Structural Reinforcement of a Large Macrocyclic Ligand. A Structural, Molecular Mechanics, and Thermodynamic Study†

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The complex of the macrocycles L^5 (1,10-dioxa-4,7,13,16-tetra-azacyclo-octadecane), L^6 (4,13-dioxa-1,7,10,16-tetra-azabicyclo[14.2.2]eicosane) and L^7 (4,13-dioxa-1,7,10,16-tetra-azatricyclo[14.2.2.2^{7,10}]docosane) have been synthesized and their complex formation constants determined with Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}; the ions Sr^{2+} and Ba^{2+} were found not to complex with the ligands. The successive insertion of ethylene bridges into the 1,4-diaminoethane units in L^5 enhances the selectivity of the ligand for large metal ions, with L^7 binding only to Pb^{2+}. The selectivity of these ligands and the depression of the formation constants with all metal ions upon successive insertion of the ethylene bridges are rationalised with the aid of molecular mechanics calculations. The crystal structure of the free ligand of L^7 has been determined: space group $P2_1/n$, monoclinic, with $a = 6.053(2)$, $b = 14.190(8)$, $c = 10.346(6)$ Å and $\beta = 106.82(4)°$, and $Z = 2$. The final conventional R factor was 0.0627.

In past papers[1] we have discussed the design of ligands that should be selective for the lead(II) ion, for use in treatment of lead intoxication. The main objective in such ligand design is to achieve high selectively for this large ion (radius, $r^+ = 1.18$ Å in octahedral co-ordination[2]) over the small Zn^{II} ($r^+ = 0.74$ Å). Currently used chelating agents such as edta or 2,3-dimercaptopropanol show only poor selectivity for Pb^{II}.[3] Lehn and Montavon[4] have suggested several macrobicyclic ligands which show excellent selectivity for Pb^{2+} over Zn^{2+}, but no further reports on their utilisation have appeared.

The fact of the large difference in r^+ between Pb^{II} and Zn^{II} seems to suggest the use of macrocycles, with their size-match selectivity, to discriminate between the two metal ions. Size-match selectivity means here that a macrocycle with a large cavity such as L^5 should show a strong preference for the large Pb^{II}, which more nearly matches the size of the cavity. However, past studies[5,6] have shown that macrocycles are not nearly as rigid as might be imagined, and that factors other than size-match selectivity, such as the size of the chelate ring,[7] are more important in controlling metal-ion selectivity. Structural studies[8] have shown that a macrocycle such as L^3 co-ordinates well[9] to small metal ions such as Ni^{II} because the ligand is able to fold so as to co-ordinate to the small metal ion in an octahedral fashion.

What is required to sharpen up the size selectivity of macrocyclic ligands is structural reinforcement to prevent the folding which allows co-ordination to small metal ions. More structurally rigid ligands[10] such as L^2 have recently been examined[11] for their co-ordinating properties, and found to have much sharper selectivity for metal ions which fit their cavities than is found for non-reinforced ligands such as L^1. In this paper the reinforcement of the ligand L^5 to give L^6 and L^7 is reported. The stability constants of the complexes of L^6 and L^7 with Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Pb^{II} are reported. Metal ions such as Sr^{II} and Ba^{II} were also investigated for their complexing properties with these ligands, but were found to bind very weakly, if at all, which would appear to relate to their low affinity for the nitrogen donor atom. It became apparent that reinforced ligands such as L^7 complexed fairly weakly with metal ions, possibly due to the energy required to change the ligand from its presumed lower-energy chair–chair conformer, with both piperazine rings in the chair form, to the boat–boat conformer. To investigate this possibility, an X-ray crystallographic study was carried out on the free ligand L^7, and molecular mechanics calculations were carried out on the conformers of the free ligand. To examine the effect of metal-ion size on the strain energy of ligands of the L^5 type as ethylene bridges were added to provide reinforcement, molecular mechanics calculations were carried out on the complexes of Zn^{II} and Pb^{II} with L^5 to L^7.

Experimental

Materials.—The metal-ion solutions used in the formation constant study were made up from the AR nitrate salts and standardised by the usual procedures.

Ligand Synthesis.—Preparation of L^5. The reported[12] synthesis of L^5 yielded no product. The synthesis was modified and is detailed below.

