Inorganica Chimica Acta, 96 (1985) 91–97

Quantum Chemical Calculations on Structure and Bonding of Macrocyclic Complexes of Li(I) and Na(I)

BERND M. RODE and SUPOT V. HANNONGBUA

Institut für Anorganische und Analytische Chemie, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

Received April 7, 1984

Abstract

Quantum chemical calculations within the *ab initio* Hartree–Fock framework have been carried out for the complexes of Li(I) and Na(I) ions with both 1,4,7,10-tetraaza- and 1,4,7,10-tetraoxa-cyclododecane, optimizing the conformation of ligands and complexes. In agreement with experimental findings, *ab initio* calculations predict the alternate and maxidentate as being the most stable structures of the poly-N and poly-O ligands respectively. These conformations are also maintained in both complexes. The conformational changes to suit the metal being complexed consume only minor energies. When compared to the open chain analogues, the results show that much more energy input is necessary to change the structure of the open chain ligands to the optimal form for metal binding, especially in the case of polyethers.

It is understood, therefore, that the peculiar stability of the complexes with macrocyclic ligands is mainly due to the rigid pre-strained conformation of these specific ligand types, 'containing' already the amount of strain energy which otherwise reduces the gain of energy by metal bonding considerably.

Introduction

The theoretical study of complexes of simple cyclic nitrogen and oxygen donor ligands is of considerable interest, as they can serve as models for natural and synthetic macrocyclic complexes. The term 'macrocyclic effect' was first introduced to specify the peculiar stability of metal complexes with cyclic ligands compared to analogous noncyclic ligands [1]. Various conclusions were drawn concerning the factors influencing this effect. Some suggested that it is entirely due to the entropy term [2–5], while others [6] assumed that the enthalpy term should predominate. Summarizing all data, both enthalpy and entropy contributions seem to participate in this effect [7–9].

It is generally agreed that some extra stability arises from the smaller configurational entropy of the macrocycle. Margerum *et al.* [6] suggested that it arose from the lower degree of solvation of the cyclic ligands. Fabbrizzi and co-workers [2], however, showed that ligand desolvation effects were overestimated. Some other groups [8, 10–12] assigned special importance to a higher 'ligand field strength' of macrocycles compared to linear ligands. Other workers [8, 13] concluded that special stability is given because the cyclic ligand is pre-strained or pre-oriented, *i.e.* already in the conformation required for complex formation.

At present, a few theoretical studies of macrocyclic complexes have been made [14–17]. In our work we have considered 1,4,7,10-tetraaza-cyclododecane (L_{1a}) and 1,4,7,10-tetraoxa-cyclododecane (L_{1b}), which have been compared with their analogous linear ligands, 2,5,8,11-tetraaza-dodecane (L_{2a}), 2,5,8,11-tetraoxa-dodecane (L_{2b}), 2,5-diazahexane (L_{3a}), and 2,5-dioxa-hexane (L_{3b}). Li(I) and Na(I) were selected as ions, having the same charge but different atomic radii (Li(I) = 0.60 Å, Na(I) = 0.95 Å), so that the metal size effect could also be studied.

The investigations included: (i) the conformation of the compounds in the form of free ligands and metal complexes, (ii) complexation energies of the cyclic ligands compared to that of the open chain ligands, and (iii) an analysis of the factors contributing to the 'macrocyclic effect'.

Method

Ab initio MO–SCF computations were performed using a minimal Gaussian lobe basis set [18]. Although stabilization energies computed with this small basis set are usually over-emphasized, quantitative features of relative stabilities are satisfactorily reproduced in almost every case [16, 19–21]. On the other hand, the size of the system under consideration did not allow the use of extended basis sets because of the enormous computation time that would have been required. For the same reason the experimental geometries of references [22–24] (Table I) were used, and only the metal-ligand distances, the torsion angles, (and thereby the ring size) were optimized with respect to total energy.

