In memory of S. M. Nelson

Molecular Mechanics Studies of a Series of Dicopper Complexes of a 20-Membered Macrocycle containing Differing Types of Bridges between the Metal Centres *

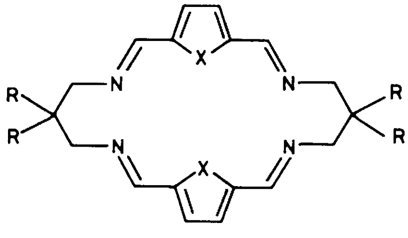
Michael G. B. Drew and Paul C. Yates
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

The molecular mechanics method has been used to investigate a series of metal complexes of the macrocycle L^1 {23,24-dioxa-3,7,14,18-tetra-azatricyclo[18.2.1.1^{9,12}]tetracosa-1(22),2,7,9,11,13,-18,20-octaene}, which are model compounds for Type 3 dicopper proteins. The macrocycle hole-size profile has been calculated for L^1 and shows that with one metal atom in a central position, the minimum-energy conformation of the macrocycle has metal–donor atom distances of 2.75 Å. Force-field calculations have also been carried out on several dicopper complexes of the 20-membered macrocycle L^1 in which the metal co-ordination spheres show a variety of co-ordination numbers and geometries and the metal atoms are bridged by zero, one, two, or three atoms. These calculations indicate that many of the properties of these complexes of L^1 can be explained by the steric effect of imposing a particular metal co-ordination geometry within the macrocycle.

Several binucleating ligands have been synthesised over the last few years and used to prepare dicopper complexes [1–11] which simulate most of the properties [12–14] of the active metal sites in Type 3 copper proteins. In our work we have concentrated on the macrocyclic ligand L^1 and its analogues L^2 and L^3 and have demonstrated [15–21] that several of its complexes contain copper atoms in sites comparable to those observed in the proteins. These complexes are also of interest because some of them function as catalysts for the oxidation of organic substrates. As part of this work, a series of crystal structures of complexes of L^1, L^2, and L^3 have been determined and are listed in Table 1. In these structures each metal atom is bonded to two nitrogen atoms of the macrocycle but not to the furan oxygen atoms; the Cu · · · O distances are generally *ca.* 3.0 Å. In addition the metal atoms are bonded to one or more bridging atoms and/or terminal groups. The macrocycle is flexible enough to accommodate metal co-ordination numbers of three to five with several different geometries. In all these structures, the four nitrogen atoms remain coplanar and therefore the different conformations can be characterised by the deviations of the metal atoms and the furan rings from the N_4 plane (Table 1).

We now report molecular mechanics calculations on metal complexes of macrocycle L^1. Molecular mechanics has been successfully applied to organic molecules for a number of years [22] but recently there has been increasing interest in using force-field methods to calculate strain energies in metal complexes.[23–33] This work has usually concentrated on mononuclear complexes though there has been a previous study on binuclear complexes [30] which contain a metal–metal bond.

Here we investigate the particular requirements for studying binuclear complexes by molecular mechanics and use the results to explain several features of the chemistry of L^1. The present method described here could be used to evaluate the ability of other macrocycles to mimic the various properties of Type 3 copper proteins and hence enable other model compounds to be designed.



L^1 ; X = O , R = H
L^2 ; X = O , R = Me
L^3 ; X = S , R = H

Experimental

Molecular mechanics calculations were performed with a version of the MM2 program [34] modified to allow for co-ordination numbers greater than four [31] and to include periodicity at metal angles. Computations were carried out on the Amdahl V7 computer at the University of Reading.

Force-field parameters used for C, N, O, and H atoms in the macrocycle were taken from values in the MM2 program with the exception of those for the furan ring which were not provided. In this part of the macrocycle, O–C–C and C–C–C angles within the ring were given ideal angles (θ_0) of 108°, and for external angles θ_0 was set at 126°. However the usual values for the bending force constants (k_b) at trigonal carbon and oxygen were included. We used Allinger's method [35] for the treatment of torsion angles within aromatic rings.

Metal parameters used are listed in Table 2. Bond stretching parameters for metal atoms are described in the appropriate

---

* *Supplementary data available* (No. SUP 56691, 20 pp.): details of molecular mechanics calculations. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

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

Table 1. Summary of the crystal structures of binuclear complexes containing L^1, L^2, or L^3

Complex	Structure type (see text)	Bridge type	M–M/Å	N_4 planar to within (Å)	Distance (Å) of M from N_4 plane	Distance (Å) of O from N_4 plane	Angle between furan rings and N_4 plane	Ref.
$[Cu_2L^1(NCMe)_2]^{2+}$	**(2b)**	None	3.39	0.00*	0.55, −0.55	0.05, 0.05	8.9, 8.9	17
$[Cu_2L^2(NCMe)_2]^{2+}$	**(2a)**	None	3.69	0.00*	0.70, −0.70	0.01, −0.06	8.9, 8.9	37
$[Cu_2L^3(NCMe)_2]^{2+}$	**(2)**	None	4.65	0.00*	0.91, −0.91	0.25, −0.25	18.5, 18.5	38
$[Cu_2L^1(SCN)_2]$	**(3c)**	2 × SCN	2.80	0.00*	0.07, −0.07	0.05, −0.05	3.9, 3.9	15
$[Co_2L^1(OEt)(NCS)_3]$	**(3j)**	OEt + NCS	3.12	0.00*	0.57, −0.57	0.02, −0.02	5.6, 5.6	16
$[Co_2L^1(OMe)(N_3)_3]$	**(3j)**	OMe + NNN	3.20	0.00*	0.60, −0.60	0.00, −0.00	7.1, 7.1	16
$[Cu_2L^1(OEt)_2(NCS)_2]$	**(3j)**	OEt + OEt	3.20	0.00*	0.57, −0.57	0.02, −0.02	8.3, 8.3	17, 46
$[Cu_2L^1(OMe)_2(NCMe)_2]^{2+}$	**(3j)**	OMe + OMe	3.12	0.00*	0.51, −0.51	0.15, −0.15	7.1, 7.1	46
$[Cu_2L^1(pyz)_2]^{2+}$	**(4a)**	2 × pyz	3.20	0.04	1.09, 1.06	−0.82, −0.85	52.8, 49.8	3, 44
$[Cu_2L^2(pydz)_2]^{2+}$	**(4b)**	2 × pydz	3.39	0.00	0.20, −0.20	0.12, −0.12	5.5, 5.5	3, 45
$[Cu_2L^1(PPh_2CH_2PPh_2)]^{2+}$	**(5e)**	$PPh_2CH_2PPh_2$	3.27	0.16	0.92, 0.92	−0.81, −0.77	59.8, 45.4	38
$[Cu_4L^1_2(CCPh)]^{3+}$	—	CCPh shared with 4 × Cu						
		(two macrocycles in asymmetric unit) ring A	2.95	0.08	0.77, 0.82	−0.81, −0.88	28.9, 51.5	19
		ring B	2.88	0.12	0.62, 0.79	−0.76, −0.75	41.3, 37.7	19
$[Cu_5L^2_2(dmt)_2]^{3+}$	—	dmt	3.34	0.05	0.82, 0.88	−0.60, −0.63	37.2, 43.5	20
$[BaL^1_2(H_2O)_2]^{2+}$ ring A	—	—		0.03	0.79	−0.78. −0.70	48.1, 35.3	18
ring B	—	—		0.03	1.69	−1.05, −1.12	80.4, 87.8	18

* Structure contains a crystallographic centre of symmetry.

section. An ideal metal co-ordination geometry was assumed in all calculations and θ_0 values were fixed accordingly.

As is usual in force-field calculations involving metal atoms, torsional barriers about co-ordinate bonds were assumed to be negligible. Non-bonded interaction parameters for the metal atoms were estimated from ref. 36. The calculations were carried out using barium and copper as the metals in the macrocycle. However the parameters used are not specific to the metal and should give similar results for other metals. Molecular mechanics for inorganic molecules is not sufficiently sophisticated for minor differences in the properties of metals to be characterised by different parameters.

For each calculation, preliminary co-ordinates were obtained from crystal structures wherever possible but from models otherwise. We used specific types of bridging groups in our calculations but the method adopted is sufficiently general to be applicable to any type of bridge, particularly as the bridge atoms rarely had any significant interactions with the macrocycle. A number of these species are positively charged and therefore would be accompanied by anions in a crystal. These anions were ignored.

