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POLYPYRAZOLIC MACROCYCLES—II

A STUDY OF THEIR COMPLEXING PROPERTIES WITH ALKALI CATIONS

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Abstract—Polypyrazolic macrocycles are shown to be excellent complexing agents for the alkali metal cations. The study is particularly focussed on the stoichiometry of the isolated complexes, as well as the rates of cation transport across a liquid membrane.

We have previously reported[1-3] the syntheses of some new macrocyclic systems, including porphyrinogen related species. As previously indicated, one of the important properties of these compounds is their ability to complex with the alkali metal cations.

A more extensive study has now been performed in order to determine the factors influencing this complexing power as well as to classify these compounds relative to those existing in the literature and in particular to the ethylene diamines[4] and the crown ethers[5].

The macrocycles discussed in the present work are shown in Fig. 1. For the purpose of simplification the abbreviations shown in Fig. 1 are used hereinafter (tetraaza for tetraazaporphyrinogen, Py-6 and Py-8 for the structures possessing 6 and 8 pyrazole groups respectively).

Experimentally, when a chloroform solution of one of these three compounds is mixed with an alkali metal salt and on subsequent filtration a recrystallisable complex is generally obtained. Stoichiometry (as deduced from the elemental analysis) and ^{1}H NMR spectra are shown in Tables 1–3.

As these tables show the complexing ability of these new macrocycles is quite general, which raises the question of the nature of the complexes obtained. In particular this complexing ability could be due to the presence of an electronegative cavity (as with the crown ethers) or to a chelating effect (as with the polyamines). In order to clarify this point, a number of linear pyrazolic compounds were studied under the same experimental conditions. Their structures (one being the non-cyclic equivalent of tetraaza-**1**) are shown in Fig. 2.

Since the linear analogues of Py-6 and Py-8 presented synthetic difficulties, it seemed that if these molecules form complexes of the chelate-type then the pyrazolylpyrazole **8** should behave similarly.

The results of ^{1}H NMR studies of the complexation of these compounds are shown in Table 4.

Several conclusions can be drawn from the results presented in the above tables. The pyrazolylpyrazole and dipyrazolylmethane moieties form chelates with the lithium cation. The absence of any such effect with Na^+ (regardless of the anion used) is analogous to reported studies of the polyamines. The tetraaza-Ki^+, Py-6-Li^+ and Py-8-Li^+ complexes can thus be compared in nature to those formed by the polyamines (TMEDA); this is indeed supported by the fact that only soft anions (I^-) associated to the lithium allow such complexation. It is known that the lattice energy is one of the determining factors in chelation of polyamines with inorganic salts.[6]

In the case where complexes are obtained with anions of different hardness (tetraaza-Na^+, tetraaza-K^+, Py-6-Na^+, Py-6-K^+, Py-6-Cs^+) the concept of chelating behaviour by one or several moieties is discarded in favour of an interaction as for the crown ethers due to the existence of an electronegative cavity formed by the sp^2 pyrazolic nitrogen lone pairs.

Complexation studies by liquid–liquid extraction

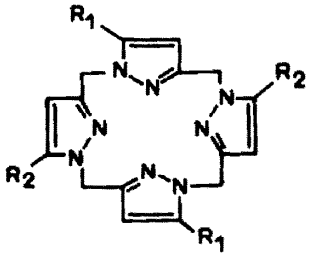
In order to better understand the relative stabilities of the various complexes the technique of liquid–liquid extraction[7-10] was used for the three macrocycles, tetraaza, Py-6 and Py-8; and the results are shown in Fig. 3 for two of them.

From these curves the equilibrium percentage extraction is obtained as a quantitative measure of the complexing power of the various macrocycles (Table 5).

Under the same experimental conditions the linear compounds **4–8** led to no extraction whatsoever, thus showing that such systems which chelate the lithium cation have a relatively weak force of cohesion and cannot extract alkali cations from the aqueous phase. This is equally the case for the tetraaza-Li^+ and Py-8-Li^+ complexes, for which the extraction percentages are very low, and for these two systems it is probably not the existence of the macrocyclic cavity which is important but rather the affinity of the pyrazolylpyrazole or dipyrazolylmethane moiety for the lithium cation.