N,N'-Ditosylethylenediamine was synthesized according to the method of Fabbrizzi.[13] A solution of *N,N'*-ditosylethylenediamine (63.5 g, 172 mmol), bis(2-chloroethyl) ether (22.7 cm^3, 193 mmol), and K_2CO_3 (34.3 g) in dimethylformamide (350 cm^3) was refluxed at 170 °C for 5 h, and allowed to cool over 12 h. A large quantity of water was added to the reaction mixture while stirring slowly (the addition of the reaction mixture to water produces an unworkable suspension of product). A white solid precipitated, accompanied by pale yellow lumps, the latter yielding a white solid after grinding under water. If the lumps were too gummy to grind, they were dissolved in boiling methanol, and reprecipitated by the addition of water. The product was filtered off, washed with water, and dried under reduced pressure (2 mmHg, ≈266 Pa). Yield (75.5 g, 86 mmol, 100%). N.m.r.($CDCl_3$): 2.37 (s, aryl CH_3, 12 H), 3.10—3.53 (m, CH_2N, 24 H), 3.77—4.07 (m, CH_2O, 8 H), and 7.50 (q, aryl H, 16 H).

The tetratosylate (150.9 g, 172 mmol) was slurried in acetic acid (1.0 l) and 48% HBr (1.5 l), and refluxed for 60 h, during which all the solid dissolved and the solution turned orange. The reaction mixture was evaporated to *ca.* 10% of its original

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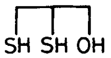
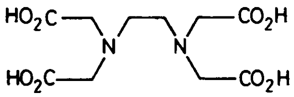
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: cal = 4.184 J.

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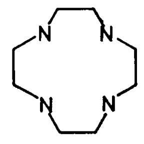
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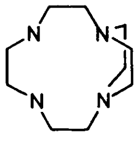
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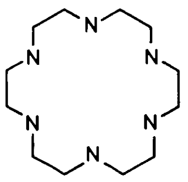
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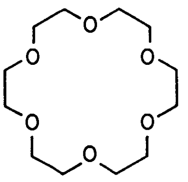
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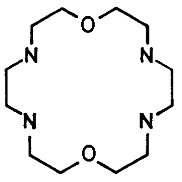
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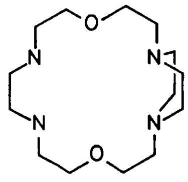
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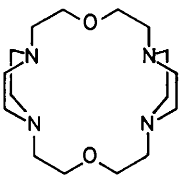
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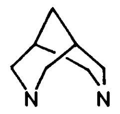
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volume. Half of that volume of ethanol was added, the solution allowed to cool, and diethyl ether added while stirring until a separate layer of ether was visible. The mixture stood for 12 h, after which the crystalline precipitate was filtered off. If the precipitate was mixed with an oil it was recrystallised from 48% HBr, producing fine, white crystals. The filtrate was dried to give 11.4 g product (19.5 mmol, 11% yield) (Found: C, 24.15; H, 5.50; N, 9.05. Calc. for $C_{12}H_{28}N_4O_2 \cdot 4HBr$: C, 24.70; H, 5.50; N, 9.60%).

The hydrobromide (11.4 g, 19.5 mmol) was dissolved in water (20 cm^3) and passed through a column containing Amberlite IRA 401 resin in the hydroxide form. The solvent was removed under reduced pressure and the resulting solid recrystallised from heptane to yield white, needle-shaped crystals (4.5 g, 17.3 mmol, 88%). Alternatively the hydrobromide was dissolved in water (20 cm^3), and sufficient NaOH (10 mol dm^{-3}) solution added to precipitate a white salt. The free base was extracted from the mixture with chloroform (4 × 50 cm^3), dehydrated (anhydrous $MgSO_4$), dried under reduced pressure, and recrystallised from heptane to yield needle-shaped crystals (2.0 g, 7.8 mmol, 40%). The best overall yield was 10%. Microanalysis and titration of a 0.01 mol dm^{-3} solution of the product with 0.05 mol dm^{-3} HNO_3 suggested that the crystals were a dihydrate of L^5.

Preparation of L^7. The ligand L^5 (0.385 g, 1.479 mmol) and 1,2-dibromoethane (1.251 g, 6.656 mmol) were refluxed in ethanol (15 cm^3) for 2 d, after which potassium carbonate (0.818 g, 5.916 mmol) was added. After refluxing for 1 d the solvent and excess of reactant were removed under reduced pressure. T.l.c. R_F 0.42, 0.29, and 0.09 (trimethylamine–methanol, 1:20). The product was recrystallised from ethyl acetate to yield yellow rods (54 mg, 0.173 mmol, 12% yield). N.m.r.($CDCl_3$): 2.43—2.93 (m, CH_2N, 24 H) and 3.43—3.70 (m, CH_2O, 8 H) (Found: C, 61.20; H, 10.55; N, 17.70. Calc. for $C_{16}H_{32}N_4O_2$: C, 61.50; H, 10.30; N, 17.95%).