0020-1693/85/$3.30

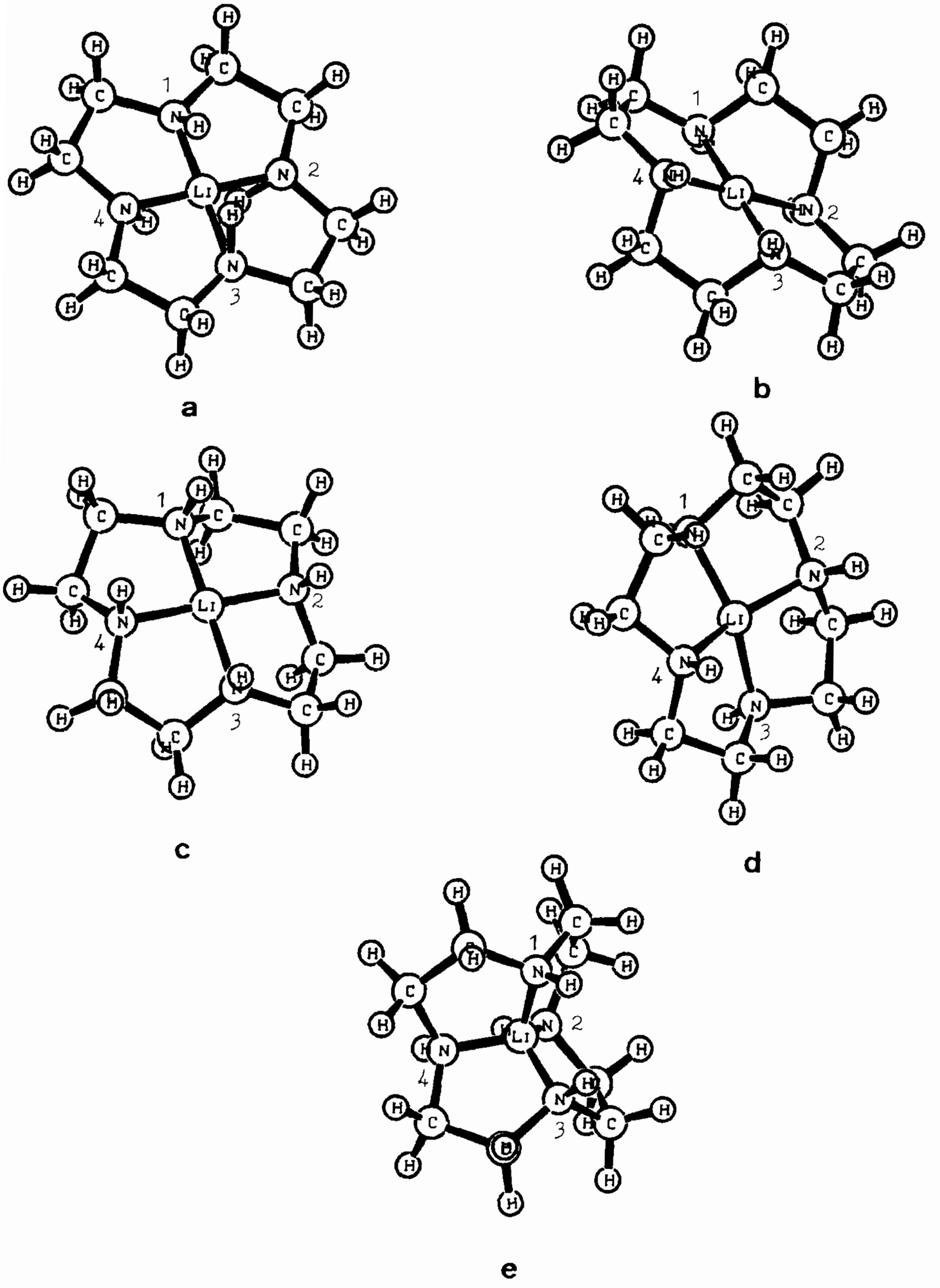

Fig. 1. The five types of possible conformations of 1,4,7,10-tetraaza-cyclododecane-metal complexes: (a) planar, (b) chair, (c) maxidentate, (d) alternate, (e) tetrahedral.