For the interaction of Py-6 with Li^+ an ambiguity exists and one can imagine that this molecule behaves like Py-8 in the presence of solid LiI (that is with chelation by the pyrazolylpyrazole moiety), whilst in view of the high percentage (57%) obtained under extraction conditions it seems that the stability of the complex obtained is due to the presence of the electronegative cavity, with formation of a complex of undetermined stoichiometry.

At the same concentration Py-6 gives extremely high percentages of extraction for each cation. Indeed this compound, which is as reactive as dicyclohexyl-18-crown-6 towards K^+, is an exceptional complexing agent of Cs^+ with a percentage of extraction of 80%. The

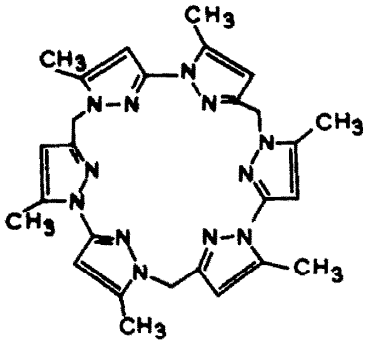


Tétraaza

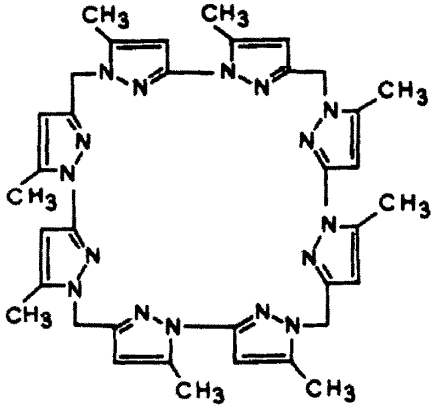
$R_1 = R_2 = CH_3$ (1)

$R_1 = CH_3, R_2 = C_6H_5$

$R_1 = R_2 = C_6H_5$

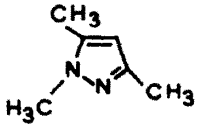


Py-6 (2)



Py-8 (3)

Fig. 1.



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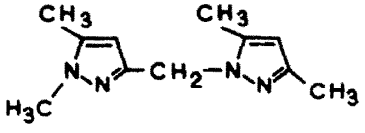

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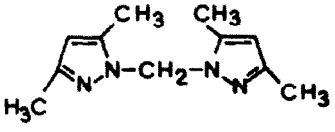

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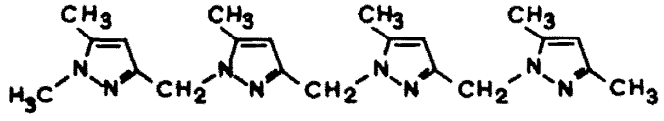

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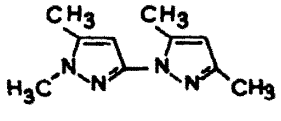

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Fig. 2.

Table 1. Complexes of tetraaza **1b** ($R_1 = CH_3$, $R_2 = C_6H_5$) with alkali cations

Cation	^1H NMR in $CDCl_3$; δ in ppm					Analysis			
	CH_3	CH_2	CH	C_6H_5	Anion	Anion	Actual Formula	Stoichiometry (tetraaza/alkali salt)
Non-complexed molecule	2.30	5.15	5.66 6.20	7.46			$C_{30}H_{28}N_8$	
Li^+	2.38	5.28 5.37	6.03 6.35	7.45	I^- [a]	Cl^- c		between 1/1 and 1/2 (poorly defined)
	2.30	5.22 5.28	5.93 6.23	7.42	Cl^-			
	2.30	5.17	5.72 6.22	7.50	CH_3COO^- 1.95 (1/2) [b]			
Na^+	2.38	5.26 5.36	5.90 6.35	7.58	OH^-	OH^- c	$C_{30}H_{28}N_8$, 1/2 NaOH	2/1
	2.33	5.20 5.27	5.80 6.27	7.48	Cl^-	Cl^- c	$C_{30}H_{28}N_8$, 1/2 NaCl, 1 H_2O	2/1
	2.32	5.18 5.27	5.85 6.20	7.47	CH_3COO^- 2.1 (2/1) [b]			
K^+	2.30	5.04 J= 12Hz 5.20 5.28 J= 14Hz 5.56	5.66 6.25	7.53	I^-	I^- c	$C_{30}H_{28}N_8$, 1/2 KI, 1H_2O	2/1
	2.30	5.25 (broad)	5.69 6.23	7.45	CH_3COO^- 2.03 (2/1) [b]			
Cs^+	Anions I^- ; NO_3^- ; NO change in the ^1H NMR spectra.							