Results and Discussion

Five categories of metal complexes were investigated:* **(1)** mononuclear complexes, **(2)** binuclear complexes with no bridging atoms, **(3)** binuclear complexes with two one-atom bridges, **(4)** binuclear complexes with two two-atom bridges, and **(5)** binuclear complexes with one or two three-atom bridges.

A summary of the results of molecular mechanics calculations in all categories **(1)**—**(5)** inclusive is given in Table 3. Full details are provided in SUP No. 56691.

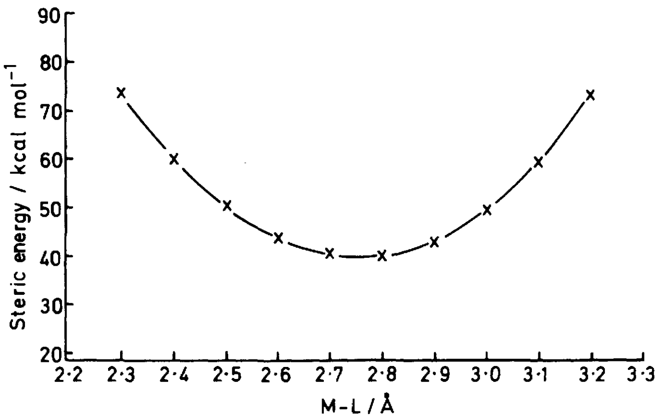


Figure 1. Plot of steric energy (kcal mol^{-1}) against M–L distance (Å) for $[BaL^1(OH_2)_2]^{2+}$, **(1)**

Mononuclear Complexes, **(1)**.—The macrocycle L^1 is prepared by the use of Ba^{2+} as a template for the cyclic [2 + 2] condensation of two molecules of 2,5-diformylfuran with two molecules of 1,3-diaminopropane to give the mononuclear complex $[BaL^1(ClO_4)_2]\cdot EtOH$.[15] We have been unable to obtain crystals of this complex suitable for *X*-ray structure determination but it seems likely that the macrocycle would provide an approximate planar donor set for the metal and a set of trial co-ordinates were calculated on that basis. The related structure of $[BaL^4(ClO_4)_2]$ (L^4 = 18-membered macrocycle formed from 2,6-diacetylpyridine and diethylenetriamine) shows that the macrocycle forms an approximately planar girdle around the barium ion with the six Ba–N distances in the range 2.84—2.89 Å.[21]

We then calculated a hole-size profile for the macrocycle L^1 using our published method.[31–33] The M–L (L = donor atoms O or N) stretching force constant (k_s) was set at 25.00 mdyn $Å^{-1}$. This ensures that the stretching of this bond becomes the

---

* Some of the experimental work and indeed some of the crystal structures listed in Table 1 have been carried out with L^2, the 5,5,16,16-tetramethyl analogue of L^1. In order to test whether the tetramethyl substitution made any difference to the calculations, we carried out molecular mechanics calculations on both $[Cu_2L^1(NCMe)_2]^{2+}$ and $[Cu_2L^2(NCMe)_2]^{2+}$. Results are discussed in the section for **(2)**. There was some difference in the strain energies but little difference in the relative values and conformations and therefore further molecular mechanics calculations were limited to structures containing L^1.

Table 2. Force-field parameters; nomenclature taken from ref. 22

(*a*) Bond stretching

Bond	Structure	k_s/mdyn Å^{-1}	r_0/Å
Ba–O(axial)	**(1)**	2.50	2.85
Cu–P	**(5e)**	2.50	2.17
C–P	**(5e)**	3.23	1.77
Cu–N(CMe)	**(2)**	2.50	1.91
Cu–N(bridge)	**(4a)**	2.00	1.94
	(4b)	2.00	2.02
M–N(CS)(bridge)	**(3a)**, **(3b)**	2.50	2.03
	(3d), **(3e)**	2.50	2.06
	(3g), **(3h)**	2.50	2.04
	(3j)	2.50	2.05
	(5a)	2.50	2.10
	(5b)	2.50	2.09
	(5c)	2.50	2.07
	(5d)	2.50	2.07
Cu–S	(**3b, c, e, f, h, i**)	2.50	2.39
	(5a)	2.50	2.37
	(5b)	2.50	2.40
	(5c)	2.50	2.37
	(5d)	2.50	2.38
M–N(macrocycle)	**(2)**	2.50	2.00
	(3a)—**(3c)**	2.50	2.00
	(3d)—**(3f)**	2.50	1.99
	(3g)—**(3i)**	2.50	1.97
	(3j)	2.50	2.05
	(4a)	2.50	2.00
	(4b)	2.50	2.03
	(5a)	2.50	2.06
	(5b)	2.50	2.07
	(5c)	2.50	2.01
	(5d)	2.50	2.01
	(5e)	2.50	2.04

(*b*) Angle bending

Angle	Structure	k_b/mdyn Å^{-1} rad^{-2}	θ_0/°
Cu–P–C	**(5e)**	0.200	109.47
C–P–C	**(5e)**	0.200	109.47
M–N–C	**(2)**	0.450	180.00
M–N–C(bridge)	(**3a, b, d, e, g, h, i**)	0.100	135.00
	(**5a, b, c, d**)	0.450	160.00
Cu–S–Cu	**(3b)**, **(3c)**	0.100	70.53
Cu–S–Cu	(**3e, f, h, i**)	0.100	90.00
Cu–S–C(bridge)	(**3b, c, e, f, h, i**)	0.100	100.00
	(**5a, b, c, d**)	0.720	95.00
Cu–N–Cu	**(3a)**, **(3b)**	0.100	70.53
Cu–S–Cu	(**3d, e, g, h, j**)	0.100	90.00
X–M–Y[a]	**(1)**	0.300	60.00, 90.00, 120.00, 180.00
X–M–Y[a]			
	(2)	0.300	120.00
	(**3a, b, c**), **(4b)**, (**5a, b**)	0.300	109.47
	(**3d, e, f, g, h, i**)	0.300	90.00, 180.00
	(3j)	0.300	90.00, 120.00, 180.00
	(4a), (**5c, d**)	0.300	90.00, 180.00

(*c*) Torsional strain[b]

Angle	Structure	V_1	V_2	V_3
			kcal mol^{-1}	
N–Cu–N–Cu	**(2a)**	0.00	10.0	0.00
	(2d)	0.00	500.0	0.00
N–Cu–S–Cu	**(2b)**	0.00	10.0	0.00
	(2e)	0.00	500.0	0.00
S–Cu–N–Cu	**(2e)**	0.00	500.0	0.00
S–Cu–S–Cu	**(2f)**	0.00	10.0	0.00

(*d*) Non-bonded parameters[c]

Atom	r^*/Å	ε/kcal mol^{-1}
Ba	2.50	0.260
Cu	2.35	0.165

[a] X–M–Y is indicative of all angles subtended at the metal. Thus X, Y = O, N, or S where appropriate. [b] Torsional barriers about metal–ligand bonds were otherwise set to zero. [c] Although different non-bonded parameters are used the calculations are essentially independent of the metal atom type and similar results will be obtained for any metal. The changes in r^* and ε have a negligible effect on the final conformations and steric energies.

dominant term in the strain energy and the M–L bond lengths will be optimised to the preset r_0 values at the expense of all other quantities. Indeed all the Ba–L bond lengths refined to this value within 0.001 Å. The resulting strain energy is therefore due primarily to strain in the macrocycle conformation which has adjusted to fit to the metal of a particular radius. The ideal M–L bond length r_0 can then be varied and the refinement repeated so that a plot of M–L against strain energy can be obtained. For this calculation, a hexagonal bipyramidal structure was assumed with the metal atom bonded to four nitrogen and two oxygen atoms of the macrocycle in the equatorial girdle and to two water molecules in axial positions. For M–OH$_2$ k_s was set at 2.50 mdyn Å^{-1} and r_0 at 2.85 Å. The force constant k_b for angles subtended at the metal atom was set at 0.300 mdyn Å^{-1} rad^{-2} with θ_0 at 60, 90, 120, or 180°.

