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Crystallographic and Molecular Mechanics Study of the Copper Perchlorate Complex of a Larger Reinforced Macrocycle†

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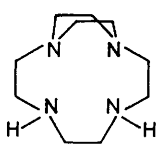
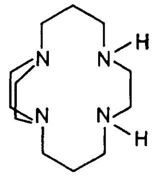
The crystal structure of the five-co-ordinate copper(II) complex of 7-methyl-7-nitro-1,5,9,13-tetra-azabicyclo[11.2.2]heptadecane, $[CuL^7(H_2O)][ClO_4]_2 \cdot H_2O$, has been determined. The blue crystals crystallised in the orthorhombic space group *Pbca* with $a = 14.625(4)$, $b = 19.083(2)$, and $c = 17.476(4)$ Å, $Z = 8$, and $R = 0.059$. The copper ion is co-ordinated to four macrocyclic nitrogen atoms with an average Cu–N distance of 2.05 Å, and a water molecule occupies an axial co-ordination site with Cu–O 2.22 Å. The conformation and chemical properties of the complex are discussed with the aid of molecular mechanics calculations.

Macrocycles structurally reinforced by inclusion of bridging alkyl groups between nitrogen atoms in the macrocyclic ring have recently been developed[1–6] (Ligands L^1—L^5). Interest in *reinforced* macrocycles has been aroused by realisation[7–9] that conventional tetra-aza-macrocycles are fairly flexible molecules, with selectivity for metal ions largely controlled by the same factors as open-chain ligands. Macrocyclic cavity size appears secondary to chelate-ring size in controlling selectivity for metal ions based on their size. Metal ions too big for the macrocyclic cavity are co-ordinated with the macrocycle buckling into conformations which allow out-of-plane co-ordination. Metal ions that do not fit the macrocyclic cavity are not necessarily disadvantaged by this, and 'size–match selectivity' is not observed. Reinforced macrocycles appear[3,4] to show size–match selectivity, since reinforcing prevents the buckling that allows out-of-plane co-ordination of the metal ion.


L^1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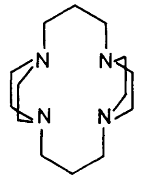
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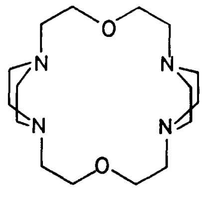
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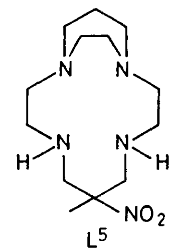
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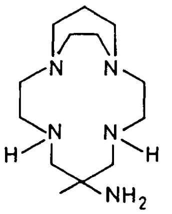
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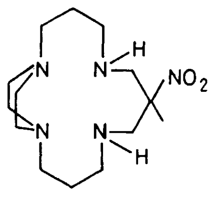
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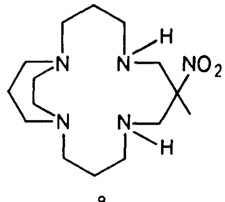
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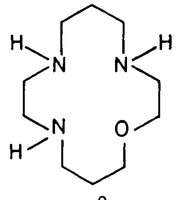
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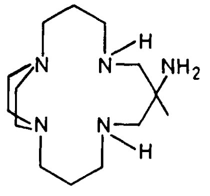
L^{10}

Reinforcing used so far has involved either piperazine[1–5] (ligands L^1—L^4) or homopiperazine[6] (L^5—L^6) bridges. These bridges effectively form double chelate rings, which have metal-ion size requirements like those of unbridged chelate rings but greatly sharpened. Simple geometric calculations on the piperazine ligand in its boat conformer show that the lone pairs on the nitrogens focus on a point such that a metal ion giving M–N bond lengths of 3.8 Å and N–M–N angles of 39° should fit best. This is in contrast to the unbridged five-membered chelate ring, where metal ions with a M–N bond length of 2.50 Å and a N–M–N of 69° fit best[9] (Scheme 1). No metal ion fulfils the bond-length or bond-angle requirements of piperazine, so that co-ordination of the piperazine bridge in reinforced macrocycles should be interesting. It has not proved possible to obtain crystal structures of complexes of ligands L^2—L^4, mainly because of disorder. The crystal structure[4] of the complex of low-spin Ni^{II} with L^1 contains a piperazine bridge, but the great mismatch in size between the metal ion and the macrocyclic cavity leads to considerable distortion of the complex, so that the observed co-ordination geometry involving the piperazine bridge may not be typical.