(a) Complex precipitated immediately
(b) The ratio tetraaza/anion acetate is indicated in brackets
(c) Analysis after recrystallisation from $CHCl_3$/Benzene

Table 2[a]. Complexes of Py-6 2 with alkali cations

Cation	NMR $^1H(CDCl_3)$, δ in ppm					Analysis		
	Anion	CH_3	CH_2	CH	Anion	Actual Formula	Stoichiometry (tetraaza/alkali salt)
non complexed molecule		2.23 2.32	5.13	5.68 5.03			
non complexed molecule [b]		2.20 2.35	5.17	6.12 5.23		$C_{27}H_{30}N_{12}$	
Li^+	Cl^-	2.23 2.38	5.23	6.00 6.10	I^-	$C_{27}H_{30}N_{12}$, 3LiI, $9H_2O$	1/3
Na^+	Cl^-	2.30 (broad)	5.10 (broad)	6.00 (broad)		$C_{27}H_{30}N_{12}$, NaSCN, $CHCl_3$, $3H_2O$	1/1
	SCN^- [b] [c]	2.20 2.35	5.17	6.12 6.29	SCN^-		
K^+	Cl^-	2.37	5.22	6.08 6.18	SCN^-	$C_{27}H_{30}N_{12}$, KSCN, $CHCl_3$, $3H_2O$	1/1
Cs^+	Cl^-	2.23 2.35	5.25	6.00 6.10	OH^- [d]	$C_{27}H_{30}N_{12}$, CsOH	1/1
	NO_3^-	2.23 2.32	5.13	5.93 6.03	I^- [d]	$C_{27}H_{30}N_{12}$, CsI	1/1

(a) The NMR spectra of the products which were soluble in $CDCl_3$ were recorded. Complexes insoluble in this solvent were identified by microanalysis.

(b) Spectrum in d_6-DMSO.

(c) The $CHCl_3$ proton was observed at 8.35 ppm with an intensity equal to 1/6 that of the CH_2 peak. The equivalence of the spectra of the "complexed" and non complexed molecule in d_6-DMSO and the nature of the $CHCl_3$ observed (chloroform free) indicate that the molecule is not actually in the form of a complex in this solvent.

(d) Product recrystallised from acetone.

Table 3[a]. Complexes of Py-8 3 with alkali cations

Cation	NMR ^1H ($CDCl_3$) δ in ppm				Analysis		
	anion	CH_3	CH_2	CH	Anion	Actual Formula	Stoichiometry (tetraaza/alkali salt)
non complexed molecule		2.37	5.10	5.95 6.12		$C_{36}H_{40}N_{16}$	
Li^+		2.40 2.50	5.58	6.17 5.22	I^-	$C_{36}H_{40}N_{16}$, 4LiI, $8H_2O$	1/4
					I^- [c]	$C_{36}H_{40}N_{16}$, 2LiI, $4H_2O$	1/2
Na^+	I^-	2.35 2.43	5.47	6.02 6.22	SCN^-	$C_{36}H_{40}N_{16}$, 2NaSCN	1/2
	SCN^-		b				

(a) No complex formation was detected for K^+ or Cs^+.

(b) The complex was insoluble in $CDCl_3$.

(c) Recrystallised from acetone.

Table 4.