All computations were performed at the CDC Cyber 74 computer of the University of Innsbruck.

Results and Discussion

Conformations

Five types of cyclic ligand conformation were considered: planar, chair, maxidentate, alternate and tetrahedral forms (Fig. 1). In the planar form (Fig. 1a), all C and N or O atoms are located in the same plane. When the opposite dimethylene bridges are moved above and below the N or O plane, one obtains the chair form (Fig. 1b). In the maxidentate form (C_4 symmetry), all dimethylene bridges are located on the same side of the N or O plane (Fig. 1c). From the maxidentate form with torsion angle

TABLE I. Experimental Values for Bond Lengths (in Å) and Angles of Polyamine and Polyether Ligands.

Polyamine			Polyether		
	(a)	(b)		(a)	(b)
C–C	1.540	1.540	C–C	1.502	1.540
C–N	1.470	1.470	C–O	1.430	1.426
C–H	1.094	1.094	C–H	1.094	1.094
N–H	1.014	1.014	C–O–C	113.60	111.50
C–N–C	118.00	109.47	O–C–C	110.75	109.47
N–C–C	104.40	109.47	Other angles	109.47	109.47
Other angles	109.47	109.47			

(a) cyclic. (b) open-chain form.

TABLE II. Total Energies (aeu) of the Various Conformations of the Macrocyclic Ligands 1,4,7,10-Tetraaza-cyclododecane (L_{1a}) and, 1,4,7,10-Tetraoxa-cyclododecane (L_{1b}) (torsion angles of the most stable alternate and maxidentate forms in parentheses).

Form	L_{1a}	L_{1b}
Chair	–452.02659	–519.30936
Planar	–452.09954	–519.25549
Tetrahedral	–451.95506	–519.23605
Maxidentate	–452.11372 (α = 60°)	–519.36377 (α = 65°)
Alternate	–452.12012 (α = 70°)	–519.35638 (α = 75°)

TABLE III. Total Energies of Li(I) and Na(I) Complexes in Various Conformations of the Macrocyclic Ligands 1,4,7,10-Tetraaza-cyclododecane (L_{1a}) and 1,4,7,10-tetraoxa-cyclododecane (L_{1b}) (torsion angles for the most stable alternate and maxidentate foms in parentheses).

Form	L_{1a}		L_{1b}	
	Li(I)	Na(I)	Li(I)	Na(I)
Chair	–458.53309	–601.01482	–525.77887	–668.44201
Planar	–458.41390 0.0^a	–600.42282 0.0^a	–525.78822 0.5^a	–668.46967 0.8^a
Tetrahedral	–458.38544	–600.24886	–525.47955	–667.21956
Maxidentate	–458.71247 (α = 60°) 0.0^a	–601.29308 (α = 74°) 0.0^a	–525.86552 (α = 55°) 0.5^a	–668.58551 (α = 65°) 1.0^a
Alternate	–458.72705 (α = 65°)	–601.31810 (α = 87°)	–525.85185 (α = 65°)	–668.52135 (α = 82°)

[a]The metal ion's out-of-plane distance (in Å) for the most stable planar and maxidentate forms.

0°, by rotating the adjacent N or O atoms to the opposite side of the plane of C atoms the alternate form (C_{2v}) is obtained (Fig. 1d). Finally, when N or O atoms are located in tetrahedral positions, one has the 'tetrahedral' form of Fig. 1e.

For finding the most stable conformation, the values of the torsion angles (α) around the C–C bond (α_{OCCO} and α_{NCCN}) for the maxidentate and alternate forms were optimized. In case of complex conformations, the metal ions were positioned in the center of the ligand and the distance between the metal ions and the N or O plane (out-of-plane distance) for the planar and maxidentate forms were also optimized. The results of these calculations are given in Tables II and III. In Table IV the minimum energy conformations for L_{1a} and L_{1b}, together with the optimized torsion angles, metal-donor atom and out-of-plane distances are summarized.

