less flexible  $\text{L}^1$  and  $\text{L}^2$ , an exception being the polymeric  $[\text{CdL}^2\text{Br}]_n^{n+}$ .

TABLE 1. Observed Metal-Ligand Bond lengths in Complexes of the Macrocycles  $\text{L}^1$ ,  $\text{L}^2$ , and  $\text{L}^3$ .

Type	Structure	M-N Bond Lengths <sup>1</sup>	Reference
(1)	$[\text{FeL}^1(\text{NCS})_2]^+$	2.20 2.26 2.25 2.21 2.22	16
	$[\text{FeL}^1(\text{NCS})_2]$	2.16 2.26 2.24 2.28 2.29	17
	$[\text{FeL}^1(\text{H}_2\text{O})\text{Cl}]^+$	2.22 2.26 2.26 2.26 2.26	18
	$[\text{FeL}^2(\text{NCS})_2]^+$	2.25 2.24 2.23 2.31 2.27	16
	$[\text{FeL}^2(\text{NCS})_2]$	2.23 2.26 2.27 2.37 2.32	17
(2)	$[\text{MnL}^3(\text{NCS})_2]$	2.31 2.38 2.35 2.43 2.38	20
	$[\text{CdL}^3\text{Br}]^+$	2.33 2.42 2.45 2.43 2.37	21
(3)	$[\text{HgL}^3\text{Br}]^+$	2.40 2.25 2.44 2.44 2.40	21
	$[\text{AgL}^3]^+$	2.39 2.50 2.51 2.40 2.41	19
		*2.36 2.55 2.49 2.40 2.55	19

Macrocycle L



$\text{L}^1$   $n = 2, m = 2$  (15-membered)  
 $\text{L}^2$   $n = 2, m = 3$  (16-membered)  
 $\text{L}^3$   $n = 3, m = 2$  (17-membered)

<sup>1</sup> Bond lengths given in the order M-N(pyridine), 2\*M-N(sp<sup>2</sup>), 2\*M-N(sp<sup>3</sup>).

\* Two molecules in the asymmetric unit.

Thus a comparison of  $[\text{FeL}^1(\text{NCS})_2]^+$ ,  $[\text{FeL}^2(\text{NCS})_2]$  and  $[\text{MnL}^3(\text{NCS})_2]$  shows the effect of varying the macrocycle ring size while keeping its conformation relatively constant, while comparing  $[\text{MnL}^3(\text{NCS})_2]$ ,  $[\text{CdL}^3\text{Br}]^+$  and  $[\text{AgL}^3]^+$  shows the effect of varying the conformation of a macrocycle of constant ring size.

### METHOD OF CALCULATION

For the determination of macrocycle hole size, only the metal complex was considered and anions and solvent molecules were ignored. All parameters used for the macrocyclic part of the complex were taken or estimated from the MM2 program (ref. 23). Force constants for metal-ligand bonds were set at  $2.50 \text{ mdyn } \text{Å}^{-1}$  and for angles subtended at the metal were  $0.50 \text{ mdyn } \text{Å}^{-1} \text{ rad}^{-2}$ . Ideal angles ( $72^\circ$ ,  $90^\circ$ ,  $144^\circ$ , or  $180^\circ$ ) for the relevant geometry were used. The torsional barriers around M-N coordinate bonds were assumed to be negligible. Nonbonded interaction parameters were estimated from ref. 24 but values for different metals are quite similar. The values of  $r_0$ , the ideal bond length, for the metal-ligand bonds were varied until the molecular mechanics calculations reproduced, as closely as possible, the actual bond lengths in each crystal structure. The results of these calculations will be referred to as the "best-fit" structures. The M-N stretching force constant was then increased to  $25.00 \text{ mdyn } \text{Å}^{-1}$ , and the steric energy determined as a function of the ideal M-N bond length, as previously reported (refs. 5, 10, 11). In each case the ideal bond length was varied through the range 2.0 to 3.1 Å (Figure 1) and a minimum obtained. The conformation corresponding to the minimum in the curve for each structure will be referred to as the "optimised" structure.