The resulting hole-size profile for L^1 is shown in Figure 1. The minimum steric energy at 40.1 kcal mol^{-1} was obtained with an M–X (X = O or N) bond length of 2.75 Å. The M–O and M–N bond lengths were then allowed to vary independently. To find starting values for r_0 the two different types of bond were given a k_s value of 0.0 mdyn Å^{-1} and the structure refined. The resulting average bond lengths were 2.4 and 2.8 Å respectively. We then fixed the M–N bond length at 2.8 Å and gave the M–O bond length a force constant of 25.00 mdyn Å^{-1}. The steric

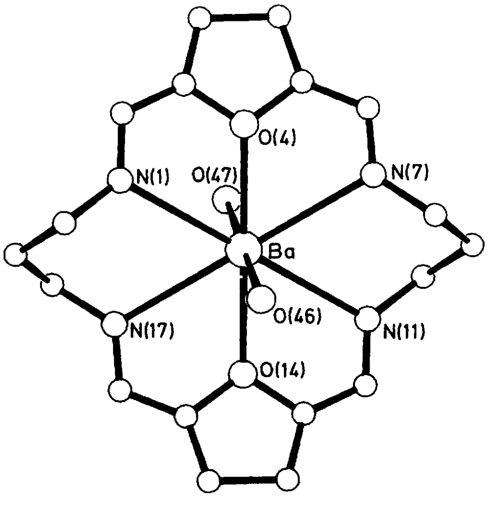


Figure 2. Structure of [BaL^1(OH$_2$)$_2$]$^{2+}$, **(1)**, as predicted by molecular mechanics calculations

Table 3. Details of the model structures obtained by force-field methods

Structure	Details	M ··· M/ Å	N_4 planar to within (Å)	Distance (Å) of M from N_4 plane	Distance (Å) of O from N_4 plane	Angle (°) between furan rings and N_4 plane	Energy/ kcal mol^{-1}
(1)	Mononuclear complex	—	0.00	0.00	−0.63, 0.63	41.7, 41.7	27.64
(2b)	Binuclear complex – no bridge	3.62	0.00	0.45, −0.45	0.00, 0.00	3.9, 3.9	25.41
(3a)	Binuclear complex, tetrahedral copper, two	2.66	0.02	0.02, −0.02	−0.05, 0.16	2.1, 10.7	33.91
(3b)	one-atom bridges *via* N,N (**3a**), N,S (**3b**), or	2.78	0.03	0.00, −0.05	0.13, 0.13	0.8, 14.6	34.43
(3c)	S,S (**3c**) atoms	2.98	0.00	0.02, −0.02	−0.06, 0.06	3.5, 3.5	35.39
(3d)	Binuclear complex, square-planar copper, two	2.79	0.01	−0.90, −0.90	1.51, 1.50	20.4, 1.50	79.85
(3e)	one-atom planar bridges *via* N,N (**3d**), N,S	2.98	0.01	−0.99, −0.99	1.56, 1.44	19.2, 32.7	93.15
(3f)	(**3e**), or S,S (**3f**) atoms	3.35	0.00	−1.01, −1.04	1.47, 1.48	38.1, 17.6	110.17
(3g)	Binuclear complex, square-planar copper, two	2.65	0.00	−0.78, −0.78	1.05, 1.05	39.5, 38.9	33.27
(3h)	one-atom non-planar bridges *via* N,N (**3g**),	2.79	0.01	−0.85, −0.85	0.98, 1.04	45.3, 42.2	36.25
(3i)	N,S (**3h**), or S,S (**3i**) atoms	2.98	0.01	−0.91, −0.91	1.03, 1.03	41.9, 41.8	42.52
(3j)	Binuclear complex, trigonal-prismatic copper, two one-atom planar bridges	3.04	0.00	0.44, −0.44	−0.01, −0.01	5.3, 2.9	26.39
(4a)*	Binuclear complex, square-planar copper, two two-atom bridges	3.45	0.01	−1.01, −1.01	0.68, 0.68	55.6, 54.5	36.93
(4b)*	Binuclear complex, tetrahedral copper, two two-atom bridges	3.30	0.00	−0.02, 0.02	0.00, 0.00	0.9, 1.4	33.38
(5a)	Binuclear complex, tetrahedral copper, two	3.74	0.01	0.19, 0.04	0.01, 0.02	1.3, 1.8	83.40
(5b)	three-atom bridges	4.18	0.00	−0.56, 0.55	0.00, 0.00	3.4, 3.4	70.07
(5c)	Binuclear complex, square-planar copper, two	4.26	0.01	−1.10, −1.26	0.52, 0.52	46.2, 45.7	43.52
(5d)	three-atom bridges	4.30	0.10	−1.18, −1.18	0.51, 0.51	46.1, 46.0	35.84
(5e)*	Binuclear complex, trigonal copper, one three-atom bridge	3.52	0.26	−0.78, −0.78	0.45, 0.45	23.1, 23.1	11.13

* Energy for these structures is not comparable with other values due to the treatment of unsaturated rings (see text).

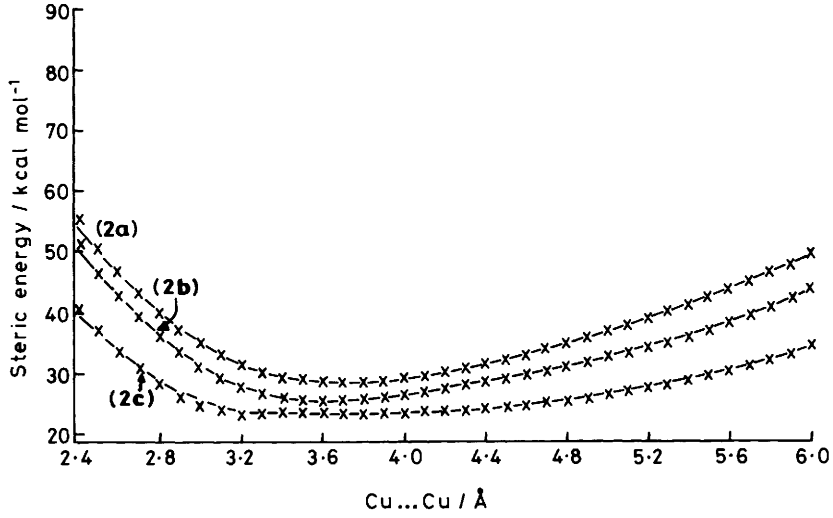


Figure 3. Plot of steric energy (kcal mol^{-1}) against Cu ··· Cu distance (Å) for $[Cu_2L^2(NCMe)_2]^{2+}$, (**2a**), and $[Cu_2L^1(NCMe)_2]^{2+}$, (**2b**), with k_b for L–Cu–L of 0.300 mdyn Å^{-1} rad^{-2}, and for $[Cu_2L^1(NCMe)_2]^{2+}$, (**2c**), with k_b for L–Cu–L of 0.030 mdyn Å^{-1} rad^{-2}

energy was then calculated over a range of r_0 values and the ideal M–O bond length was obtained from a plot of r_0 against steric energy. The M–O bond length was then fixed at this value and the process was repeated to find the ideal M–N bond length. Iterations proceeded in this manner for M–O and M–N alternately until convergence which occurred at a M–N distance of 2.86 Å and a M–O distance of 2.46 Å. The resulting steric energy was much lower at 27.6 kcal mol^{-1} than when M–O and M–N were fixed to be equivalent (40.1 kcal mol^{-1}).

The angles around the barium atom were close to the preset θ_0 values (60, 90, 120, or 180°) in the refined model (Figure 2). However the main contributions to the angle bending term came from within the macrocycle, suggesting that considerable strain is induced by adapting to this geometry. The fact that the M–N and M–O bond lengths refine to very different values suggests that L^1 is not well suited to the formation of a mononuclear complex particularly as the difference between oxygen and nitrogen covalent radii is very small, a fact confirmed by Ba–O and Ba–N distances in other structures. Another indication of strain in the minimum-energy conformation is that both furan rings are tilted at 41.7° to the N_4 plane. This is not a consequence of allowing the Ba–O and Ba–N lengths to refine to different values as with equivalent bond lengths, the angle tilts are 39.8°. These deviations are particularly noteworthy as the furan ring was coplanar with the donor atoms in the starting model. We predict that this non-planar deviation would be found in a crystal structure of $[BaL^1]^{2+}$.

There is structural evidence that a 20-membered planar macrocycle provides too large a hole for a single metal atom, even one as large as barium. In transition-metal macrocycle complexes, planar conformations are found only for 15—17-membered rings and while 18-membered rings have been found around barium,[21] larger rings need to fold to reduce the hole size so that a metal can be encapsulated.

In this 18-membered ring structure,[21] the Ba–N distances had typical values in the range 2.84—2.89 Å. The Ba–O,N distances of *ca.* 2.75 Å required in the ideal conformation of $[BaL^1]^{2+}$ are thus below the norm.