The most stable conformation of L_{1a} is the alternate form with a torsion angle of 70°. In the complex the torsion angle is not the same as in the free ligand and depends on the type of metal ion bounded. In the complex with Li(I), the macrocyclic ring is contracted (from α = 70° to α = 64°), whereas in that of Na(I) it becomes larger (to α = 87°). In experimental investigations with various types of metal ions, approximate *cis*-octahedral forms were observed [25–31]. The exact *cis*-octahedral form is included

TABLE IV. Torsion Angles α, Metal–Donor Distances d (Å) and $N_1 \cdots N_3$ ($O_1 \cdots O_3$) Distances D (Å) for the Most Stable Conformations of 1,4,7,10-Tetraaza-cyclododecane (L_{1a}) and 1,4,7,10-Tetraoxa-cyclododecane (L_{1b}), and Their Complexes with Li(I) and Na(I) Ions.

Form	L		L + Li(I)			L + Na(I)		
	α	D	α	d	D	α	d	D
L_{1a} Alternate	70	3.78	64	1.88	3.72	87	2.08	4.09
L_{1b} Maxidentate[a]	65	4.10	56	2.04	4.08	65	2.28	4.10

[a] For the maxidentate form, Li(I) and Na(I) ions are located out of the O plane 0.5 Å and 1.0 Å respectively.

in our optimization of the alternate form, but our results indicate that this form of the L_{1a} complex is more or less distorted, in agreement with X-ray data showing N–M–N angles deviating from the exact *cis*-octahedral angles [32].

Some other data [30, 31] indicate that for L_{1a} complexes more or less distorted square coplanar conformations can be observed with increasing temperature and ionic strength of the solvent. In this case our calculations predict that the maxidentate conformation (four N atoms are in the same plane) should be formed, as the energy difference between the most stable alternate to the maxidentate form is small, amounting to 9.2 and 15.1 kcal/mol for Li(I) and Na(I) complexes (Table II). Upon this conformational rearrangement the M^+–N distance changes only in the case of Na(I) (from 2.08 Å to 2.01 Å).

No experimental data have been reported on these complexes. Although it is obviously not sufficient to consider only the relative size of the metal ions and the aperture of the free ligand, it is interesting to compare the M–N distances of 1.90, 1.93 and 2.03–2.10 Å measured for Ni(II) [8], Co(II) [32] and Cu(II) [33] complexes with our data (atomic radii; Li(I) = 0.60 Å, Ni(II) = 0.69 Å, Co(II) = 0.70 Å, Na(I) = 0.95 Å and Cu(II) = 0.96 Å).

Our $N_1 \cdots\cdots N_3$ distance characterizing the ring size for free L_{1a} (3.88 Å) is significant larger than that calculated by Busch *et al.* [14]. In their calculations (3.66 Å), however, the four N atoms are in a square planar arrangement (corresponding to a maxidentate form with torsion angle of 50° in our calculations), which is surely not the most stable form. Complexes of this structure have never been isolated [5, 8, 23, 24, 35].

For 1,4,7,10-tetraoxa-cyclododecane, L_{1b}, the minimum conformation is the maxidentate form (Table III). The conformation of its complex with Na(I) ion is the same as that of the free ligand (α = 65°, $O_1 \cdots\cdots O_3$ = 4.10 Å), whereas Li(I) makes the ring smaller and changes the ligand conformation from α = 65° to α = 56° ($O_1 \cdots\cdots O_3$ = 3.96 Å). Apparently the structure of this ligand is ideal for sodium ions, as can be seen from the stabilisation energy data in Table VI. In this compound, Li(I) and Na(I) ions stay above the plane of the O atoms (0.5 Å for Li(I) and 1.0 Å for Na(I)), rather than to induce a larger deformation of the ligand.

The experimental results [22] and other calculations [15, 17, 19] obtainable for this ligand are similar to our findings. Fukui *et al.* [17] using the CNDO/2 method, suggested the maxidentate form for both free ligand and its Na(I) complex, Na(I) out of plane by 1.5 Å. Pullman *et al.* [15] performed *ab initio* calculations using another minimal (STO-3G) basis set. Almost the same stabilization energy for maxidentate and alternate forms was obtained for both free and Li(I)-bound ligands (Li(I) out of plane by 0.4 Å in the alternate form). Some small discrepancies may be due to the geometrical data of large compounds being used for the ligand in their calculations.