Sargeson and co-workers[10] have reported template syntheses of macrocycles involving condensation with formaldehyde and nitroethane. This simple route to macrocycles has already been used[6] for the synthesis of the bridged macrocycles L^5 and L^6, and is used here for the synthesis of L^7 (Scheme 2). Apart from its simplicity of synthesis the resulting complex has some useful aspects. The bulky nitro and alkyl groups appear[6] to inhibit disorder, and the nitro group is easily reduced to an amine which is a synthetically useful point of attachment, either of the complex to polymeric supports for use in catalysis or ion

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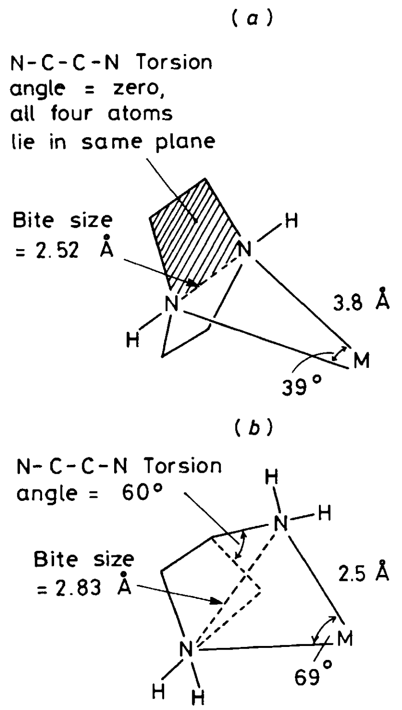
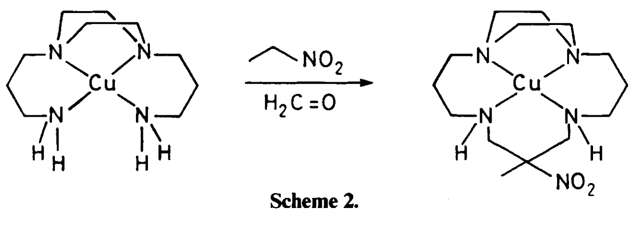
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.
Non-S.I. units employed: dyn = 10^{-5}N, cal = 4.184 J.



Scheme 1. Minimum strain geometries for (*a*) piperazine ring and (*b*) ethylenediamine ring



Scheme 2.

exchange, or of additional ligating groups such as pyridyl or imidazole for increasing the denticity of the ligand.

In this paper we report the synthesis of the complex $[CuL^7(H_2O)][ClO_4]_2 \cdot H_2O$, the determination of its crystal structure, and a molecular mechanics (m.m.) analysis of its structure and metal-ion size preferences.

Experimental

Synthesis of the Complex $[CuL^7(H_2O)][ClO_4]_2 \cdot H_2O$.—This is analogous to that of the capped cryptands described by Comba *et al.*[10] To $Cu(ClO_4)_2 \cdot 6H_2O$ (4.8 g) in methanol (50 cm^3) was added bis(aminopropyl)piperazine (Aldrich, 4.8 g) in methanol (100 cm^3), plus water (6 cm^3) to dissolve the reactant complex. The mixture was stirred and heated to reflux, and nitroethane (5 cm^3), then triethanolamine (5 cm^3), added dropwise. Formaldehyde (38%, 5 cm^3) in methanol (20 cm^3) was added dropwise over 2 h. The solution was allowed to cool for 12 h, when deep blue crystals formed. The crystals were collected by filtration, washed with ethanol, and recrystallised from hot water (4.02 g, 55% yield). U.v. (aqueous solution): $\lambda_{max.} = 574$ nm, $\varepsilon = 407$ dm^{-3} mol^{-1} cm^{-1}. I.r. (KBr pellet): 3 300—3 150 (br, O–H of H_2O); 1 550 and 1 360 cm^{-1} (ν_{asym} and ν_{sym} of NO_2 respectively) (Found: C, 28.50; H, 5.50; N, 11.65. Calc. for $C_{14}H_{33}Cl_2CuN_5O_{12}$: C, 28.10; H, 5.55; N, 11.70).