This result also confirms that a large cation is required to enable the template preparation of the macrocycle to proceed. Clearly a transition metal such as copper will not fit into the 20-membered macrocycle in the same way as barium. We attempted to model a structure in which one copper atom was encapsulated into the macrocycle bonded only to the four nitrogen atoms but it proved impossible to minimise this structure successfully.

Binuclear Complexes with no Bridge, (**2**).—The crystal structures of three similar complexes of this type have been determined, *viz.* $[Cu_2L(NCMe)_2]^{2+}$, where L = L^1,[17] L^2,[37] or L^3.[38] In the two structures with L^1 and L^2, the two copper atoms are three-co-ordinate with approximately trigonal-planar environments. Although the conformations are similar (Table 1), the Cu ··· Cu distances differ significantly, being 3.39 Å with L^1 and 3.69 Å with L^2. In each structure the metal atoms are bonded to two nitrogen atoms (N_m) of the macrocycle and to a nitrogen atom (N_t) of the methyl cyanide molecule in an approximately trigonal-planar geometry {dimensions in $[Cu_2L^1(NCMe)_2]^{2+}$ are:[17] Cu–N_m 1.96, 1.97 Å, Cu–N_t 1.91 Å; N_m–Cu–N_m 101.4, N_m–Cu–N_t 129.7, 124.7°; the copper atom 0.23 Å above the plane of the three nitrogen atoms}. In $[Cu_2L^3(MeCN)_2]^{2+}$, a Cu ··· Cu distance of 4.65 Å has been observed.[38] However in this structure there are weak Cu ··· S interactions (2.89, 3.07 Å) that give rise to a more irregular co-ordination sphere.

In order to study these complexes (and the other binuclear complexes) we used a variation of the 'hole-size' method described for (**1**) above. A Cu–Cu 'dummy bond' was included in the calculation instead of a van der Waals interaction between the two metal atoms.*

At first the bond stretching energy force constant for this bond was set to 0.00 mdyn Å^{-1}. We then varied r_0 for the Cu–N bonds (and Cu–S bonds where present) until either the bond lengths in a particular crystal structure were obtained on refinement, or in the absence of this information, when the bond lengths obtained were appropriate to the oxidation state and co-ordination number of the copper atoms. When there was doubt about the correct values, parameters were chosen so that bond lengths of 2.05 Å for Cu–N and 2.39 Å for Cu–S were obtained upon refinement. In these calculations the k_s value was 2.50 mdyn Å^{-1}. Slightly different values of r_0 were obtained in each structure and as is common in molecular mechanics, these values were usually less than the observed bond lengths. Having obtained values of r_0 (Cu–L) in this fashion k_s for the Cu ··· Cu distance was set to 25.0 mydn Å^{-1} so that in the calculation the Cu ··· Cu distance was fixed at the set r_0. The strain energy therefore indicates how well the macrocycle conformation has adjusted to fit to the particular Cu ··· Cu distance. The Cu ··· Cu length was then varied and a plot produced of Cu ··· Cu distance against the steric energy of the complex.

This method was first applied to the binuclear complexes with no bridge. Calculations were carried out on $[Cu_2L^2(NCMe)_2]^{2+}$, (**2a**), and $[Cu_2L^1(NCMe)_2]^{2+}$, (**2b**), with input co-ordinates taken from the known crystal structures.[17,38] We first used k_b values for N–Cu–N angles of 0.30 mdyn Å^{-1} rad^{-2} giving the plots of steric energy against Cu ··· Cu distance shown in Figure 3 [(**2a**) and (**2b**)]. Both curves are very shallow and show the wide range of Cu ··· Cu distances that can be accommodated within the macrocycle when there are no bridges between the metal atoms. The shapes of these curves contrast markedly with the deep minimum found in the mononuclear complex (Figure 1). The curves have slightly different minima (at 3.72 and 3.62 Å) but the overall shape is similar and we decided in subsequent calculations to work solely with L^1. We have no explanation for the different Cu ··· Cu distances of 3.69 and 3.39 Å found in the two crystal structures with L^2 and L^1 but note that there is only 4.0 kcal mol^{-1} difference in steric energy over a considerable range of Cu ··· Cu distance (3.10—4.50 Å).

We then repeated the calculation for $[Cu_2L^1(NCMe)_2]^{2+}$ with a k_b value of 0.03 mdyn Å^{-1} rad^{-2} [curve (**2c**)], in order to investigate possible correlations between Cu ··· Cu distance and N–Cu–N angles. There proved to be a strong interdependence, with mean angles for N_m–Cu–N_m and N_m–Cu–N_t of 107, 87° respectively at Cu ··· Cu 2.40 Å; 105, 115° at 3.40 Å; 102, 129° at 4.20 Å; 97, 129° at 4.90 Å; and 88, 122° at 6.00 Å.

With the more realistic value for k_b of 0.30 mdyn Å^{-1} rad^{-2}, the N–Cu–N angles vary less from 120° but follow a similar trend to the distortions obtained for k_b = 0.03 mdyn Å^{-1} rad^{-2}. For the largest Cu ··· Cu distances, the furan rings twist considerably out of the plane to give N–C–C–O torsion angles of −38.5, −42.5° (at Cu ··· Cu 6.00 Å). In most structures, these torsion angles are close to zero. However there is one precedent for this rotation; in a structure of a complex containing a trimethine unit formed from 2,6-diacetylpyridine,[39] one of the N–C–C–N torsion angles is −83°, so that the nitrogen atom is twisted right out of the plane. Though the ligand involved in this complex is not a macrocycle, this twist does suggest that the structure postulated at larger Cu ··· Cu distances cannot be ruled out. Although all the observed structures containing L^1 have Cu ··· Cu distances between 2.80 and 3.39 Å (Table 1), the structures of $[Cu_2L^2(NCMe)_2]^{2+}$ (Cu ··· Cu 3.69 Å) and $[Cu_2L^3(NCMe)_2]^{2+}$ (Cu ··· Cu 4.65 Å) suggest that longer Cu ··· Cu distances are also possible for L^1, particularly as the conformations of the macrocycle in these structures are very similar to those found for L^1.

However while in principle the macrocycle can accommodate a wide range of Cu ··· Cu distances, in practice the distance is limited by any bridge between the atoms and by the metal co-ordination geometry.

Binuclear Complexes with Two One-atom Bridges, (**3**).—For the one-atom bridge system with macrocycle L^1, a number of structures have been determined but only one has four-co-ordinate copper atoms, namely $[Cu_2L^1(SCN)_2]$. This structure contains tetrahedral Cu^I atoms bridged through sulphur by two thiocyanate ligands.[15] Nine sets of calculations were carried out for complexes of this type with four-co-ordinate copper atoms bridged by two thiocyanate groups.

Force-field parameters for the bridge were difficult to estimate,

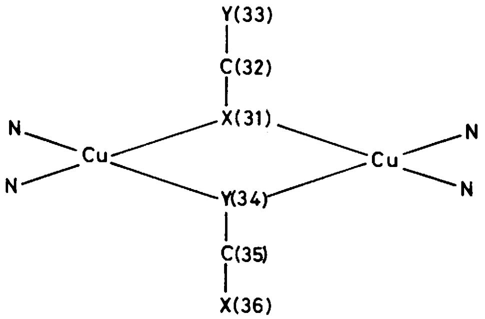
---

* Inclusion of the dummy bond instead of a non-bonded interaction for the Cu ··· Cu interaction has the advantage that it can be easily fixed at a particular value. In addition if the metal atoms are sufficiently close that the interaction between them is repulsive, inclusion of the dummy bond allows them to move closer than would otherwise be the case. This allows the calculation to proceed without making prior assumptions about whether a metal ··· metal bond is present.

Tetrahedral environment: (**3a**) bridging atoms N, N
(**3b**) bridging atoms N, S
(**3c**) bridging atoms S, S

Square-planar environment: (**3d**) bridging atoms N, N
(planar bridge) (**3e**) bridging atoms N, S
(**3f**) bridging atoms S, S

Square-planar environment: (**3g**) bridging atoms N, N
(non-planar bridge) (**3h**) bridging atoms N, S
(**3i**) bridging atoms S, S



because there are few precedents for di-μ-1,1-thiocyanate bridges and also because the angles to some extent depend upon the Cu ··· Cu distances. A search of the Cambridge Crystallographic Centre files[40] produced several structures containing Cu–S–Cu bridges [all involving Cu^{I}] with Cu–S–Cu angles ranging from 69 to 115° correlated with Cu ··· Cu distance. In view of the short Cu ··· Cu distance (2.80 Å) found in the structure of [$Cu_2L^1(SCN)_2$], and because the Cu_2S_2 bridge was planar, it was decided to set θ_0 for Cu–S–Cu to 70.46° (*i.e.* 180—109.54°) and for Cu–S–C to 100°.