Product	Cation	Anion	^{1}H N M R in $CDCl_3$; δ in ppm			
			CH_3	NCH_3	CH_2	CH
4	non complexed molecule		2.20(br)	3.73	-	5.78
	Li^+	I^-	——— a			
5	non complexed molecule		2.18 2.23	3.7	5.12	5.78
	Li^+	I^-	1.77 2.28 2.38	3.43	5.17	5.78 6.23
	Na^+	SCN^-	——— a			
6	non complexed molecule		2.17 2.40	-	6.07	5.80
	Li^+	I^-	1.82 2.55	-	6.37	5.83 6.37
7	non complexed molecule		2.20(br)	3.73	5.18	5.80
	Li^+	I^-	2.33	3.97	5.22 5.23 5.63	5.80 6.05(I=2H) 6.10
	Na^+	I^-, SCN	——— a			
8	non complexed molecule		2.27 2.38	3.73	-	5.9 6.13
	Li^+	I^-	2.17 2.42 2.52	3.73	-	6.05 6.22
	Li^+	Cl^-	——— a			
	Na^+	I^-, SCN	——— a			

(a) No chelate formation.

Table 5. Limiting percentage of extraction[a]

Compound	Li^+	Na^+	K^+	Cs^+
Tetraaza	4	56	27	8
Py-6	57	42	72	80
Py-8	0	0	1	4
Dibenzo-18-crown-6	0	2	30	5

(a) Values obtained after 2 hours.

complexing power of these pyrazolic macrocycles was attributed above to the existence of sp^2 lone pairs forming an electronegative internal cavity. In order to verify this the extraction technique was applied to a previously described[11] compound **9** which possesses pyridine-type sp^2 nitrogens and a cyclic structure with an internal cavity of a comparable size to that of 18-crown-6 (Fig. 4).

All extraction attempts with this compound gave negative results regardless of the cation used (Cs^+, K^+, Na^+ or Li^+). This serves to emphasise the novel peculiarity of the macrocyclic structures containing linked pyrazole groups.

Decomplexation studies

Chloroform solutions of the complexes obtained from equilibrium with aqueous inorganic salts as describec above were then put in contact with an equal volume o pure water. The passage of the alkali metal picrate int the aqueous phase was then followed thus giving th decomplexation curves shown below (Fig. 5). Whereas i general the quantity of picrate which moves into th aqueous phase on decomplexation is the same as tha observed on extraction, this is not the case with the Py- complexes with K^+ and Cs^+ for which the stabilities ar such that only partial decomplexation is observed by thi method.

Transport of cations across a membrane

As an extension of the ability of these macrocycles t extract or release (according to the conditions) alkali met

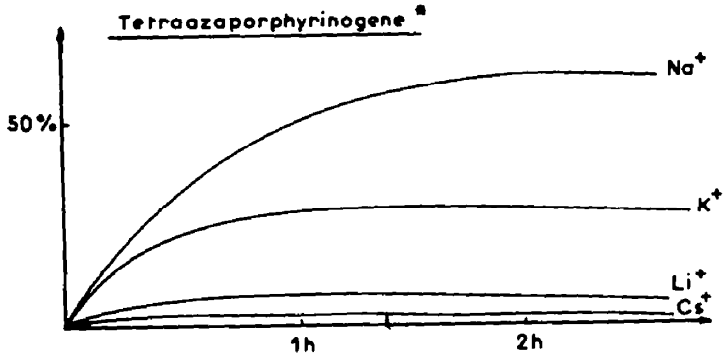

Fig. 3(a).

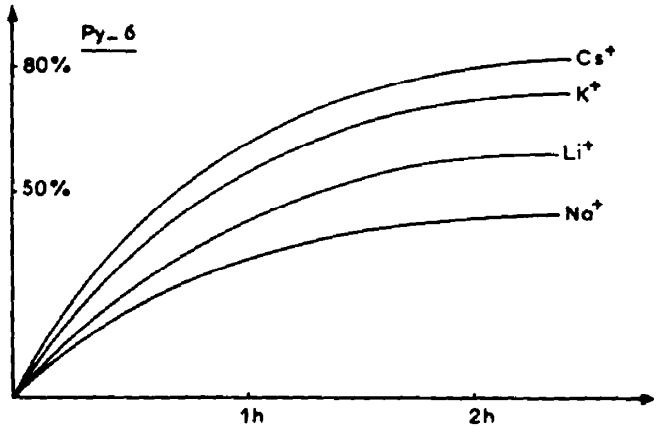

Fig. 3(b).