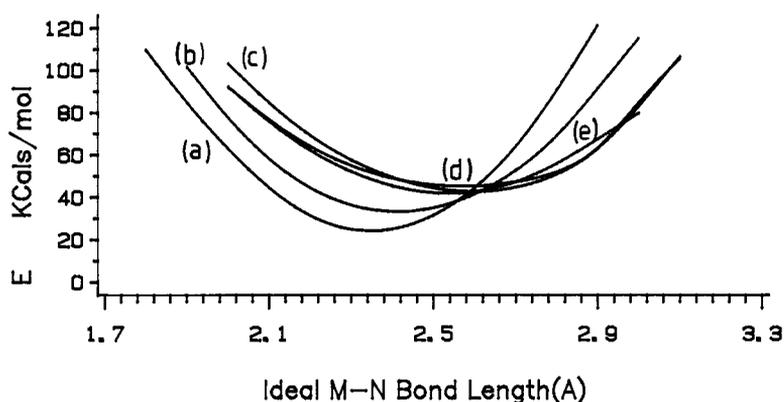


Fig. 1. Steric energy as a function of ideal M-N bond length for (a)  $L^1$ , (b)  $L^2$ , (c)  $L^3$  in type (2), (d)  $L^3$  in type (3) and (e)  $L^3$  in type (4) complexes.

### DISCUSSION OF RESULTS

Figure 1 shows the hole size energy profile for the five compounds studied. The steric energies of the "optimised" and "best fit" structures are given in Table 2, together with the corresponding average M-N bond lengths within the macrocycle. This method for the determination of the optimum hole size of the macrocycle in each structure is essentially independent of the nature of the metal ion present; hence the bond lengths obtained from the calculation are those which would result if an ion of "perfect radius" for that conformation of the macrocycle were to be present. A comparison of the optimum bond lengths  $r_1$  with those observed in the crystal  $r_c$  provides a measure of how well the particular metal ion fits a given macrocycle. A "goodness of fit" parameter

$$R_A/R_p = (\text{bonding cavity radius})/(\text{Pauling covalent radius}) \text{ has been defined (ref. 25).}$$

However the quantity

$$F_r = r_c/r_1 = (\text{average bond length in observed structure})/(\text{average optimised bond length})$$

is easier to calculate. A value of unity for either  $R_A/R_p$  or  $F_r$  denotes a perfect match of the metal ion for the bonding cavity. However, the great advantage of calculating hole sizes with molecular mechanics is that it is possible to compare the energies of the optimised and the best fit structures, i.e. the ideal and crystal structures. We thus define a second "goodness of fit" parameter

$$F_E = E_c - E_1$$

where  $E_c$  is effectively the steric energy of the conformation found in the crystal and  $E_1$  is the steric energy of the ideal conformation.  $F_E$  is the additional steric energy of the macrocyclic structure which is due to the deviation of the ion radius from the ideal for the macrocycle. Table 2 lists the values of  $F_r$  and  $F_E$  for the structures.

For the iron and manganese complexes, it can be seen that the average bond lengths (and hence the hole sizes) increase as extra carbon atoms are added to the macrocycle and the metal ion stereochemistry remains constant. However, the values for  $[\text{FeL}^1(\text{NCS})_2]^+$  and  $[\text{FeL}^2(\text{NCS})_2]^+$  are closer than are those for  $[\text{FeL}^2(\text{NCS})_2]^+$  and  $[\text{MnL}^3(\text{NCS})_2]$  which is as expected as the same metal ion is involved in the former pair. The Fe-N bond lengths in the complex must be similar due to the identical nature of the bonding. In the optimised structures, the steric energy increases with increasing ring size. This effect appears to be additive with an increase of about 9 kcal mol<sup>-1</sup> for each additional carbon atom introduced to the ring. All energy terms, with the exception of that due to dipole interactions, increase with increasing ring size. These individual increases are due to a combination of small terms, although the distorted geometry around the manganese atom is a major source of strain in  $[\text{MnL}^3(\text{NCS})_2]$ .