Crystallography.—The complex $[CuL^7(H_2O)][ClO_4]_2 \cdot H_2O$ was recrystallised from hot water to yield dark blue crystals. These were rather small, but repeated efforts to produce larger crystals were hampered by decomposition of the complex. The density was determined by flotation in dichloroethane and dibromoethane. A good diffraction-quality crystal was selected using standard oscillation and Weissenberg techniques. The data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Cell dimensions were obtained from least-squares refinement of 24 reflections ($16 < \theta < 17°$). Three standard reflections were monitored and showed a 2.9% variation over the data collection. Empirical absorption corrections[11] were made. The structure was solved and refined with Patterson and Fourier difference techniques using the SHELX 76 program.[12] All non-hydrogen atoms were refined anisotropically before the hydrogen atoms were located. The hydrogen atoms were refined with a common isotropic thermal parameter. Those hydrogen atoms that were not located on the Fourier difference map were placed. One perchlorate ion was disordered, and was refined as a disordered pair with a common chlorine atom. The crystal data are reported in Table 1, fractional atomic parameters in Table 2, and important bond lengths and angles in Table 3. The

Table 1. Crystal data for $[CuL^7(H_2O)][ClO_4]_2 \cdot H_2O$

Formula	$C_{14}H_{33}Cl_2CuN_5O_{12}$
M	597.87
Crystal colour	Blue
Crystal dimensions/mm	$0.13 \times 0.13 \times 0.21$
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
a/Å	14.625(4)
b/Å	19.083(2)
c/Å	17.476(4)
U/Å^3	4 877.36
Z	8
D_c/g cm^{-3}	1.63
D_m/g cm^{-3}	1.53
μ/cm^{-1}	1.17
λ(Mo-K_α)/cm^{-1}	0.710 73
F(000)	2 312
Scan mode	ω—2θ
Scan speed range/° min^{-1}	1.38—8.25
θ Range/°	$1 < \theta < 25$
Octants	$0 < h < 17, 0 < k < 20, 0 < l < 22$
Transmission factor range/%	90.55—99.28
Reflections measured	4 786
Unique reflections	3 258
Reflections used	1 926 [$F > 4\sigma(F_o)$]
Parameters refined	343
Final *R* factor	0.059
Maximum shift/e.s.d.	0.677
Residual density/e Å^{-3}	0.79, −0.47

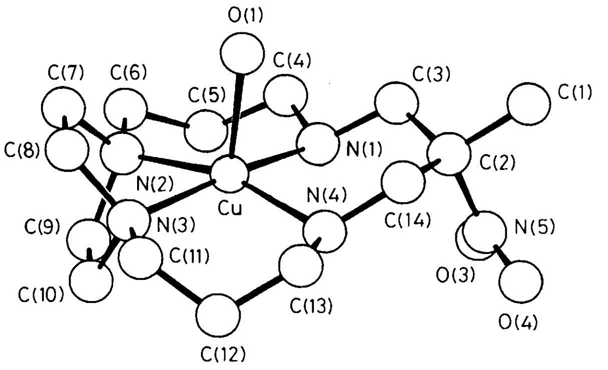


Figure 1. ORTEP[18] drawing of the cation $[CuL^7(H_2O)]^{2+}$, showing the numbering scheme

Table 2. Fractional co-ordinates (× 10^4) for $[CuL^7(H_2O)][ClO_4]_2 \cdot H_2O$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	2 540(1)	1 387(1)	750(1)
N(1)	3 049(5)	2 287(4)	1 232(4)
N(2)	3 760(6)	988(4)	397(5)
N(3)	2 246(6)	606(4)	−23(6)
N(4)	1 249(5)	1 800(5)	812(5)
N(5)	1 462(8)	3 318(6)	1 336(6)
O(1)	2 414(7)	820(4)	1 851(5)
O(2)	3 900(9)	928(7)	2 750(8)
O(3)	1 955(7)	3 804(6)	1 460(7)
O(4)	886(8)	3 318(5)	846(6)
C(1)	1 208(9)	2 907(7)	2 645(7)
C(2)	1 563(7)	2 674(6)	1 859(6)
C(3)	2 595(7)	2 523(5)	1 948(5)
C(4)	4 064(7)	2 308(7)	1 407(7)
C(5)	4 644(6)	2 047(6)	748(7)
C(6)	4 642(6)	1 251(6)	712(7)
C(7)	3 689(8)	221(5)	554(7)
C(8)	2 745(9)	−12(6)	290(8)
C(9)	2 755(8)	860(6)	−720(7)
C(10)	3 709(8)	1 080(6)	−455(6)
C(11)	1 284(9)	406(6)	−223(8)
C(12)	655(8)	1 037(7)	−256(7)
C(13)	485(7)	1 345(7)	524(7)
C(14)	980(7)	2 078(6)	1 567(7)
Cl(1)	576(3)	5 435(2)	7 369(2)
O(5)[a]	818(3)	6 101(2)	7 699(2)
O(6)[a]	−397(3)	5 411(2)	7 245(2)
O(7)[a]	1 044(3)	5 349(2)	6 651(2)
O(8)[a]	837(3)	4 882(2)	7 883(2)
O(9)[b]	−12(3)	5 447(2)	8 030(2)
O(10)[b]	196(3)	4 970(2)	6 803(2)
O(11)[b]	1 469(3)	5 191(2)	7 589(2)
O(12)[b]	645(3)	6 129(2)	7 056(2)
Cl(2)	2 276(2)	−1 921(1)	−747(1)
O(13)	2 850(2)	−2 492(1)	−504(1)
O(14)	2 822(2)	−1 404(1)	−1 135(1)
O(15)	1 583(2)	−2 181(1)	−1 259(1)
O(16)	1 847(2)	−1 607(1)	−89(1)