Fig. 3. Percentage extraction curves for (a) tetraazaporphyrinogen, (b) Py-6 as a function of time. Identical results were obtained for all substituents.

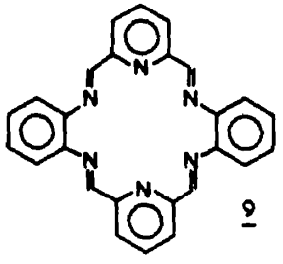

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Fig. 4.

cations, their role as transfer agents across a liquid membrane was studied.

These experiments were performed using a modification of a method previously described,[9] on the various products studied by (liquid–liquid) complexation, again including dibenzo-18-crown-6 for comparative purposes. In each case there was no transfer of picrate ion across the membrane in the absence of the macrocycle.

The transfer was also followed by conductimetry which is more general since it can detect transfer of inorganic salts which do not absorb in the UV region. This technique was used in two cases: (a) For the cation K^+ and tetraazaporphyrinogen ($R_1 = CH_3$; $R_2 = C_6H_5$) (Picrate: 7×10^{-4} mole/l; nitrate: 10^{-1} mole/l) and (b) in the absence of picrate.

These experiments showed the reliability of the UV method (since identical results were obtained by the two methods) and the preference for picrate anion transfer compared to that of nitrate (or hydroxide), in accord with the literature.[7,9] Experiment (b) showed that the nitrate anion has a transfer rate across the membrane four times lower than that of picrate. This can be attributed to the difference in the free energy of solubilisation of the two anions on complexation.

The non-cyclic compounds 4-8 were also studied but in each case no transport of cation was observed. This demonstrates once again that the chelating character of the pyrazolylpyrazole and bipyrazolylmethane systems is not sufficient to explain the properties of the macrocycles.

For the transfer by cryptates possessing tertiary amines, Lehn *et al.*[7] have demonstrated the existence of protonation of these ligands to a significant extent. In the

Table 6. Cation transport rates across a liquid membrane

Compound	Cation	Transfer rate in mole/hour x 10^7	Transfer Selectivity Li/Na	Transfer Selectivity Cs/Na
tetraaza ($R_1 = CH_3$, $R_2 = C_6H_5$)	Li^+	7,6	0,37	0,24
	Na^+	20,2		
	K^+	18,5		
	Cs^+	5,0		
Py-6	Li^+	35,3	1,17	1,45
	Na^+	30,2		
	K^+	26,9		
	Cs^+	24,4		
Py-8	Li^+	very low	-	3,04
	Na^+	2,5		
	K^+	4,2		
	Cs^+	7,6		
Dibenzo 18-crown-6	Li^+	0,8 (0,29)	0,32	5
	Na^+	2,5 (4,62)M		
	K^+	22,5 (73,5)M		
	Cs^+	12,6		

M Values obtained by Y. KOKUBE et al.[13]. The differences between the two sets result from the different experimental conditions (in particular we have noted that the speed of rotation and the type of magnetic bar used, not quoted by the above authors[13], have a significant effect on the transport rates, which are diffusion derived[11]).

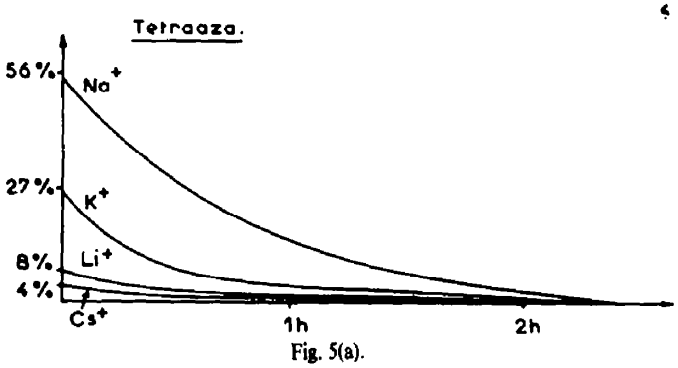

Fig. 5(a).