Preparation of L^6. This was identical to that above except that the L^6 was largely removed by crystallisation from ethyl acetate, and the products in the mother-liquor were separated by chromatography on silica, with gradient elution from 2 to 20% isopropylamine in $CHCl_3$. The solvent was removed under reduced pressure to reveal a white, hygroscopic solid in 15% yield. N.m.r.($CDCl_3$): 1.95 (s, HN, 2 H), 2.43—2.93 (m, CH_2N, 20 H), and 3.43—3.70 (m, CH_2O, 8 H) (Found: C, 59.05; H, 10.20; N, 19.30. Calc. for $C_{14}H_{30}N_4O_2$: C, 58.70; H, 10.55; N, 19.55%).

Potentiometric Studies.—The formation constant studies were all conducted using glass-electrode potentiometry as described previously.[14] The potentiometric titration data were all refined using the programs EQUILIBRIA[15] or MINIQUAD.[16] The formation and protonation constants determined are in Table 4.

Crystallography.—The compound L^7 was recrystallised from ethyl acetate to yield pale yellow rods. The density was determined by flotation in benzene and 1,2-dichloroethane. A good diffraction-quality crystal was selected using standard oscillation and Weissenberg techniques. The data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. The cell dimensions were obtained from least-squares refinement of 25 reflections ($16 < \theta < 20$). Three standard reflections were monitored and showed a 0.6% variation over the data collection. Lorentz polarisation and absorption corrections (based on θ scan of nine reflections) were made. The structure was solved and refined with Patterson and Fourier difference techniques using the SHELX program.[17] Least squares weights were defined by $w = k/\sigma^2$. All non-hydrogen atoms of the molecule were refined anisotropically before the hydrogen atoms were located. The crystal data are given in Table 1, fractional atomic co-ordinates in Table 2, and important bond lengths and angles in Table 3. The numbering scheme is shown in Figure 1.

Table 1. Crystal data for L^7

Formula	$C_{16}H_{32}N_4O_2$
M	312.46
Crystal colour	Light yellow
Crystal dimensions	0.60 × 0.50 × 0.40 mm
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	6.053(2)
b/Å	14.190(8)
c/Å	10.346(6)
β/°	106.82(4)
U/Å^3	850.5
Z	2
D_c/g cm^{-3}	1.220
D_m/g cm^{-3}	1.218
T/K	298
μ/cm^{-1}	0.70
λ(Mo-K_α)/Å	0.710 73
F(000)	344.00
Scan mode	ω
Scan speed range (° min^{-1})	0.9—5.50
θ Range/°	$2 < \theta < 30$
Octants	$-8 < h < 8, 0 < k < 20, 0 < l < 14$
Transmission factor range/%	91.5—100
Reflections measured	2 704
Unique reflections	2 186
Reflections used ($F > 4\sigma F$)	1 659
Parameters refined	149
R'	0.0676
R	0.0627
Maximum shift/e.s.d.	0.0062
Residual density (max., min.)/e Å^3	0.27, 0.35

Table 2. Fractional co-ordinates (× 10^4) for L^7

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
O(1)	1 104(4)	9 604(2)	7 029(2)
N(1)	1 043(4)	8 604(2)	9 443(3)
N(2)	1 949(4)	8 860(2)	2 283(3)
C(1)	1 944(7)	8 659(3)	−2 753(4)
C(2)	1 011(7)	8 094(2)	−1 779(4)
C(3)	3 369(5)	8 789(3)	311(4)
C(4)	3 308(6)	9 350(3)	1 531(3)
C(5)	−387(5)	8 692(3)	1 401(3)
C(6)	−273(6)	8 104(2)	207(4)
C(7)	2 044(7)	9 300(3)	3 571(3)
C(8)	−1 324(6)	9 673(3)	−3 570(4)