There was only one structure containing two Cu–N–Cu bridges in the Cambridge Data files [involving a di-μ-azido-dicopper(II) moiety within a 24-membered ligand[41]] which has Cu–N–Cu angles between 100 and 105° with a Cu ··· Cu distance of 3.162 Å. We also noted the structure of [$\{Re(NCS)_4\}_2(\mu\text{-}NCS)_2$][42] in which dimensions were Re–Re 2.613 Å, Re–N–Re 77.3, and Re–N–C 138.9—143.0°. We set θ_0 for Cu–N–Cu to 70.46° to conform to a planar bridge and then θ_0 for Cu–N–C was set at 135° as most structures contained nitrogen in an almost trigonal-planar environment. In view of the uncertainty of ideal values, the bridge angles were assigned a low bending force constant (0.100 mydn Å^{-1} rad^{-2}) so that deviations of up to 15° had little effect on the total energy. The S–C–N angle on the other hand was given the more usual force constant of 0.400 mdyn Å^{-1} rad^{-2}.

All these crystal structures in the Cambridge Data Centre files showed a Cu_2X_2 planar bridge (maximum deviation of any atom <0.02 Å). In order to provide such a constraint, a large two-fold torsional barrier, V_2, of 10.0 kcal mol^{-1} was included for the Cu–X–Cu–Y torsion angles and this indeed kept them within 3° of 0°.

Steric energy was then calculated for particular Cu ··· Cu distances in the manner described for (**2**). The resulting steric energies for structures (**3d**), (**3e**), and (**3f**) (square-planar copper atoms in a planar bridge), were very large (*ca.* 80 kcal mol^{-1}) and it seems unlikely that such structures could be prepared. The planar constraint on the bridge was therefore removed and the energies then became comparable to those for models containing tetrahedral copper (*ca.* 40 kcal mol^{-1}). Plots of steric energy against Cu ··· Cu distance for (**3a**), (**3c**), (**3g**), and (**3i**) are given in Figure 4.

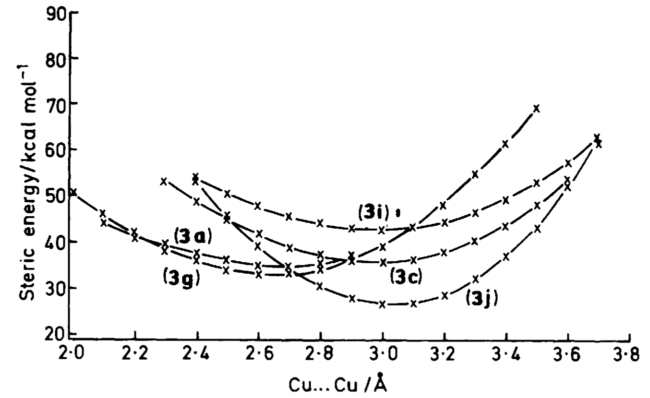


Figure 4. Plot of steric energy (kcal mol^{-1}) against Cu ··· Cu distance (Å) for various structures of [$Cu_2L^1(NCS)_2$] containing two 1,1-dithiocyanate bridges between metal centres. Copper atoms in tetrahedral environments: (**3a**) N,N bridges, (**3c**) S,S bridges. Copper atoms in square-planar environments: (**3g**) N,N bridges, (**3i**) S,S bridges. Copper atoms in trigonal-bipyramidal environments, [$Cu_2L^1(NCS)_4$]: (**3j**) N,N bridges

There is little difference between the minimum energies in the tetrahedral structures (**3a**), (**3b**), and (**3c**) although as expected the position of the Cu ··· Cu distance at the minimum increases from 2.66 Å for two N bridges, to 2.78 Å for N and S bridges, to 2.98 Å for S bridges. These values were dependent to some extent on the parameterisation of the bridge and, to take an extreme case, if θ_0 for Cu–S–Cu was changed to 120°, the minimum for Cu ··· Cu changed to 3.17 Å. However our choice of parameters ensured that the calculations were realistic.

As a test for the method, the aforementioned copper(II) structure with di-μ-1,1-azide bridges[41] was investigated. We used as far as possible the same parameters as in (**3a**) but in this structure there were weak Cu–O interactions at *ca.* 2.65 Å in axial positions which complicated the calculations. Parameters involving these bonds were therefore given small force constants (k_s 0.10 mdyn Å^{-1}, k_b 0.10 mdyn Å^{-1} rad^{-2}). A curve of Cu ··· Cu distance against steric energy showed a minimum energy at a Cu ··· Cu distance of 3.10 Å compared to an observed value of 3.16 Å in the crystal structure. This result indicated that this present modelling technique should work for a wide variety of macrocyclic complexes for not only did our method confirm the different steric requirements of the two types of macrocycle but also successfully predicted different Cu ··· Cu distances at the minimum-energy conformation despite the uncertainty over the parameterisation of the bridge.*

The results for (**3a**)—(**3c**) suggest an explanation for the unexpected structure of [$Cu_2L^1(SCN)_2$][15] which exhibited S-bonded thiocyanate rather than N-bonded thiocyanate. In order to accommodate N-bonded thiocyanate the ideal Cu ··· Cu distance at 2.66 Å would involve a metal–metal bond; while in S-bonded thiocyanate the interaction is considerably less; indeed a Cu ··· Cu distance of 2.98 Å is ideal. It is

---

* One of the hazards of molecular mechanics calculations is that only local minima are found and therefore an accurate input model can be crucial. We hoped that our method (of imposing a dummy Cu ··· Cu bond of a particular length) might overcome this problem by forcing the macrocycle to accommodate a particular Cu ··· Cu distance. To test the validity of our method we used two different models as input to structure (**3a**). The first model used the co-ordinates from the crystal structure of [$CuL^1(SCN)_2$]. For the second model, a different set of co-ordinates were obtained from the tetrahedral two-atom bridge structure (**4b**). The curves, of steric energy against Cu ··· Cu distance, for the two models were similar as were the conformations of the macrocycle. This result was encouraging as it suggests that the starting geometry may not be too important in the calculation of the ideal metal–metal distance by this method.

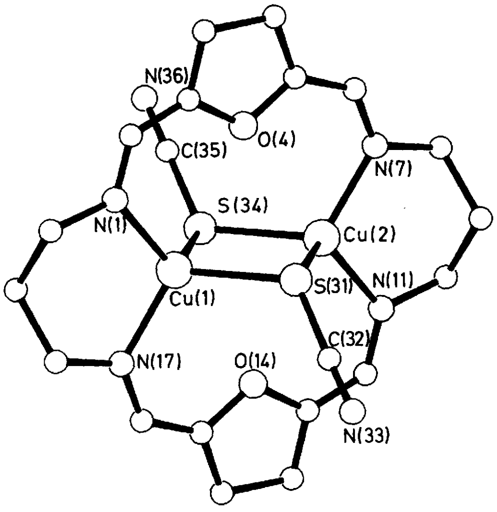


Figure 5. The structure of $[Cu_2L^1(SCN)_2]$, (**3c**), as predicted by molecular mechanics calculations

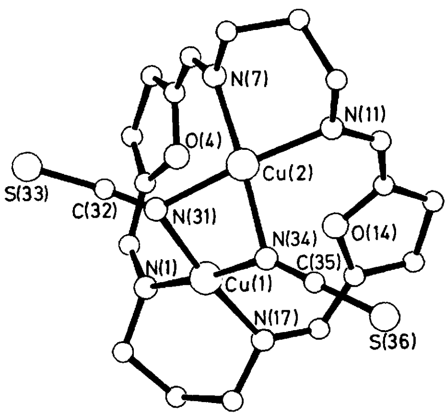


Figure 6. The structure of $[Cu_2L^1(NCS)_2]^{2+}$, (**3g**), as predicted by molecular mechanics calculations

interesting that the Cu ··· Cu distance in the crystal structure is significantly less, at 2.80 Å, and this must indicate some weak Cu ··· Cu interaction. As no such interaction had been included in these calculations of preferred Cu ··· Cu distance in $[Cu_2L^1(SCN)_2]$, we calculated the force constant necessary to minimise the steric energy at a Cu ··· Cu distance of 2.80 Å and this proved to be 1.5 mdyn $Å^{-1}$, together with an r_0 of 2.75 Å. Molecular orbital calculations[43] on $[Cu_n]^{n+}$ ($n = 2$ or 4) model systems have shown that while there will be closed-shell repulsions between the d^{10} shells, these may be opposed by a slight attractive interaction through mixing of metal s and p orbitals.