[a] Site occupancy 60.9%. [b] Site occupancy 29.1%.

Table 3. Bond lengths (Å) and angles (°) for $[CuL^7(H_2O)]^{2+}$

Cu–N(1)	2.053(8)	Cu–N(2)	2.036(8)
Cu–N(3)	2.055(9)	Cu–N(4)	2.048(8)
Cu–O(1)	2.215(9)	N(1)–C(3)	1.487(12)
N(1)–C(4)	1.516(12)	N(2)–C(6)	1.490(13)
N(2)–C(7)	1.491(13)	N(2)–C(10)	1.501(14)
N(3)–C(8)	1.49(2)	N(3)–C(9)	1.51(2)
N(3)–C(11)	1.50(2)	N(4)–C(13)	1.501(14)
N(4)–C(14)	1.48(2)	N(5)–O(3)	1.20(2)
N(5)–O(4)	1.20(2)	N(5)–C(2)	1.54(2)
C(1)–C(2)	1.53(2)	C(2)–C(3)	1.545(14)
C(2)–C(14)	1.51(2)	C(4)–C(5)	1.52(2)
C(5)–C(6)	1.52(2)	C(7)–C(8)	1.52(2)
C(9)–C(10)	1.53(2)	C(11)–C(12)	1.52(2)
C(12)–C(13)	1.51(2)		

N(1)–Cu–N(2)	96.8(3)	N(1)–Cu–N(3)	162.1(3)
N(2)–Cu–N(3)	73.3(3)	N(1)–Cu–N(4)	89.5(3)
N(2)–Cu–N(4)	165.4(4)	N(3)–Cu–N(4)	97.0(4)
N(1)–Cu–O(1)	94.7(3)	N(2)–Cu–O(1)	98.8(3)
N(3)–Cu–O(1)	101.5(3)	N(4)–Cu–O(1)	93.8(4)
Cu–N(1)–C(3)	115.9(6)	Cu–N(1)–C(4)	117.4(6)
C(3)–N(1)–C(4)	105.0(8)	Cu–N(2)–C(6)	121.4(6)
Cu–N(2)–C(7)	104.5(6)	C(6)–N(2)–C(7)	108.9(8)
Cu–N(2)–C(10)	102.3(6)	C(6)–N(2)–C(10)	111.7(8)
C(7)–N(2)–C(10)	107.1(8)	Cu–N(3)–C(8)	103.3(7)
Cu–N(3)–C(9)	101.3(6)	C(8)–N(3)–C(9)	108.0(9)
Cu–N(3)–C(11)	122.3(7)	C(8)–N(3)–C(11)	110.1(8)
C(9)–N(3)–C(11)	110.9(9)	Cu–N(4)–C(13)	116.4(7)
Cu–N(4)–C(14)	115.5(6)	C(13)–N(4)–C(14)	108.0(8)
O(3)–N(5)–O(4)	123.5(12)	O(3)–N(5)–C(2)	117.0(11)
O(4)–N(5)–C(2)	119.5(10)	N(5)–C(2)–C(1)	105.6(9)
N(5)–C(2)–C(3)	107.6(8)	C(1)–C(2)–C(3)	107.2(8)
N(5)–C(2)–C(14)	110.3(9)	C(1)–C(2)–C(14)	109.2(9)
C(3)–C(2)–C(14)	116.4(9)	N(1)–C(3)–C(2)	114.1(7)
N(1)–C(4)–C(5)	112.7(9)	C(4)–C(5)–C(6)	111.0(9)
N(2)–C(6)–C(5)	110.7(8)	N(2)–C(7)–C(8)	107.1(9)
N(3)–C(8)–C(7)	108.9(9)	N(3)–C(9)–C(10)	107.1(9)
N(2)–C(10)–C(9)	108.3(9)	N(3)–C(11)–C(12)	112.1(9)
C(11)–C(12)–C(13)	112.1(10)	N(4)–C(13)–C(12)	114.0(9)
N(4)–C(14)–C(2)	115.0(9)		