Table 3. Bond lengths (Å) and angles (°) for L^7

O(1)–C(1)	1.429(4)	O(1)–C(8)	1.423(4)
N(1)–C(2)	1.451(4)	N(1)–C(3)	1.458(4)
N(1)–C(6)	1.459(4)	N(2)–C(4)	1.460(4)
N(2)–C(5)	1.463(4)	N(2)–C(7)	1.458(4)
C(1)–C(2)	1.518(5)	C(3)–C(4)	1.502(5)
C(5)–C(6)	1.508(4)		
C(1)–O(1)–C(8)	114.1(3)	C(2)–N(1)–C(3)	113.2(3)
C(2)–N(1)–C(6)	111.0(2)	C(3)–N(1)–C(6)	109.6(3)
C(4)–N(2)–C(5)	109.7(3)	C(4)–N(2)–C(7)	113.8(3)
C(5)–N(2)–C(7)	114.5(3)	O(1)–C(1)–C(2)	114.6(3)
N(1)–C(2)–C(1)	113.7(3)	N(1)–C(3)–C(4)	111.1(3)
N(2)–C(4)–C(3)	110.5(3)	N(2)–C(5)–C(6)	109.6(3)
N(1)–C(6)–C(5)	109.7(3)		

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

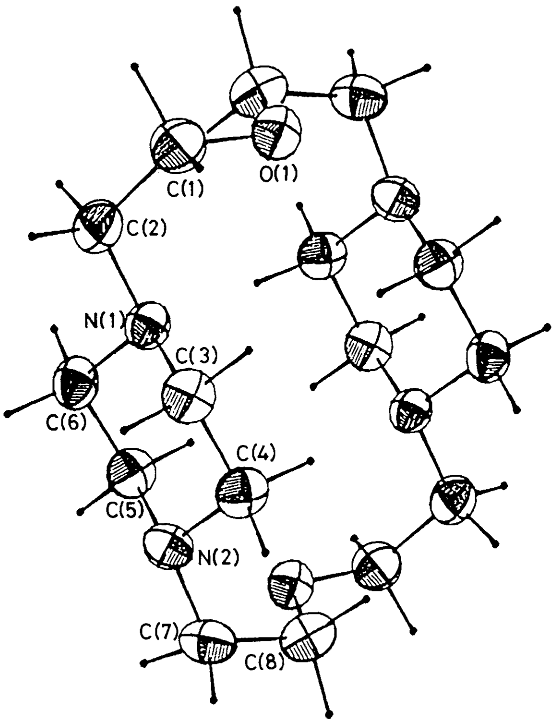

Figure 1. Crystal structure of L^7 showing the atom numbering scheme

Molecular Mechanics Calculations.—The program used for the molecular mechanics calculations was MOLBLD-3 due to Boyd *et al.*,[18] which was locally modified to reproduce the united-atom force field AMBER,[19] which was used in all the calculations. To test the validity of the modification, the results reported by Wipff *et al.*[20] on alkali-metal-ion complexes of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane) were successfully reproduced. Where crystallographic co-ordinates were not available, the structures were generated by ALCHEMY (Tripos Inc.). Ether torsion parameters were taken from ref. 20, as were non-bonded parameters for K^+. Non-bonded parameters appropriate to C, N, O, and Zn^{2+} were taken from Vedani and Dunitz,[21] the latter requiring further modification. The dielectric constant was taken to be unity in all calculations, as done by Wipff *et al.*[20] The partial charges on oxygen were taken to be −0.6, as used by Wipff *et al.*[20] The partial charges on nitrogen were taken to be the same as on oxygen. The cut-off distance for non-bonded interactions was set to 7 Å, and the refinements were all terminated when the root-mean-square (r.m.s.) shifts in co-ordinates were less than 0.2 Å.

Non-bonded parameters for Zn^{2+} have been reported by Vedani and Dunitz.[21] When these parameters were used in calculations on substituted 18-membered azacrown ethers[22] the Zn–O and Zn–N bond lengths were consistently calculated to be about 1.7 Å, shorter than the normal van der Waals distances of 2.0 Å.[21] A similar result was obtained by Vedani and Dunitz in their calculations on human carbonic anhydrase, and they overcame the problem by using a strongly distance-dependent dielectric constant ($=4r$), which has the effect of quenching the electrostatic component of the force field. Since the dielectric constant in this work is taken to be equal to 1, this approach could not be used and the effective ionic radius of Zn^{2+} in the Slater-Kirkwood equations[23] was simply increased to 1.4 Å, when more reasonable bonding distances were observed.