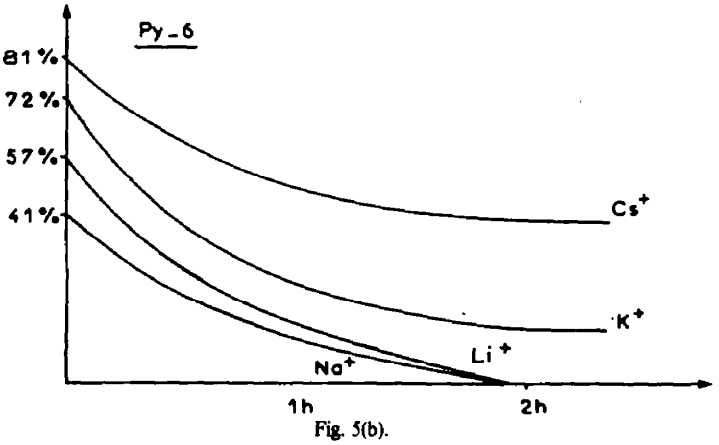

Fig. 5(b).

present case such a possibility can be excluded since identical results were obtained for 0.1 M nitrate solution and 0.1 M hydroxide solution.

From the above studies the transfer rates were calculated (from the linear part of the curve) and are shown in Table 6.

Several conclusions can be drawn from the above values: (a) the observed rates for tetraaza are about 24 times superior to those found for the furanic analogues;[9] (b) the transfer rates of tetraaza and Py-6 are of the same order (or superior) to those of dibenzo-18-crown-6. However these high rates are not accompanied by significant selectivities towards the various cations. Tetraaza does however discriminate Na^+ and K^+ against Li^+ and Cs^+ which is in accord with observations made in the complexation studies; (c) for the macrocycle Py-6 there is a decrease in the transport rates on passing from Li^+ to Cs^+, which is the inverse order to that of the observed percentages of extraction (Table 5). This effect, previously noted,[9] shows the importance of the relative ease of release of the cation in decomplexation (see the curves in Fig. 3).

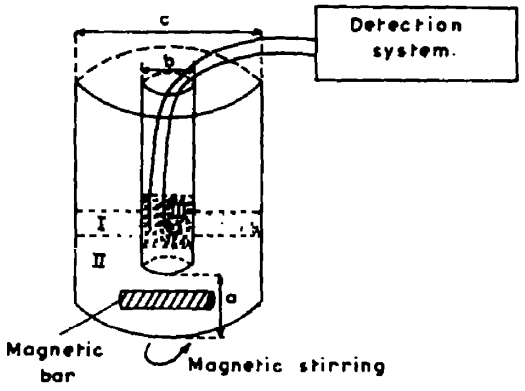

Fig. 6.

Other complexes of the tetraazaporphyrinogen

As an additional aspect of the properties of these polypyrazolic macrocycles it was decided to study the

Table 7. ^1H NMR spectra of tetraaza complexes with transition metal salts

R_1	R_2	CH_3COO^-	CH_3	CH_2	CH	C_6H_5	Cation	Anion	Stoichiometry[a]
CH_3	C_6H_5	2,02	2,50	5,30 5,50	6,27 6,67	7,50	Hg^{++} (b)	CH_3COO^-	1/4
C_6H_5	C_6H_5	2,02	-	5,45	6,60	7,53	Hg^{++}	CH_3COO^-	1/4
CH_3	C_6H_5	-	2,37	5,37 5,60	5,98 6,47	4,50	Ag^+	NO_3^-	-
C_6H_5	C_6H_5	-	-	5,48	6,27	7,53	Ag^+	NO_3^-	-
CH_3	CH_3	-	2,30	5,03	5,57	-	Ag^+	NO_3^-	-
CH_3	C_6H_5	2,02	2,28	5,22 5,33	5,88 6,22	7,48	Ag^+	CH_3COO^-	1/2
CH_3	CH_3	2,02	2,25	5,18	5,92	-	Ag^+	CH_3COO^-	1/2
CH_3	C_6H_5	2,03	2,37	5,2 broad: 5,83broad:	6,0 6,30	7,45	Cd^{++}	CH_3COO^-	1/1

(a) Stoiechiometry deduced by integration of the acetate methyl peak relative to the other signals.