In the square-planar structures (**3g**), (**3h**), and (**3i**) the minimum steric energy (33.27, 36.25, or 42.52 kcal mol^{-1}) and the Cu ··· Cu distance at the minimum (2.65, 2.79, or 2.98 Å) increases as the number of bridging sulphur atoms increases.

It is interesting that the steric energy for sulphur bridges, (**3c**), is less than that of nitrogen bridges, (**3a**), in tetrahedral dicopper structures but the reverse is true for the square-planar case. This provides good evidence that steric effects cause the thiocyanates to bridge through sulphur in $[Cu_2L^1(NCS)_2]$ although preference for sulphur may also be due to the class b or 'soft' nature of the Cu^I ion.

The macrocycle conformations within each group of structures are very similar. In the tetrahedral case (Figure 5), the metal atoms are coplanar with N_4 and the furan rings almost parallel, while for the square-planar structures (Figure 6) both copper atoms lie on the same side of the N_4 plane and the furan rings are inclined at angles of *ca.* 40° to this plane. Indeed the conformation is similar to that found for the two two-atom bridges in the section for (**4a**) for square-planar copper.

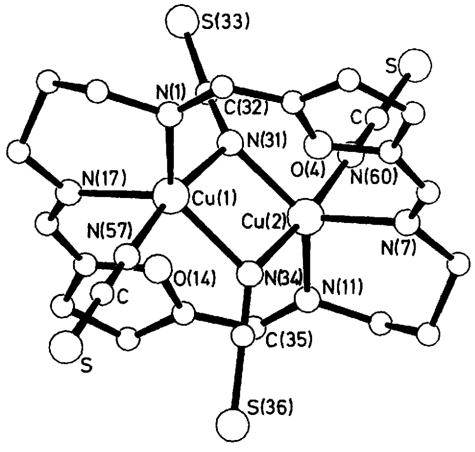


Figure 7. The structure of $[Cu_2L^1(NCS)_4]$, (**3j**), as predicted by molecular mechanics calculations

These results support the suggestion in ref. 15 that in a structure containing square-planar copper atoms, the bridge would be folded. Indeed the electronic spectrum of the $[Cu_2L^1(OMe)_2]^{2+}$ cation suggests a square-planar co-ordination geometry with –OMe bridges.[15] However all attempts to prepare crystals of this (or similar) cations have failed, often because the metal ions add solvent to become five-co-ordinate. Thus when we attempted to recrystallise $[Cu_2L^1(OMe)_2]^{2+}$ in methyl cyanide the five co-ordinate $[Cu_2L^1(OMe)_2(NCMe)_2]^{2+}$ was formed. Several crystal structures have been determined of such five-co-ordinate complexes. In all, the metal atoms have trigonal-bipyramidal environments with the bridge atoms in axial and equatorial sites. Figure 4 includes a plot of steric energy against Cu ··· Cu distance for $[Cu_2L^1(NCS)_4]$ (**3j**) in which both copper atoms have five-co-ordinate trigonal-bipyramidal environments. In this calculation θ_0 values were set at 90, 120, or 180° and k_b values for N–Cu–N set at 0.300 mdyn $Å^{-1}$ rad^{-2}. The minimum energy was 24.4 kcal mol^{-1}, significantly lower by *ca.* 10 kcal mol^{-1} than the values found for any of the other one-atom bridged structures [(**3a**)—(**3i**) inclusive]. This difference is mainly due to a decrease in bending strain at the copper atom and a smaller number of significant van der Waals 1,4 interactions (interactions between atoms connected by two other atoms). The Cu_2N_2 bridge remains planar with the furan rings parallel to the N_4 plane (Figure 7). The copper atoms are displaced on opposite sides of the N_4 plane. Four structures have been determined with this geometry, two with M = Co^{16} (mean Co ··· Co distance 3.16 Å) and two with M = $Cu^{II\,17,37}$ (mean Cu ··· Cu distance 2.98 Å). These M ··· M distances lie in the low-energy part of the curve and the steric energy is much less than for the comparable four-co-ordinate structures. In contrast to calculation (**3c**), for these structures, the M ··· M distances at minimum energy obtained from the molecular mechanics calculation agree well with the crystal structures and it therefore seems unlikely that any metal ··· metal interaction is present.

Binuclear Complexes with Two Two-atom bridges, (**4**).—Two calculations were carried out with the metal atoms in square-

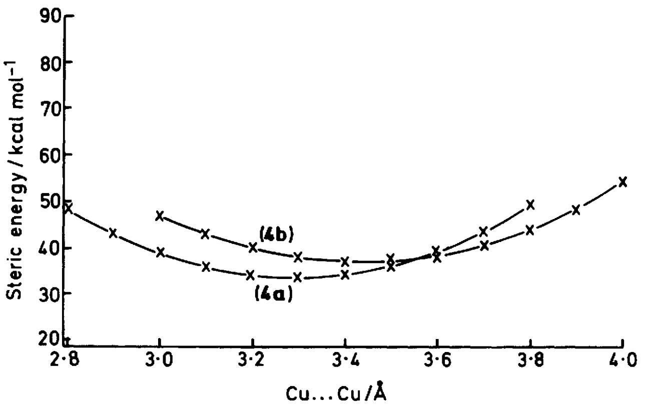


Figure 8. Plot of steric energy (kcal mol^{-1}) against Cu ··· Cu distance (Å) for $[Cu_2L(L\text{–}L)_2]^{2+}$ with L–L bidentate ligand: (**4a**) with Cu in a square-planar environment, (**4b**) with Cu in a tetrahedral environment

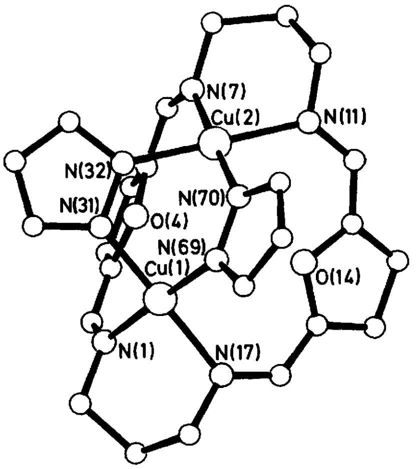


Figure 9. Structure of $[Cu_2L^1(pyz)_2]^{2+}$, (**4a**), as predicted by molecular mechanics calculations

planar, (**4a**), and tetrahedral, (**4b**), environments. Starting co-ordinates were taken from two crystal structures, namely $[Cu_2L^1(pz)_2]^{2+}$ (Hpz = pyrazole)[44] and $[Cu_2L^2(pydz)_2]^{2+}$ (pydz = pyridazine).[45] The same bridging ligands were used in the molecular mechanics calculations as in the crystal structures. The ligands were parameterised as unsaturated rings using Allinger's method.[35] This results in highly negative torsion angles terms; direct quantitative comparisons with other structures are therefore not possible. For the Cu–N–N angles in the ring, parameters were as follows; $\theta_0 = 120°$, $k_b = 0.30$ mdyn Å^{-1} rad^{-2} and the Cu–N–N–Cu torsion angle was set to be equivalent to the C–C=C–C torsion angle in the MM2 program but no other restrictions were placed on the bridge geometry.

Plots of steric energy against Cu ··· Cu distance are shown in Figure 8. The optimum geometry of the macrocycle occurs at a higher energy and a larger Cu ··· Cu distance in (**4a**), the complex with square-planar copper (36.9 kcal mol^{-1}, 3.45 Å) than in (**4b**), the complex with tetrahedral copper (33.4 kcal mol^{-1}, 3.30 Å). These Cu ··· Cu distances in the minimum-energy conformations can be compared to values found in the crystal structures of 3.20 and 3.39 Å respectively.

The two structures with the minimum energy exhibit quite different conformations of the macrocycle. In (**4a**) the copper atoms are both positioned on the same side of the N_4 plane and the macrocycle is folded (Figure 9). In (**4b**) the copper atoms are coplanar with the N_4 plane and the furan rings are almost parallel (Figure 10). These results agree with the arrangements in the crystal structures; in the pyrazolate structure[44] the furan rings intersect the N_4 plane at angles of 49.8 and 52.8° respectively and the copper atoms both lie on the same side of the N_4 plane, at distances of 1.06 and 1.09 Å respectively. In the pyridazine structure[45] both furan rings intersect the N_4 plane at an angle of 5.5°.