The non-bonded parameters for Pb^{2+} were taken to be identical to those developed[20] for K^+, and were found to

Table 4. Protonation and complex formation constants (log K_1) of ligands discussed*

Ligand	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Sr^{2+}	Ba^{2+}
L^5	9.36(2)	8.40(2)	6.27(2)	5.25(2)	16.27(1)	12.25(1)	10.51(1)	10.90(1)	9.01(1)	<2	<2
L^6	8.63(1)	6.73(1)	3.20(1)	1.33(1)	7.04(1)	<2	<2	4.79(1)	5.36(3)	<2	<2
L^7	8.57(2)	7.63(2)	2.65(2)	2.08(2)	<2	<2	<2	<2	4.73(1)	—	—

* At 25 °C in 0.1 mol dm^{-3} $NaNO_3$ in water.

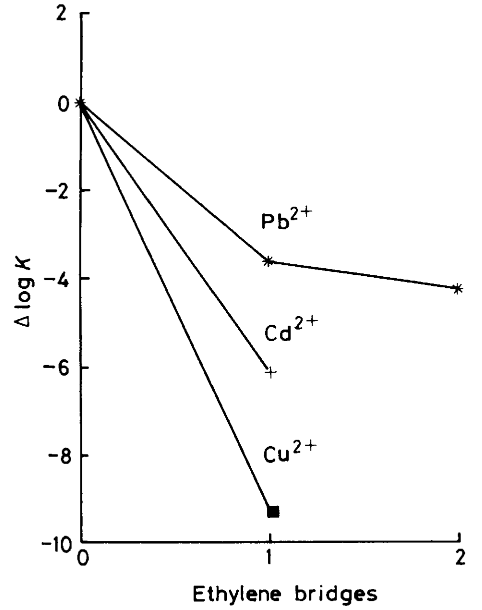

Figure 2. Variation in stability of metal complexes relative to L^5 as a function of added ethylene bridges

Table 5. Strain energy of the zinc(II) and lead(II) complexes of some sexidentate macrocycles as a function of the number of double bridges between donor atoms

	Total calculated energy of hydrated complexes (kcal mol^{-1})		
Metal	L^5	L^6	L^7
Zn^{2+}	−230.9	−166.6	−89.0
Pb^{2+}	−170.6	−148.6	−125.9

reproduce tolerably the structure of $[PbL^5][SCN]_2$ reported by Metz and Weiss.[24] The trial co-ordinates for L^5 with Pb^{2+} were taken from the structure of $[KL^4]^+$ [25] with two axial H_2O molecules added using ALCHEMY. The trial co-ordinates of $[ZnL^5]^{2+}$ were taken from the structure[8] of $[CoL^3]^{2+}$. The structures of $[PbL^6(H_2O)_2]^{2+}$ and $[PbL^7]^{2+}$ were built using ALCHEMY with the structure[25] of $[KL^4]^+$ as a guide. The structures of the bridged ligands with Zn^{2+} were obtained using those of Pb^{2+} as initial guides, and refining with the non-bonded parameters developed for Zn^{2+}.

Results and Discussion

Formation Constants.—The stability constants of the complexes of L^5 were determined by Luboch *et al.*[26] with Cu^{2+} (log K = 15.5), Ni^{2+} (log K = 12.49), and Zn^{2+} (log K = 10.9). These formation constant determinations were repeated here and the results agree well with the literature values, except in the case of Cu^{2+} (see Table 4).

The relative variation in stability of metal complexes is shown in Figure 2 as a function of the number of ethylene bridges in the macrocycle. It can be seen that introducing a single bridge into L^5 results in a decrease in log K for Cu^{2+} of 9.2, for Cd^{2+} of 6.1, and for Pb^{2+} of 3.65 log units. The ions Ni^{2+} and Zn^{2+} are not measurably complexed once ethylene double bridges are introduced into the ligand. The decrease in stability upon bridging is largest for the smaller metal ions. The change in affinity of the ligand for Ba^{2+} and Sr^{2+} could not be accurately gauged, because of the low formation constant even with L^5. Introducing the second bridge to L^5 decreases the complex formation constant with Pb^{2+} by a further 0.6 log units, and totally eliminates the complexation of other metal ions. It is seen that addition of the double bridges to a large cavity macrocycle results in selectivity for large metal ions. Also that the introduction of the extra ethylene bridge between 1,2-diaminoethane moieties to make piperazine units results in an overall reduction of complex stabilities, leading to the conclusion that the piperazine-containing macrocycles are as free ligands at a low level of preorganisation. The most probable cause of this low level of preorganisation would be the adoption of the chair conformer by the piperazine bridges of the bridged ligands, rather than the usually higher-energy boat conformers which would be required for co-ordinating to a metal ion.