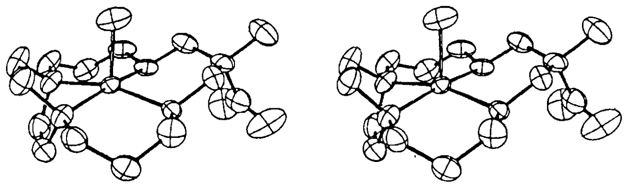


Figure 2. Stereoview[18] of the cation $[CuL^7(H_2O)]^{2+}$

numbering scheme is shown in Figure 1, and a stereoview of the complex in Figure 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Molecular Mechanics Calculations.—These were performed using the MOLBLD-3 M.M. program of Boyd *et al.*[13] The force-field parameters[14] for high-spin nickel(II) adequately described the square-pyramidal copper(II) ion, with some modifications. The unstrained M–N bond length for Cu^{II} was taken as 2.03 Å, as suggested[15,16] previously for tetragonally distorted Cu^{II}. A *trans* N–Cu–N bond angle constraint was included, with an unstrained angle of 180°, and a force constant of 0.1 mdyn Å rad^{-1}. The force field appropriate to the organic part of the complex was as used previously.[14] This adequately reproduces the structures of $[CuL^7(H_2O)]^{2+}$ and of the previously reported[8] $[CuL^9(Br)]^{2+}$, both containing square-pyramidal Cu^{II}. Trial structures for the force-field program were either derived from crystallographic co-ordinates or generated by the molecular modelling program ALCHEMY (Tripos Associates, St. Louis, Missouri).

Results and Discussion

Work on the nickel(II) complex of L^6 has shown it to be highly resistant to demetallation, surviving refluxing in cyanide or sulphide solutions for a week. It seems this inertness is kinetic, and derives from the inability of the ligand to fold into the types of intermediates postulated[17] for the demetallation reactions of

Table 4. Observed and calculated bond lengths (Å) and angles (°) in $[CuL^7(H_2O)]^{2+}$, from molecular mechanics and crystallography (this work)

	Calc.	Obs.		Calc.	Obs.
Cu–N(1)	2.083	2.053	Cu–N(4)	2.083	2.048
Cu–N(2)	2.068	2.036	Cu–O(1)	2.224	2.215
Cu–N(3)	2.068	2.055			
N(1)–Cu–N(2)	96.4	96.8	N(1)–C(3)–C(2)	113.5	114.1
N(1)–Cu–N(4)	91.4	89.5	N(1)–C(4)–C(5)	112.8	112.7
N(2)–Cu–N(3)	73.9	73.3	N(2)–C(6)–C(5)	112.4	110.7
N(3)–Cu–N(4)	96.4	97.0	N(2)–C(7)–C(8)	108.5	107.1
N(1)–Cu–N(3)	166.5	162.1	N(2)–C(10)–C(9)	108.3	108.3
N(2)–Cu–N(4)	166.5	165.4	N(3)–C(8)–C(7)	108.5	108.9
N(1)–Cu–O(1)	92.7	94.7	N(3)–C(9)–C(10)	108.3	107.1
N(2)–Cu–O(1)	97.6	98.8	N(3)–C(11)–C(12)	112.4	112.1
N(3)–Cu–O(1)	97.6	101.5	N(4)–C(13)–C(12)	112.8	114.0
N(4)–Cu–O(1)	92.8	93.8	N(4)–C(14)–C(2)	113.5	115.0
Cu–N(1)–C(3)	114.6	115.9	N(5)–C(2)–C(1)	108.1	105.6
Cu–N(1)–C(4)	116.6	117.4	N(5)–C(2)–C(3)	110.9	107.6
Cu–N(2)–C(6)	122.8	121.4	N(5)–C(2)–C(14)	110.9	110.3
Cu–N(2)–C(7)	105.7	104.5	C(3)–N(1)–C(4)	108.0	105.0
Cu–N(2)–C(10)	97.0	102.3	C(6)–N(2)–C(7)	109.7	108.9
Cu–N(3)–C(8)	105.7	103.3	C(6)–N(2)–C(10)	111.5	111.7
Cu–N(3)–C(9)	97.0	101.3	C(7)–N(2)–C(10)	108.8	107.1
Cu–N(3)–C(11)	122.8	122.3	C(8)–N(3)–C(9)	108.8	108.0
Cu–N(4)–C(13)	116.6	116.4			
Cu–N(4)–C(14)	114.6	115.5			