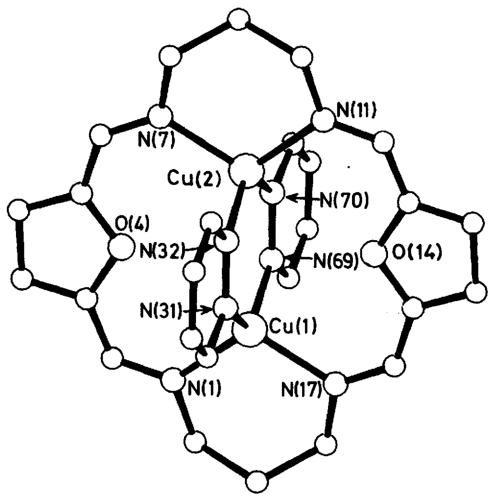
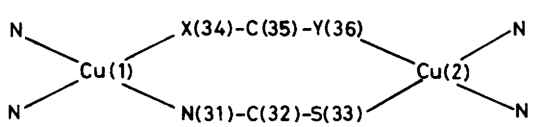


Figure 10. Structure of $[Cu_2L^1(pydz)_2]^{2+}$, (**4b**), as predicted by molecular mechanics calculations

The crystal structure of one related compound has been determined, *viz.* $[Cu_5L^2{}_2(dmt)_2]^{3+}$ (dmt = 3,5-dimethyl-1,2,4-triazolate anion) and shows only one two-atom bridge between two three-co-ordinate copper atoms.[20] The geometry of the macrocycle is similar (Table 1) to that observed in (**4a**) for square-planar copper(II). The dmt bridge is however bonded to a third copper atom and we have not carried out any calculations on this complicated and unique molecule.

Binuclear Complexes with Three-atom Bridges.—Four different calculations were carried out for two 1,3-thiocyanate ligands bridging two copper atoms in the macrocycle.



Tetrahedral copper: (**5a**) X = N, Y = S
(**5b**) X = S, Y = N
Square-planar copper: (**5c**) X = N, Y = S
(**5d**) X = S, Y = N

There are no known complexes of L^1 which contain two three-atom bridges but the structure of $[Cu_2L^1(PPh_2CH_2PPh_2)]^{2+}$ has been determined[38] in which the two copper atoms are bridged by one $-PPh_2-CH_2-PPh_2$ group and this is considered later as structure (**5e**). A search of the Cambridge Data Centre files[40] showed that di-μ-1,3-thiocyanate bridges are known, although more commonly for other transition metals than copper (only one Cu^I and one Cu^{II} example). All structures had the centrosymmetric arrangement with each metal bonded to both N and S. However a recent structure determination of a Pb–Mn complex in a 24-membered macrocycle has shown the lead atom to be bonded to both sulphur atoms and the

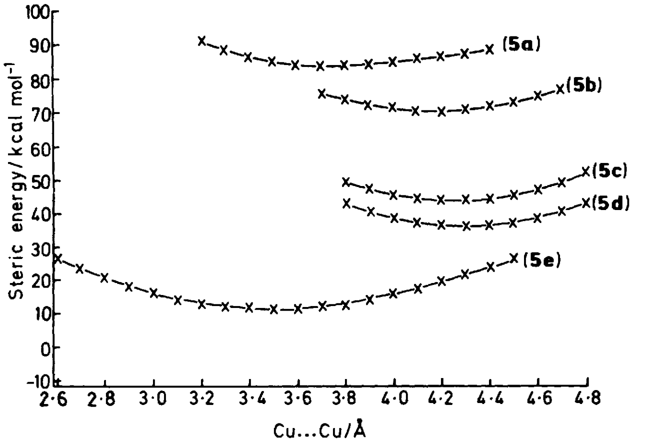


Figure 11. Plot of steric energy (kcal mol^{-1}) against Cu $\cdots$ Cu distance (Å) for [$Cu_2L^1(NCS)_2$] assuming two 1,3-dithiocyanate bridges between metal centres. Two copper atoms in a tetrahedral environment with: (**5a**) one copper bonded to N and N and the other to S and S, (**5b**) both bonded to N and S. Two copper atoms in square-planar environment with: (**5c**) one copper bonded to N and N and the other to S and S, (**5d**) both bonded to N and S. Two copper atoms in a trigonal environment in [$Cu_2L^1(PPh_2CH_2PPh_2)]^{2+}$, (**5e**), containing a single Cu–P–C–P–Cu bridge

manganese atom to both nitrogen atoms of a di-μ-1,3-thiocyanate bridge.[46] In this structure the M $\cdots$ M distance is only 4.72 Å, considerably less than the range 5.3—5.8 Å found in the centrosymmetric bridged-thiocyanate structures. In the two copper structures of di-μ-1,3-thiocyanate bridges, the Cu–S–C angles were *ca.* 95—100 and Cu–N–C angles 160° and these values were used for θ_0.

The eight-membered rings formed by the copper atoms and thiocyanate groups were approximately planar; deviations of the copper atoms from the $(NCS)_2$ plane were between 0.2 and 0.3 Å. However in the molecular mechanics calculations we were unable to introduce a satisfactory torsional energy term to include this planar restriction and so no constraint was applied. Initial co-ordinates were obtained by adjusting those of the two two-membered bridges in (**4**).

Plots of steric energy against Cu $\cdots$ Cu distance for the four different configurations are shown in Figure 11. The results for (**5a**) and (**5b**) are very different with minimum-energy conformations at Cu $\cdots$ Cu distances of 3.74 and 4.18 Å respectively. The calculations were then repeated with k_b set at 0.00 mdyn Å^{-1} rad^{-2} for angles subtended at the bridging nitrogen and sulphur atoms; but this gave similar minima positions. These results suggest that the difference in Cu $\cdots$ Cu distance for the minimum-energy conformation of (**5a**) and (**5b**) is significant and due to the different arrangements of the –NCS bridges.

As expected, the centrosymmetric arrangement (**5b**) is less strained than (**5a**) but both energies are far too high for these tetrahedral complexes to be sterically stable.

However the steric energies for the square-planar structures (**5c**) and (**5d**) are considerably less. As in the tetrahedral examples, the centrosymmetric bridging type is less strained [(**5d**) 35.8, (**5c**) 43.5 kcal mol^{-1}] although both structures show a minimum energy at a Cu $\cdots$ Cu distance of 4.30 Å. In (**5d**) the deviations of the copper atoms from the $(NCS)_2$ least-squares planes are at 1.32, 1.32 Å rather larger than those observed experimentally.[40]

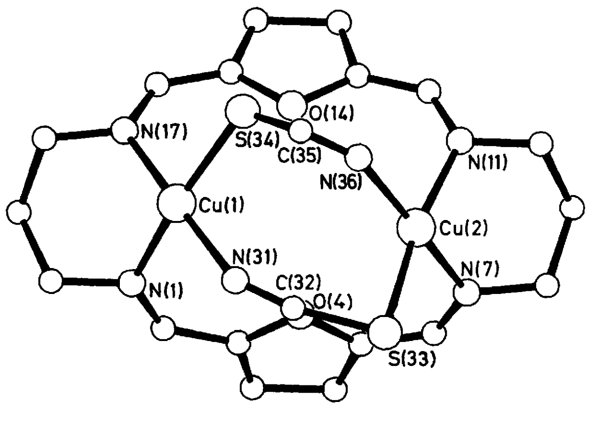


Figure 12. The structure of [$Cu_2L^1(NCS)_2]^{2+}$, (**5d**), as predicted by molecular mechanics calculations

In structures (**5c**) and (**5d**) the macrocycle is folded with both copper atoms lying on the same side of the N_4 plane. The conformation (Figure 12) is similar to that found in the other square-planar structures [(**3g**), (**3h**), (**3i**), and (**4a**)], although the Cu $\cdots$ Cu distance (4.30 Å) found for the minimum in (**5d**) is much shorter than the norm (5.3—5.8 Å[40]) for M $\cdots$ M distances in such bridged structures. This imposes considerable distortion upon the geometry of the copper co-ordination spheres. But the energy for (**5d**) is quite small, even at these larger Cu $\cdots$ Cu distances and it may be that such a compound would be sterically stable. It seems more likely that in complexes of L^1, the di-μ-1,1-thiocyanate bridge [(**3g**), (**3h**), or (**3i**)] would be preferred though its steric energy is only slightly less than for (**5d**). The tetrahedral binuclear complex can be ruled out, the steric energy being much higher than for the μ-1,1-thiocyanate bridges [(**3a**), (**3b**), or (**3c**)].