Crystal Structure of L^7.—The crystal structure of the free ligand L^7 (Figure 1) shows that the two piperazine-type bridges in the macrocyclic ring do indeed adopt the 'chair,' rather than the 'boat' form observed in the structure of $[NiL^2]^{2+}$. The chair–chair conformer of L^7 has two nitrogen lone pairs pointing away from the macrocyclic cavity, and two methylene groups for each piperazine unit which obstruct the macrocyclic cavity.

While the free ligand L^2 appears to be too small to allow the piperazine unit to assume the chair form, the macrocyclic ring of L^7 is large enough for the piperazine units to assume the chair–chair form. For all donor atoms to be co-ordinated to a metal, the ligand would have to adopt the boat-boat form on complexation, and thus the free ligand is not well preorganised, since it has to undergo a major conformation change during complexation.

Molecular Mechanics Calculations.—Molecular mechanics calculations on L^7 in the chair–chair and the boat–boat form show that the former is more stable than the latter by 21.2 kcal mol^{-1}. This is the energy penalty for altering conformation to that which is needed for complexation of metal ions. Energy minimisations were performed on the complexes of L^5 to L^7 with Pb^{2+} with two co-ordinated water molecules present to give a more realistic co-ordination number of eight to the Pb^{II}. No co-ordinated water molecules were added to the Zn^{II}, since this metal ion is normally only six-co-ordinate in its complexes. Energy minimisations on the 'space invader' and 'deck-chair' conformers of the lead complex of L^7 (Figure 3) indicated that the 'deck-chair' conformation was the one preferred.

The lowest-energy conformers found for the zinc(II) complexes of L^5 to L^7 are seen in Figure 4. It is of interest that for the L^7 complex the very high strain energy has led to one of the nitrogen donor atoms being entirely non-co-ordinated.

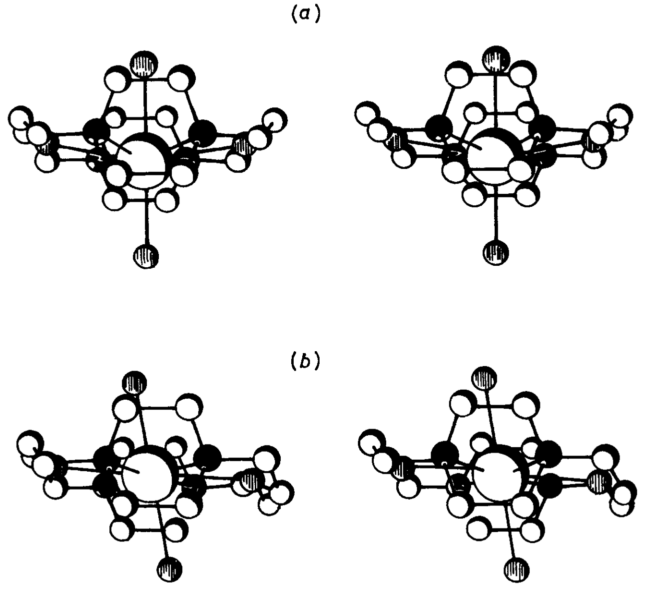

Figure 3. 'Space invader' (*a*) and 'deck-chair' (*b*) conformations of $[PbL^7]^{2+}$. Large central atom is lead, all others are carbon, except for solid circles (nitrogen) and shaded circles (oxygen)

Figure 5 shows the variation is strain as a function of the number of ethylene bridges. The zinc complexes increase dramatically in strain as the extra ethylene bridges are added, whereas those of Pb^{2+} increase much less in energy. That the stability of the complex of Pb^{2+} in solution differs so little upon adding a single or a double bridge must be attributable to the increase in donor strength upon further alkyl substitution of the nitrogen donors.

Conclusions

Poor size selectivity of the unsubstituted crown- and aza-crown ethers is attributed to the flexibility of the macrocycles, which results in poor preorganisation of the ligands.