The  $F_r$  values of < 1.0 in Table 2 show that a larger metal ion in each case would give a better fit to all three macrocycles. Iron(III) is a slightly better fit to  $L^1$  than to  $L^2$ , but manganese(II) is a poorer fit to  $L^3$  than iron(III) is to either  $L^1$  or  $L^2$ . The  $F_E$  values confirm this trend. The hole sizes of the three different conformations of the macrocycle  $L^3$  are similar, as evidenced by the average bond lengths in Table 2. This is a somewhat unexpected result as in previous work we had found variations in hole size of up to 0.4 Å for different conformations of the same macrocycle (ref. 11). As different metals are present in each structure, a small variation in hole size is only to be expected; the ionic radii for  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ag}^+$  are estimated at 0.82, 0.95 and 1.15 Å respectively (ref. 26). Silver(I) actually gives the best fit to the macrocycle, having the lowest  $F_E$  value, 1.95 kcal mol<sup>-1</sup>, of the  $L^3$  complexes in Table 2, and the  $F_r$  value closest to unity (0.96). The match between a metal and a macrocycle conformation is more likely in this case to be due to the preferred stereochemistry rather than differences in size. Since all the  $F_r$  values are less than unity, it appears that all the ions are smaller than the ideal size for these conformations of  $L^3$ . The optimised structures are close in steric energy with  $[\text{CdL}^3\text{Br}]^+$  being the most strained, a major contribution to the total being bending strain at the cadmium(II) ion. The best-fit molecular mechanics calculation only gives a poor fit to the crystal structure for this complex, and it may be that the use of 1,3-nonbonded interactions instead of the angle bending term would improve the fit and give a lower steric energy (ref. 9).

TABLE 2. Goodness of Fit Parameters  
Distances in Å, energies in kcal mol<sup>-1</sup>.

compound	$r_c$	$r_i$	$F_r$	$E_c$	$E_i$	$F_E$
$[\text{FeL}^1(\text{NCS})_2]^+$	2.23	2.35	0.95	31.55	24.20	7.35
$[\text{FeL}^2(\text{NCS})_2]^+$	2.26	2.40	0.94	41.15	33.30	7.85
$[\text{MnL}^3(\text{NCS})_2]$	2.37	2.60	0.91	53.38	42.73	10.65
$[\text{CdL}^3\text{Br}]^+$	2.40	2.57	0.93	47.92	45.31	2.61
$[\text{AgL}^3]^+$	2.44	2.54	0.96	43.86	41.91	1.95

TABLE 3.  $F_r$  values for complexes of L.

Structure	Geometry Type	Ionic Radius (Å)	$F_r$
$[\text{FeL}^1(\text{NCS})_2]^+$	(1)	0.65	0.95
$[\text{FeL}^1(\text{NCS})]_2$	(1)	0.78	0.96
$[\text{FeL}^1(\text{H}_2\text{O})\text{Cl}]^+$	(1)	0.78	0.96
$[\text{FeL}^2(\text{NCS})_2]^+$	(1)	0.65	0.94
$[\text{FeL}^2(\text{NCS})_2]$	(1)	0.78	0.96
$[\text{CdL}^2\text{Br}]_n^{n+}$	(1)	0.95	1.00
$[\text{MnL}^3(\text{NCS})_2]$	(2)	0.82	0.91
$[\text{CdL}^3\text{Br}]^+$	(3)	0.95	0.93
$[\text{HgL}^3\text{Br}]^+$	(3)	1.02	0.93
$[\text{AgL}^3]^+$	(4)	1.15	0.96