(b) analysis : $C_{30}H_{28}N_8\left[Hg(CH_3COO)_2\right]_4\ 1H_2O$.

Table 8.

LIGAND	Alkali metal salt (a)																	
	Li^+			Na^+				K^+				Cs^+						
	I^-	Cl^-	CH_3COO^-	I^-	Cl^-	CH_3COO^-	SCN^-	I^-	Cl^-	CH_3COO^-	SCN^-	I^-	Cl^-	NO_3^-				
Tetraaza R_1=CH_3, R_2=C_6H_5 1	B	A	A	-	A	A	-	A	-	A	-	-b	-b	-				
Py-6 2	B	A	-	-	A	-	B	-	A	-	-	B	B	A	A			
Py-8 3	B	-b	-	B	-b	-	B	-b	-b	-b	-	-b	-b	-b				

(a) : the complexes with OH^- as anion were isolated in the synthesis of the macrocycles

(b) : both methods gave a negative result.

interaction of tetraaza with various cations such as Cd^{2+}, Hg^{2+} and Ag^{+}. These results are shown in Table 7.

It should be noted that for the Hg^{2+} complexes, the macrocycle coordinates four cations which indicates that each pyrazole ring associates one cation. This is a known phenomenon for Hg^{2+}-pyridine complexes.[12]

This type of complex (with Hg^{2+} and Ag^{+}) cannot be compared directly with these obtained with the alkali metal cations. However it does demonstrate the wide application of the macrocycles discussed in the present work for which three types of complexes have been shown to exist: (1) complexation by the sp^2 nitrogen lone pair of one pyrazole group; (2) complexation by the pyrazolylpyrazole or bipyrazolylmethane moiety (analogous to the polyamines); (3) complexation by the electronegative cavity (analogous to the crown ethers).

EXPERIMENTAL

Preparation of starting materials

The following products were prepared according to the literature method: tetraazaporphyrinogen 1;[2] Py-6 2;[3] Py-8 3;[3] 1,3,5-trimethylpyrazole;[13] 3,5,3',5'-tetramethyl-1,1'-dipyrazolylmethane 6;[3] 1',5',3,5-tetramethyl-3'-pyrazolyl-1-pyrazole 8;[3] the pyridine macrocycle 9.[11]

1',5',3,5-Tetramethyl-3',1-dipyrazolylmethane 5. Methylation of 3,5,5'(3')-trimethyl-1,3'(5')-dipyrazolylmethane[14] by the literature method[13] gave two isomeric products, 1',5,3,5-tetramethyl-3',1-dipyrazolylmethane 5 (yield 55%) m.p. 75-76° (petroleum ether); ^1H NMR ($CDCl_3$) 2.17 and 2.20, 3-, 5- and 5'-CH_3 (addition of several drops of C_6D_6 produced two coupled peaks (J = 0.7 Hz) and one uncoupled methyl peak); 3.67, N-CH_3; 5.08, CH_2; 5.77; 4- and 4'-H. 1',3',3,5-tetramethyl-5',1-dipyrazolylmethane (yield 25%) m.p. 72–73° (petroleum ether); ^1H NMR ($CDCl_3$) 2.17, 3-, 5- and 3'-CH_3 (similarly the addition of several drops of C_5D_6 produced an uncoupled methyl peak (I = 6H) assigned to the two methyls in positions 3 and 3' and a coupled peak (J = 0.7 Hz) due to the 5-CH_3); 3.73, N-CH_3; 5.12, CH_2; 5.80, 4- and 4'-H.