The attempt to reduce the flexibility of compound L^5 by introducing successive ethylene bridges across bis(aminoethyl) structures to form piperazine units was successful. The insertion of a single ethylene bridge reduced the stability of the complexes of smaller metal ions relative to lead, with the drop in stability being more severe the smaller the metal ion studied. The insertion of two ethylene bridges resulted in total size selectivity for lead among the metal ions studied.

Though good metal-ion discrimination was achieved by this ligand on the basis of size, the stability of the lead complex was low. The crystal structure of the free ligand showed that the piperazine subunits responsible for making the complexed ligand size selective assumed an energetically much lower chair conformation, rather than the boat conformation necessary for complexation. The ligand is thus still poorly preorganised from the point of view of increase in strain energy on complex formation, although the cavity size is better controlled.

It therefore seems that to achieve better size selectivity in the future, while retaining high complex stability, better preorganised bridging units will be needed. We are currently examining the use of bispidine bridging units (L^8) as potentially better preorganised bridging units.

Acknowledgements

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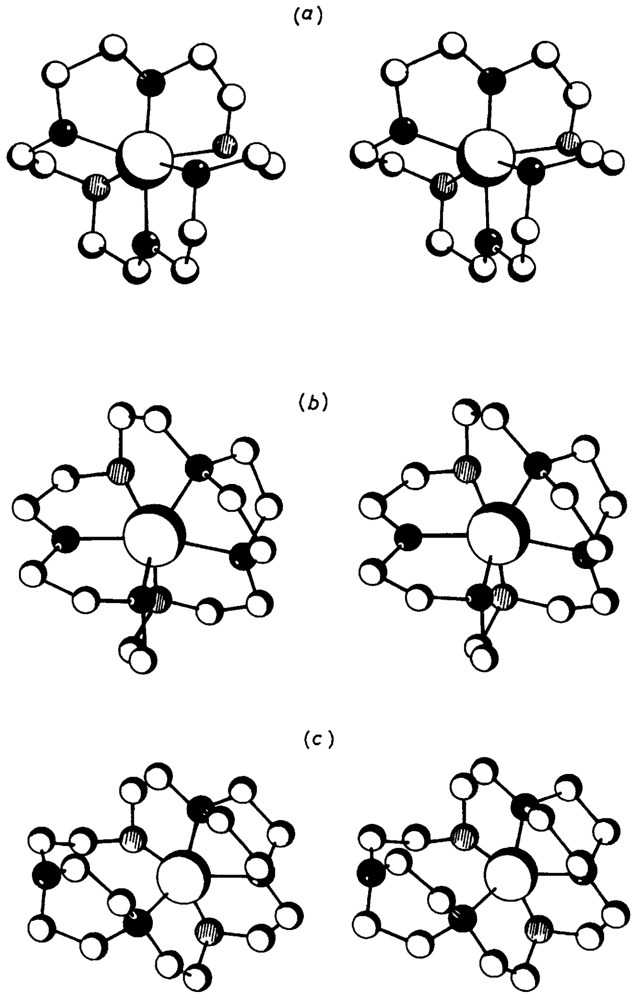

Figure 4. Lowest-energy conformations of (*a*) $[ZnL^5]^{2+}$, (*b*) $[ZnL^6]^{2+}$, and (*c*) $[ZnL^7]^{2+}$. The extreme left nitrogen in (*c*) is not co-ordinated to the Zn^{2+}. Large central atom is zinc, all others are carbon, except for solid circles (nitrogen) and shaded circles (oxygen)

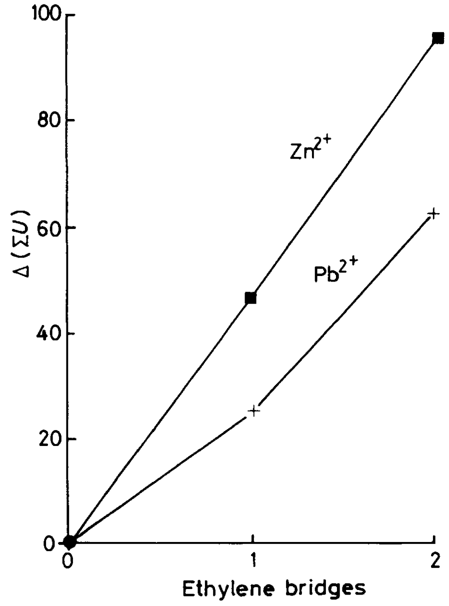

Figure 5. Variation in strain energy of metal complexes relative to L^5 as a function of added ethylene bridges

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