TABLE V. Total Energies (aeu) of Li(I) and Na(I) Ions Complexes with Open Chain Ligands.

(a) 2,5,8,11-Tetraaza-dodecane (L_{2a}) and 2,5,8,11-Tetraoxa-dodecane (L_{2b})

Form	L_{2a}	L_{2b}
Li(I) ion	–6.40997	–6.40997
Na(I) ion	–149.12772	–149.12772
L(expand.)	–453.12195	–520.41694
L(contract. a)	–453.09368	–520.34534
L(contract. b)	–453.08922	–520.35027
L(contract. a) + Li(I)	–459.67507	–526.85291
L(contract. b) + Na(I)	–602.27994	–669.56121

(b) 2,5-diaza-hexane (L_{3a}) and 2,5-dioxa-hexane (L_{3b})

Form	L_{3a}	L_{3b}
L(*trans*)	–227.05951	–260.70744
L(*cis*)	–227.05666	–260.69937
2L(dimer a)	–454.15970	–521.33661
2L(dimer b)	–454.16495	–521.33794
2L(dimer a) + Li(I)	–460.62256	–527.85392
2L(dimer b) + Na(I)	–603.24158	–670.53783

TABLE VI. Energy Balance for Complex Formation Processes of Li(I) and Na(I) Complexes with Cyclic and Open Chain Ligands.

(a) Macrocyclic Ligands, L_{1a} and L_{1b} process	L_{1a}		L_{1b}	
	Li(I)	Na(I)	Li(I)	Na(I)
1a) L(conf. 1) $\longrightarrow$ L(conf. 2)	+0.9	+8.9	+5.3	0.0
2a) L(conf. 2) + M$^+$ $\longrightarrow$ ML$^+$	−123.6	−43.5	−57.6	−59.0
3a) overall process: L + M$^+$ $\longrightarrow$ ML$^+$	−122.7	−34.6	−52.3	−59.0
(b) open chain ligands, L_{2a} and L_{2b} process	L_{2a}		L_{2b}	
	Li(I)	Na(I)	Li(I)	Na(I)
1b) L(expand.) $\longrightarrow$ L(contract.)	+17.7	+20.5	+44.9	+41.8
2b) L(contract.) + M$^+$ $\longrightarrow$ ML$^+$	−107.6	−39.5	−61.3	−52.2
3b) overall process: L(expand.) + M$^+$ $\longrightarrow$ ML$^+$	−89.9	−19.0	−16.3	−10.4
c) open chain ligands, L_{3a} and L_{3b} process	L_{3a}		L_{3b}	
	Li(I)	Na(I)	Li(I)	Na(I)
1c) L(*trans*) $\longrightarrow$ L(*cis*)	+1.8	+1.8	+5.1	+5.1
2c) 2L(*cis*) $\longrightarrow$ L_2(dimer)	+29.1	+32.4	+39.0	+38.2
3c) L_2(dimer) + M$^+$ $\longrightarrow$ M(L_2)$^+$	−90.3	−28.4	−67.4	−45.3
4c) overall process: 2L(*trans*) + M$^+$ $\longrightarrow$ M(L_2)$^+$	−59.4	+4.8	−23.3	+2.0