In the structure of [$Cu_2L^1(PPh_2CH_2PPh_2)]^{2+}$,[38] the Cu^I atoms have a distorted trigonal-planar environment, being strongly bonded to two nitrogen atoms (Cu–N 2.14, 2.21 Å) and one phosphorus atom (Cu–P 2.21 Å). In addition there are two weak Cu $\cdots$ O (furan) interactions at 2.62, 2.69 Å. These short distances are unique among structures of L^1. Results for this structure (**5e**) are also shown in Figure 11 though as we used Allinger's method[35] for the treatment of benzene rings, direct comparisons of energy with (**5a**)—(**5d**) are not possible. The resulting curve is very shallow, with variations in energy of < 1.0 kcal mol^{-1} for changes in r_0 over 0.5 Å, thus indicating that this arrangement of a three-atom bridge is very flexible. The conformation of the macrocycle at the minimum is similar to that of square-planar structures [(**3g**), (**3h**), (**3i**), (**5c**), and (**5d**)]. The Cu $\cdots$ Cu separation is 3.52 Å at the energy minimum compared to 3.27 Å in the crystal structure.

In these calculations, the atoms involved in the weak Cu $\cdots$ O interactions were not treated as bonded but as independent atoms. Naturally in the refinement the Cu $\cdots$ O distances increased markedly because of van der Waals repulsions. We then repeated the calculations with a k_s (Cu–O) value of 0.03 mdyn Å^{-1} obtaining an energy minimum at 3.35 Å, a value considerably closer to that observed in the crystal structure. This suggests that with a trigonal geometry where there is considerable space around the metal atom and L $\cdots$ L repulsions are small, the force constant for L–M–L angles should be lower than for higher co-ordination numbers. It is clear from this structure that the effect of the three-atom bridge with four bulky phenyl rings is to cause the macrocycle to fold to exclude a second bridging ligand.

Conclusions

We have demonstrated that molecular mechanics can be used to study complexes of the macrocycle L^1, in particular the binuclear copper complexes (with tetrahedral Cu^{I} or square planar Cu^{II}) which contain either one or two, one-, two-, or three-atom bridges and to predict which types of compound will be sterically stable.

This method as described above can be used to investigate the viability of various other macrocycles for acting as model compounds for Type 3 copper proteins, but can generally be applied to all sorts of complexes which contain two or more metals.

Acknowledgements

We are grateful to the late Professor S. M. Nelson for introducing us to the macrocycle L^1 and his interest and encouragement in this work. We also thank the S.E.R.C. for a studentship (to P. C. Y.).

References

1 J. E. Bulkowski, P. L. Burk, M-F. Ludman, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1977, 498.
2 P. L. Burk, J. A. Osborn, M-T. Youinou, Y. Agnus, R. Louis, and R. Weiss, *J. Am. Chem. Soc.*, 1977, **99**, 411.
3 R. R. Gagne, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, 1977, **99**, 7170.
4 M. G. Burnett, V. McKee, and S. M. Nelson, *J. Chem. Soc., Chem Commun.*, 1980, 829.
5 M. G. Simmons, C. L. Merrill, L. J. Wilson, L. A. Bottomley, and K. M. Kadish, *J. Chem. Soc., Dalton Trans.*, 1980, 1827.
6 K. D. Karlin, P. L. Dahlstrom, S. N. Cozette, P. M. Scensny, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1981, 881.
7 V. McKee, J. V. Kagdigian, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.*, 1981, **103**, 7000.
8 T. N. Sorrell, M. R. Malachowski, and D. L. Jameson, *Inorg. Chem.*, 1982, **21**, 3252.
9 H. M. Hendricks, P. J. M. W. L. Birker, J. van Rihn, G. C. Verschoor, and J. Reedijk, *J. Am. Chem. Soc.*, 1982, **104**, 3607.
10 Y. Nishida, N. Oisha, H. Kuramoto, and S. Kida, *Inorg. Chim. Acta*, 1982, **57**, 253.
11 K. Moore and G. S. Vigee, *Inorg. Chim. Acta*, 1982, **66**, 125.
12 E. I. Solomon, in 'Copper Coordination Chemistry, Biochemical and Inorganic Perspectives,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1983, p. 1.
13 E. I. Solomon, in 'Copper Proteins,' ed. T. G. Spiro, Wiley-Interscience, New York, 1981.
14 S. M. Nelson, J. Trocha-Grimshaw, A. Lavery, K. P. McKillop, and M. G. B. Drew, in 'Biological and Inorganic Copper Chemistry,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1985, p. 27.
15 M. G. B. Drew, S. M. Nelson, and F. S. Esho, *J. Chem. Soc., Chem. Commun.*, 1981, 388.
16 M. G. B. Drew, F. S. Esho, A. Lavery, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1984, 545.
17 S. M. Nelson, F. S. Esho, A. Lavery, and M. G. B. Drew, *J. Am. Chem. Soc.*, 1983, **105**, 5693.
18 M. G. B. Drew, F. S. Esho, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1983, 1653.
19 M. G. B. Drew, F. S. Escho, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 1347.
20 M. G. B. Drew, P. C. Yates, J. Trocha-Grimshaw, K. P. McKillop, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1985, 262.
21 M. G. B. Drew, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1679.
22 U. Burkert and N. Allinger, 'Molecular Mechanics,' A.C.S. Monograph, No. 177, American Chemical Society, Washington D.C., 1982.
23 J. F. Endicott, G. R. Brubaker, T. Ramasami, K. Kumar, K. Dwarakanath, J. Cassel, and D. Johnson, *Inorg. Chem.*, 1983, **22**, 3754.
24 V. J. Thom, C. C. Fox, J. C. A. Boeyens, and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 5947.
25 Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4029.
26 G. R. Brubaker and D. W. Johnson, *Coord. Chem. Rev.*, 1984, **54**, 1.
27 K. R. Adam, L. G. Brigden, K. Henrick, L. F. Lindoy, M. McPartlin, B. Mimnagh, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1985, 710.
28 A. M. Bond, T. W. Hambley, and M. R. Snow, *Inorg. Chem.*, 1985, **24**, 1920.
29 D. J. Brecknell, D. J. Raber, and D. M. Ferguson, *J. Mol. Struct.*, 1985, **124**, 343.
30 J. C. A. Boeyens, F. A. Cotton, and S. Han, *Inorg. Chem.*, 1985, **24**, 1750.
31 M. G. B. Drew, S. Hollis, and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1985, 1829.
32 M. G. B. Drew, D. A. Rice, S. bin Silong, and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1986, 1081.
33 M. G. B. Drew and D. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1986, 1543.
34 N. L. Allinger and Y. H. Yuh, MM2, Q.C.P.E. Program No. 423, Quantum Chemistry Program Exchange, Indiana University Chemistry Department, Indiana U.S.A. 1977, Modified version 1980.
35 N. L. Allinger, Q.C.P.E. Bulletin, Indiana University Chemistry Department, Indiana, 1983, vol. 3, no. 2, p. 32.
36 N. L. Allinger, *Adv. Phys. Org. Chem.*, 1976, **13**, 1.
37 M. G. B. Drew and S. M. Nelson, unpublished work.
38 P. C. Yates, Ph.D. Thesis, University of Reading, 1986.
39 S. M. Nelson, A. Lavery, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1986, 911.
40 Cambridge Crystallographic Data Centre files, 1986 update.
41 J. Comarmond, P. Plumere, J-M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, and I. Morgenstern-Badaran, *J. Am. Chem. Soc.*, 1982, **104**, 6330.
42 F. A. Cotton, A. Davidson, W. H. Ilsley, and H. S. Trop, *Inorg. Chem.*, 1979, **18**, 2719.
43 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, 1978, **17**, 2187 and refs. therein.
44 M. G. B. Drew, P. C. Yates, J. Trocha-Grimshaw, A. Lavery, K. P. McKillop, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, in the press.
45 M. G. B. Drew, P. C. Yates, F. S. Esho, J. Trocha-Grimshaw, A. Lavery, K. P. McKillop, S. M. Nelson, and J. Nelson, unpublished work.
46 J. Nelson, B. P. Murphy, M. G. B. Drew, P. C. Yates, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, in the press.

Received 29th December 1986; *Paper* 6/2482