unbridged tetra-aza-macrocycles. On the other hand the complexes of L^1 are only slightly more kinetically inert than their unbridged analogues. The $[NiL^1]^{2+}$ complex is highly strained, and the metal ion extruded some 0.2 Å from the plane of the nitrogen donors. The complex $[CuL^7]^{2+}$ is readily demetallated by cyanide or sulphide, and reduction with hydrogen in an autoclave produces copper metal plus the reduced ligand. In contrast the copper complexes of L^8 are much more difficult to demetallate, and the copper is not reduced to metal in an autoclave under hydrogen.

The Structure of $[CuL^7(H_2O)][ClO_4]_2\cdot H_2O$.—A stereoview of the complex cation is seen in Figure 2.[18] The Cu^{II} is co-ordinated to the four macrocyclic nitrogen atoms, with an average Cu–N distance of 2.05 Å. A water molecule occupies the axial co-ordination site with a Cu–O bond length of 2.22 Å. The Cu^{II} lies 0.25 Å above the plane of the donor nitrogens. The N–Cu–N *trans* angles are almost equal, averaging 164°, and the N–Cu–N angle subtending the piperazine bridge is 73°. The N–Cu–N angles adjacent to the piperazine bridge are 97°, and that involving the chelate ring containing the nitro-group is 90°. The co-ordination geometry around the metal is thus a distorted square pyramid. The metal complex crystallises as a dihydrate. The water molecule co-ordinated directly to the metal is hydrogen-bonded to the non-co-ordinated water molecule, and to a disordered perchlorate ion. The non-co-ordinated water molecule is hydrogen-bonded to two oxygen atoms of a symmetry-related disordered perchlorate. The perchlorate anion that is not hydrogen-bonded does not appear to be disordered.

The most striking feature of the complex is the small N–Cu–N angle of 73° involving the nitrogens of the piperazine bridge. This small angle is related to the small 'bite' (2.52 Å) of piperazine, and its requirement of a metal ion with a M–N bond length of 3.8 Å and N–M–N angle of 39°. An interesting feature of the structures of $[NiL^1]^{2+}$ and $[CuL^7(H_2O)]^{2+}$ is that the bite size of the piperazine is compressed down from a strain-free value of 2.52 Å to values of 2.40 and 2.45 Å respectively. This effect is reproduced in the m.m. calculations on both complexes. It seems that compression of the bite of the piperazine bridge is brought about so as to focus the lone pairs on the nitrogens on a point allowing for more overlap with the orbitals on the metal ion. In $[CuL^9(Br)]^+$ the copper also lies out of the plane of the donor atoms, which appears to be related to the cavity of the ligand being too small for Cu^{II}. The cavity of L^7 is actually too large for Cu^{II}, so that extrusion of the metal ion from the cavity may relate to the need for longer Cu–N bonds so as to satisfy the needs of the piperazine bridge.

The six-membered chelate rings of $[CuL^7(H_2O)]^{2+}$ are all in the lower-energy chair form. In the crystal structure the nitro-group is axially placed on a six-membered chelate ring, whereas the geminal methyl group is substituted equatorially. This is surprising since the nitro-group is composed of larger atoms and might be expected to be in the equatorial position. The explanation is unlikely to lie in interactions with the co-ordinated water molecule since it lies too far away.