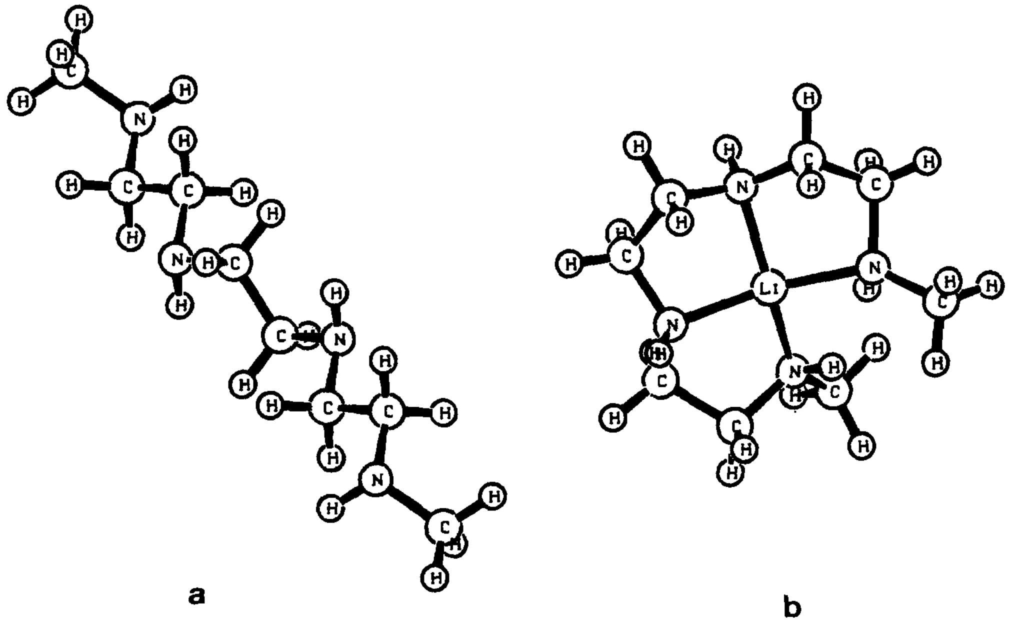

Fig. 2. 2,5,8,11-tetraaza-dodecane configurations: (a) expanded form, (b) contracted form with Li(I) ion.

Macrocyclic Effect

The complexation energies of the macrocyclic ligands and their open chain analogues are given in Table VI. The conformations 1 and 2 represent the most stable free and metal-bonded cyclic ligands, respectively. A negative energy sign denotes a net gain of energy in the reaction.

The conformation of the open chain ligands is shown in Fig. 2a (L_{2a}) and Fig. 3a (L_{3a}). Before complexation, L_{2a} and L_{2b} have to be contracted