We have used our optimised structures to calculate  $F_r$  values for all the complexes listed in Table 1, assuming that each one represents the ideal situation for all the complexes in that group of given macrocycle and metal atom stereochemistry. Table 3 shows the  $F_r$  values for each complex, together with the estimated ionic radius of the metal ion (ref. 26). Thus for the macrocycle  $L^1$ , where the metal ion has a pentagonal bipyramidal geometry, the best fit of ion to macrocycle will occur with a metal with an ionic radius greater than 0.78 Å. In fact, both  $L^1$  and  $L^2$  form complexes with ions with radii ranging from 0.65 to 1.15 Å (ref. 22). The results in Table 3 indicate that the "goodness of fit" increases with ionic radius to  $\text{Cd}^{2+}$ , radius 0.95 Å, which gives a perfect fit with  $F_r=1.00$ . This is in good agreement with a value of 0.92 Å which is the mid-point of the observed range of ions (ref. 22). Finally, where a metal forms complexes with  $L^3$  in a pentagonal pyramidal environment, the best fit will occur for a metal with an ionic radius somewhat less than 0.95 Å. Complexes of  $L^3$  have been prepared having metal ions with radii between 0.82 and 1.18 Å.

We have presented a method for making quantitative estimates of the "goodness of fit" between a metal ion and a macrocyclic ligand, which we believe is superior to other, purely geometric, forms of calculation. Our method has the advantage of allowing the macrocycle conformation to vary as the hole size changes, and gives good agreement with the known crystal structures of this series of macrocycles.

In general, many authors have shown in different ways that it is possible to obtain significant results from molecular mechanics studies of inorganic molecules. Fortunately the uncertainties in the metal parameters often have only a marginal effect on the end result particularly in comparisons of various possible conformations.

## MODELLING OF INTERACTIONS BETWEEN MOLECULES

The whole area of inclusion compounds of molecular transition metal hosts has recently been reviewed (ref. 27). The modelling of interactions between molecules is more difficult than modelling individual molecules and computer graphics plays an essential role in the building up of starting structures. A simple example is the insertion of solvent guest molecules within a macrocycle host. Clearly this is analogous to, but more complicated than, the insertion of a metal atom. Molecular mechanics can be used to minimise the individual molecules and then the solvent molecule or molecules can be docked into the host in various positions while monitoring the energy of interaction. Several systems have been studied in this way including 18-crown-6 (ref. 28), a disilver cryptand (ref. 13) and cavitands (ref. 29). These latter are synthetic organic host molecules that contain enforced rigid cavities of dimensions large enough to include simple organic and inorganic guest species. In the example (Fig. 2) redox-active centres (in this case ferrocene) have been incorporated into these hydrophobic hosts as part of a project to prepare molecular sensory devices capable of electrochemically detecting the inclusion of a guest in the cavitand cavity (ref. 30). Fig. 2 shows a recent crystal structure (ref. 29) of a dichloromethane molecule incorporated within the cavitand. Such experimental results are very useful in the refining of modelling techniques and this molecule as well as other guest molecules such as  $\text{CH}_3\text{CN}$ ,  $\text{CS}_2$ ,  $\text{CO}_2$  and  $\text{CH}_3\text{C}\equiv\text{N}$  have been modelled within the cavity.

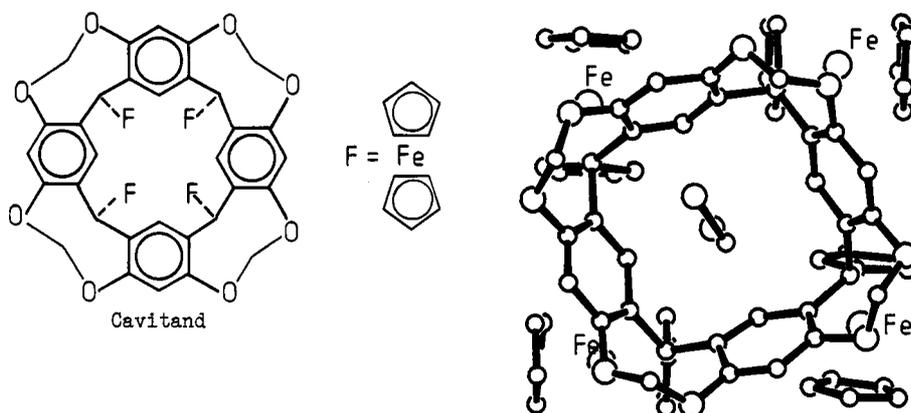


Fig. 2 The Structure of a Cavitand with dichloromethane solvent.