Linear tetrapyrazolic product 7. A solution containing 3,5,5'(3')-trimethyl-1,3'(5')-dipyrazolylmethane[14] (10^{-2} mole) and 3 - chloromethyl - 1',5',5 - trimethyl - 1,3' - dipyrazolylmethane (10^{-2} mole) (obtained by methylation of 3-hydroxymethyl-3'(5), 5-dimethyl-1, 3'(5')-dipyrazolylmethane[1] with bromomethane under the previously described[14] phase transfer catalysis conditions, followed by halogenation with thionyl chloride as previously described[1]) in DMF (100 ml) in the presence of KI (5×10^{-2} mole) was heated at 100°C for 2 hr. After filtration the DMF was removed under reduced pressure and the residue chromatographed on alumina (eluant: $CHCl_3$ + 1% ethanol): yield 65%; m.p. 123–124° (ether–petroleum ether); *m/e* 392; analysis $C_{21}H_{28}N_8$; ^1H NMR (C_6D_6) 1.53 (J: 0.7 Hz) 1.88 (J: 0.7 Hz) 1.94 (J: 0.7 Hz) 2.10 (J: 0.7 Hz) corresponding to the four methyl groups substituted at positions 5 in the pyrazole rings;[13] 2.32, CH_3's in positions 3; 3.07, N-CH_3; 5.05, 5.10 and 5.20, 3 × CH_2; 5.77, 5.83, 5.87 and 5.97, 4 × 4-H.

Preparation of the complexes

Two different methods of preparation were used: *Method A.* A mixture containing the finely ground alkali metal salt (200 mg) and the macrocycle (100 mg) in $CHCl_3$ (5 mL) was refluxed with stirring for 4 hr. After filtration and concentration of the organic phase a white solid was obtained and which was recrystallised in several cases (see discussion above). This method was used for complexes which were soluble in chloroform. *Method B.* A deuteriochloroform solution (1 ml) of the macrocycle (50 mg) was rapidly passed through a bed of the finely ground inorganic salt (200 mg). Where possible the NMR spectra of the complexes obtained by this second method were recorded immediately after filtration. Generally the filtrate gave an insoluble precipitate after several minutes, which was able to be recrystallised in certain cases. The same NMR spectra were obtained for compounds prepared by method B by simply adding 50 mg of the inorganic salt to a deuteriochloroform solution of the product studied.

For compounds which did not give a positive result by method B it was verified that a negative result was also obtained by method A.

The melting points of all the complexes isolated were greater than 300°C.

Results of complexation. With the alkali metals, see Table 8. For the linear products the only isolated complexes were obtained by method B with LiI. With Hg^{2+}, Cd^{2+} and Ag^{+} the tetraazaporphyrinogen complexes were prepared by method B.

Extraction, decomplexation and transport studies

Instrumentation. The reaction mixture was pumped through a cell in a UV spectrometer, and the absorbance changes at 355 nm were recorded as a function of time. Detector and Recorder: Elugraphe "SV". Residual volume of the system (pump, UV cell, tubing): 10 ml. Circulation rate: 20 ml/min. Agitation: magnetic bar 38 mm long and 8 mm in diameter rotating at 1 turn/sec. Standard curves have been obtained from solutions with known concentrations.

Extraction. The cylindrical reaction cell (46 mm diameter) contained a spectroscopic grade chloroform solution (50 ml) of the compound being studied (7×10^{-4} mole/l) and an aqueous solution (50 ml) of nitrate (or hydroxide) (10^{-1} mole/l) and metal picrate (7×10^{-4} mole/l). The organic phase was magnetically stirred and the complexation followed by monitoring the picrate anion concentration in the aqueous phase by UV spectrometry.

Decomplexation. The cell contained the previously produced chloroform solution of the complex and an equal volume of doubly distilled water. Decomplexation was followed by the appearance of the picrate anion in the aqueous phase.

Transport across a liquid membrane. The following apparatus was used (Fig. 6). a = 13 mm; b = 28 mm; c = 19 mm.

Phase I: aqueous solution (6 ml) of nitrate or hydroxide (10^{-1} mole/l) and alkali cation picrate (2×10^{-3} mole/l). Phase II: chloroform solution (50 ml) of the product to be studied (7×10^{-4} mole/l). Phase III: distilled water (24 ml).

The appearance of the picrate anion in phase III was followed by UV spectrometry or by conductimetry (in the latter case the electrode was immersed directly in phase III).

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