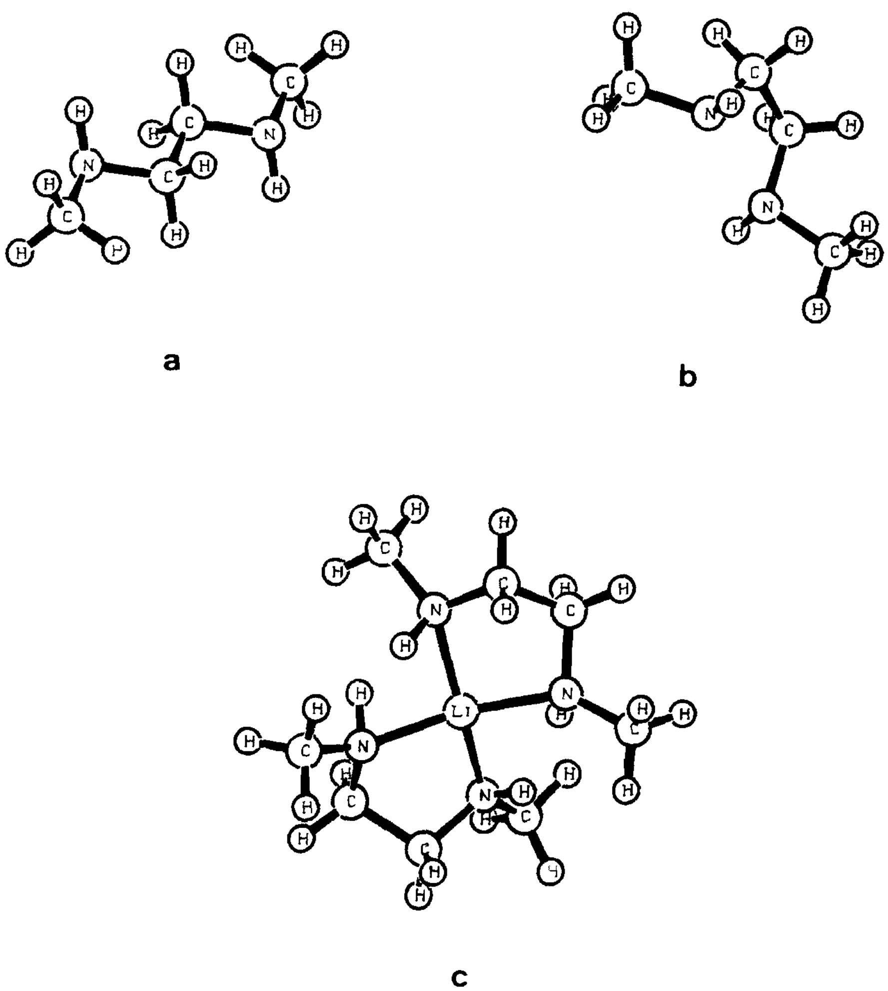

Fig. 3. 2,5-diaza-hexane configurations: (a) *trans* form, (b) *cis* form, (c) dimer form with Li(I) ion.

to a geometry suitable for complex formation (Fig. 2b) and L_{3a} and L_{3b} have to change from *trans* (Fig. 3a) to *cis* conformation (Fig. 3b) and to a 'dimer' structure as shown in Fig. 3c.

In our calculations on these contracted and dimer forms, the macrocyclic geometrical parameters were used, thus obtaining conformations analogous to metal-bound macrocyclic ligands (conformation 2).

The results are collected in Table VI. The L_{1a} complex with Li(I) is considerably more stable than the corresponding Na(I) complex (see eqns. 3a and 3b). The consumed energies are due to the conformation change (eqns. 1a and 1b) before complexation and the nature of these ions in the complex formation step (eqns. 2a and 2b). Comparing the macrocyclic ligand with the open-chain ligands L_{2a} and L_{3a}, 'macrocyclic effects' of 32.8 and 63.6 kcal/mol for Li(I) and 15.6 and 39.4 kcal/mol for Na(I) result. The analysis of energy contributions to these values shows clearly that the main factor is the strain energy (eqns. 1a, 1b and 1c + 2c, Table VI).

A smaller but still important contributing factor (especially in the Li(I)–L_{1a} complex) is the stronger binding of the metal ions by the cyclic ligand in the complexation process (eqns. 2a, 2b and 3c, Table VI), which should be due to the more flexible electron distribution in the ring system.

In the case of O-containing ligands, both Li(I) and Na(I) complexes show an opposite order (Na(I) > Li(I)) for the macrocyclic effect (36.0 and 29.0 kcal/mol for Li(I) and 48.6 and 61.0 kcal/mol for Na(I)). Apparently, the smaller intrinsic affinity of the Na(I) ion is compensated by a better fit of this ion to the ligand structure. In the case of these ligands, complex stabilization seems to be mainly due to this macrocyclic 'prestrain-energy content'.

In our calculations, solvent and entropy effects are neglected. The small basis set used might have affected the absolute stabilization energies, in the form of some over-estimation. The relative order, however, can be assumed to be quite reliable. Therefore, the conclusion that the peculiar stability of the complexes with macrocyclic ligands and thus the 'macrocyclic effect' are mainly due to the rather rigid pre-strained conformation of these specific ligands 'containing' already the amount of strain energy, which otherwise would compensate much of energy gain in the complex formation step, seems to be justified and be based on a satisfactory quantum chemical foundation.

These strain energies when taken as an enthalpic effect would correspond to entropy changes of –60 to –150 cal/mol·K. Such high values are not very likely to occur in solvation/desolvation processes. Therefore, the entropy term should be only of secondary importance concerning the extra stability of macrocyclic complexes.

Acknowledgement

Financial support for S. V. H. by the Austrian Federal Government is gratefully acknowledged.