Molecular Mechanics Calculations.—Reproduction of the structure of $[CuL^7(H_2O)]^{2+}$ by the m.m. calculations is seen in Table 4 to be satisfactory. The calculated N–Cu–N angles deviate from those in the crystal structure by at most 2°. As reported in the Experimental section, the copper(II)–nitrogen force constants were adapted from those pertaining to Ni^{II}. The copper(II)–oxygen bond force constant was left at 0.68×10^{-5} dyn cm^{-1}. At the distance that the oxygen is from the Cu^{II}, steric forces on it are negligible, so that the Cu^{II}–O bond remains at the unstrained length of 2.22 Å. This lack of steric hindrance to axial co-ordination probably explains the apparent ready co-ordination of chloride ion to give a green complex. The important feature of the complex is the N–Cu–N angle are only 73.3° involving the piperazine bridge, with the m.m. calculations predicting an angle of 73.9°.

The N–H hydrogens in the crystal structure are on the opposite side of the plane of the ligand as the co-ordinated water molecule. The m.m. minimised conformer with N–H hydrogen atoms on the same face as the co-ordinated water molecule is shown as **(B)** in Figure 3. In order for the six-membered chelate ring involving the co-ordinated secondary amine groups to retain its energetically low 'chair' conformation, the hydrogen atoms on the methylene groups have to come quite close to the

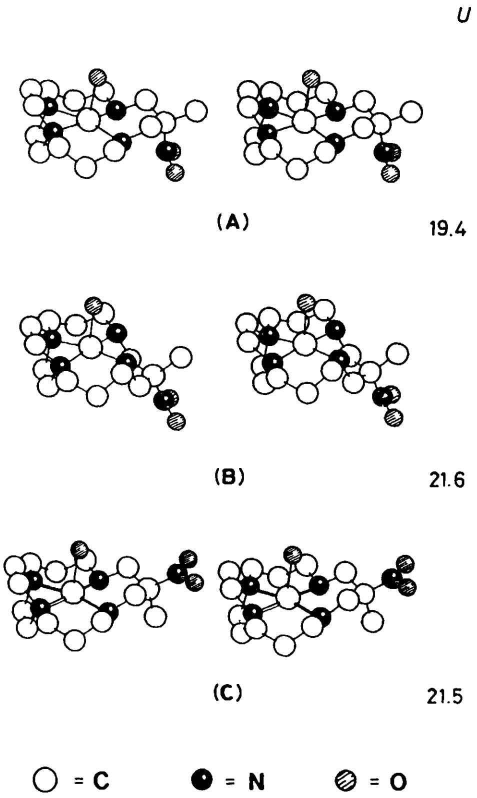


Figure 3. Stereoviews of the conformers generated by m.m. calculation for the cation $[CuL^7(H_2O)]^{2+}$. Conformer (**A**) is that of the crystallographic structure determined in this work, (**B**) is that with the water placed on the same side of the macrocyclic ring as the N–H hydrogens, and (**C**) is that with the position of the nitro- and methyl groups exchanged. The numbers shown for each conformer are the total strain energies in kcal mol^{-1}. Drawings executed by the program ALCHEMY

hydrogen atoms on the central carbons of adjacent propylene groups. The strain energy of this conformer was calculated to be 21.6 kcal mol^{-1}, 2.2 kcal mol^{-1} higher than in the observed structure, conformer (**A**) in Figure 3.

Why the NO_2 group occupies an axial rather than an equatorial site is indicated by m.m. calculations on the conformer (**C**) in Figure 3. The conformation of the macrocycle itself was kept as for the observed structure, but the methyl and nitro groups on the six-membered chelate ring opposite the piperazine bridge were exchanged. The strain energy of this conformer was calculated to be 21.5 kcal mol^{-1}, 2.1 kcal mol^{-1} higher than the observed structure. As Figure 3 shows, although the nitro-group is composed of larger atoms than the methyl group, the tetrahedral methyl group presents more steric bulk for interaction with the amine hydrogens than does the planar nitro-group, thus causing the axial nitro-group to be the observed minimum-energy configuration.

The presence of the nitro- and methyl groups on the chelate ring formed using the method of Sargeson and co-workers[10] leads according to the m.m. calculations to considerable steric crowding, and this may mean that the method will not work for synthesising macrocycles where there is larger steric bulk present. We are currently working on reducing the nitro-group on L^7 to obtain the reduced complex, from which the free ligand L^{10} can be obtained, which should allow for a study of the thermodynamics of complex formation of L^{10} with a variety of metal ions so as to determine how structural reinforcement has affected selectivity patterns.

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