In these cavitands the shape of the host is rigid but often the interaction between guest and host can affect the conformation of both molecules. A series of cryptands have recently been prepared (ref. 13) and crystal structures have been determined of the free macrocycle where the three carbimine nitrogen atoms are directed outwards from the cavity. However in dinuclear complexes, these nitrogen atoms are directed inwards and bonded to metal atoms (Fig. 3). The encapsulation of the metal atoms is thus concomitant with change in conformation. NMR studies (ref. 31) show that restricted rotation around the C-C bonds take place in solution. This has been confirmed by modelling the reaction path to show that the energy barrier is small. Molecular mechanics calculations have also shown that the experimental difficulties involved in preparing metal complexes of the analogous meta-phenyl cryptand are caused by steric repulsions involving the meta-phenyl hydrogen atoms.

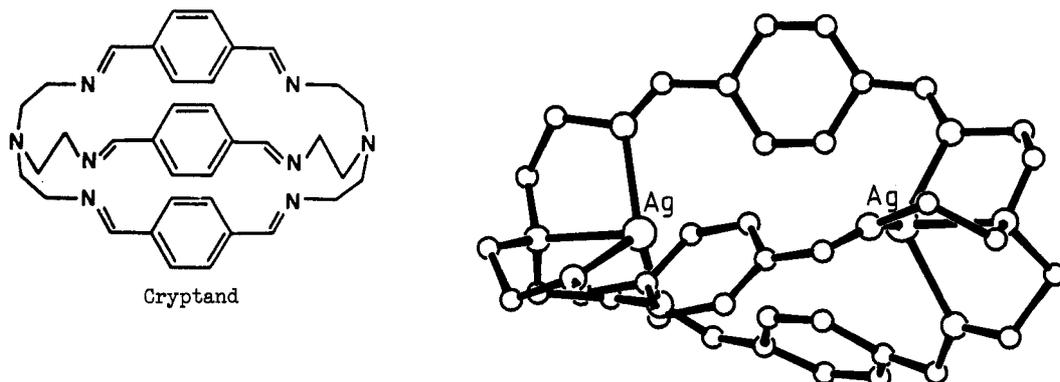


Fig. 3 Structure of  $[\text{Ag}_2(\text{cryptand})]^{2+}$

These calculations have been carried out without consideration of the solvent and this may be a significant omission as solvent molecules can change the relative steric energies of possible conformations and indeed overturn the order of preferred conformations. We are investigating the interaction of solvent water molecules with these cryptands and their role in the conformational changes observed in solution.

A final illustration on this topic is provided by the bifacial porphyrins and phthalocyanines which have been suggested as providing binuclear multielectron redox catalysts for small molecules such as O<sub>2</sub> and N<sub>2</sub> (refs. 32,33). The distance between the bifacial macrocycles can be changed by fitting bridges between them either one rigid aromatic group (e.g. anthracene (1) or biphenylene (2)) or two 4-atom more flexible amide bridges (3). Crystal structures of binuclear complexes have shown a considerable range of conformation and metal...metal distance e.g. Ni...Ni 4.566Å in (1), Cu...Cu 3.807Å in (2) and Co...Co 3.417Å in (3) with varying amounts of slippage between rings. We have modelled these various bifacial macrocycles, not only to relate the distance between macrocycles and metal centres to the linking group but also to consider the structural changes necessary for the approach of small molecules such as O<sub>2</sub> to the metal centres and their subsequent interaction (ref. 14).

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