References

1 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc., 91, 6540* (1969).
2 L. Fabbrizzi, P. Paoletti and A. B. P. Lever, *Inorg. Chem., 15,* 1502 (1976).
3 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.,* 116 (1976).
4 M. Kodama and E. Kimura, *J. Chem. Soc., Chem. Commun.,* 819 (1975).
5 A. Anichini, L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chim. Acta, 22,* L25 (1977); *24,* L21 (1977); *J. Chem. Soc., Dalton Trans.,* 1438 (1978).
6 F. P. Hinz and D. W. Margerum, *J. Am. Chem. Soc., 96,* 4993 (1974); *Inorg. Chem., 13,* 2941 (1974).
7 P. Paoletti, L. Fabbrizzi and R. Barbucci, *Inorg. Chim. Acta Rev., 7,* 43 (1973).
8 L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chem., 17,* 1042 (1978).
9 N. F. Arnaud, W. M. Schwing, R. Loues and R. Wee, *Inorg. Nucl. Chem. Lett., 14,* 367 (1970).
10 Y. Hung, L. Y. Martin, S. C. Jackels, A. M.Tait and D. H. Busch, *J. Am. Chem. Soc., 99,* 4029 (1977).
11 R. D. Hancock and G. J. McDougall, *J. Am. Chem. Soc., 102,* 6551 (1980).
12 D. H. Busch, K. Farmery, V. Goedken, V. Katovie, A. C. Melnyk, C. R. Sperati and N. Tokel, *Adv. Chem. Ser.,* 44 (1971).
13 G. J. McDougall, R. D. Hancock and J. C. A. Boeyens, *J. Chem. Soc., Dalton Trans.,* 1438 (1978).
14 L. Y. Martin, L. J. Dehayes, L. J. Zompa and D. H. Busch, *J. Am. Chem. Soc., 96,* 4046 (1974).
15 A. Pullman, C. G. Prettre and Y. V. Kruglyak, *Chem. Phys. Lett., 35,* 156 (1975).
16 G. J. Reibnegger and B. M. Rode, *Inorg. Chim. Acta, 72,* 47 (1983).
17 T. Yamabe, K. Hori, K. Akagi and K. Fukui, *Tetrahedron, 35,* 1065 (1979).
18 R. Ahlrichs, *Theoret. Chim. Acta (Berlin), 33,* 157 (1974).
19 K. P. Sagarik and B. M. Rode, *Inorg. Chim. Acta, 78,* 177 (1983).
20 K. P. Sagarik and B. M. Rode, *Inorg. Chim. Acta, 78,* 81 (1983).
21 K. P. Sagarik and B. M. Rode, *Inorg. Chim. Acta, 76,* L209 (1983).
22 P. Groth, *Acta Chem. Scand., A32(3),* 279 (1978).
23 M. F. Richardson and R. E. Siever, *J. Am. Chem. Soc., 94,* 4134 (1972).
24 L. E. Sutton, 'Table of Interatomic Distances', London, The Chemical Society, 1958.
25 J. P. Collman and P. W. Schneider, *Inorg. Chem., 5,* 1380 (1966).
26 G. A. Kalligeros and E. L. Blinn, *Inorg. Chem., 11,* 1145 (1972);
C. M. Sarter and E. L. Blinn, *Inorg. Chem., 15,* 3083 (1976).
27 L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.,* 1857 (1979).
28 F. P. Remoortere and F. P. Boer, *Inorg. Chem., 13,* 2071 (1974); *13,* 2886 (1974).
29 Y. Iitaka, M.Shina and E. Kimura, *Inorg. Chem., 15,* 1502 (1976).
30 L. Y. Martin, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc., 99,* 2968 (1977).
31 R. Smierciak, J. Passariello and E. L. Blinn, *Inorg. Chem., 16,* 2646 (1977).
32 Y. Iitaka, M. Schina and E. Kimura, *Inorg. Chem., 13,* 2886 (1974).
33 A. Anichini, L. Fabbrizzi nd R. G. Clay, *J. Chem. Soc., Dalton Trans.,* 577 (1978).
34 K. P. Wainwright, *Inorg. Chem., 19,* 1396 (1980).
35 L. Fabbrizzi, *Inorg. Chem., 16,* 2667 (1977).