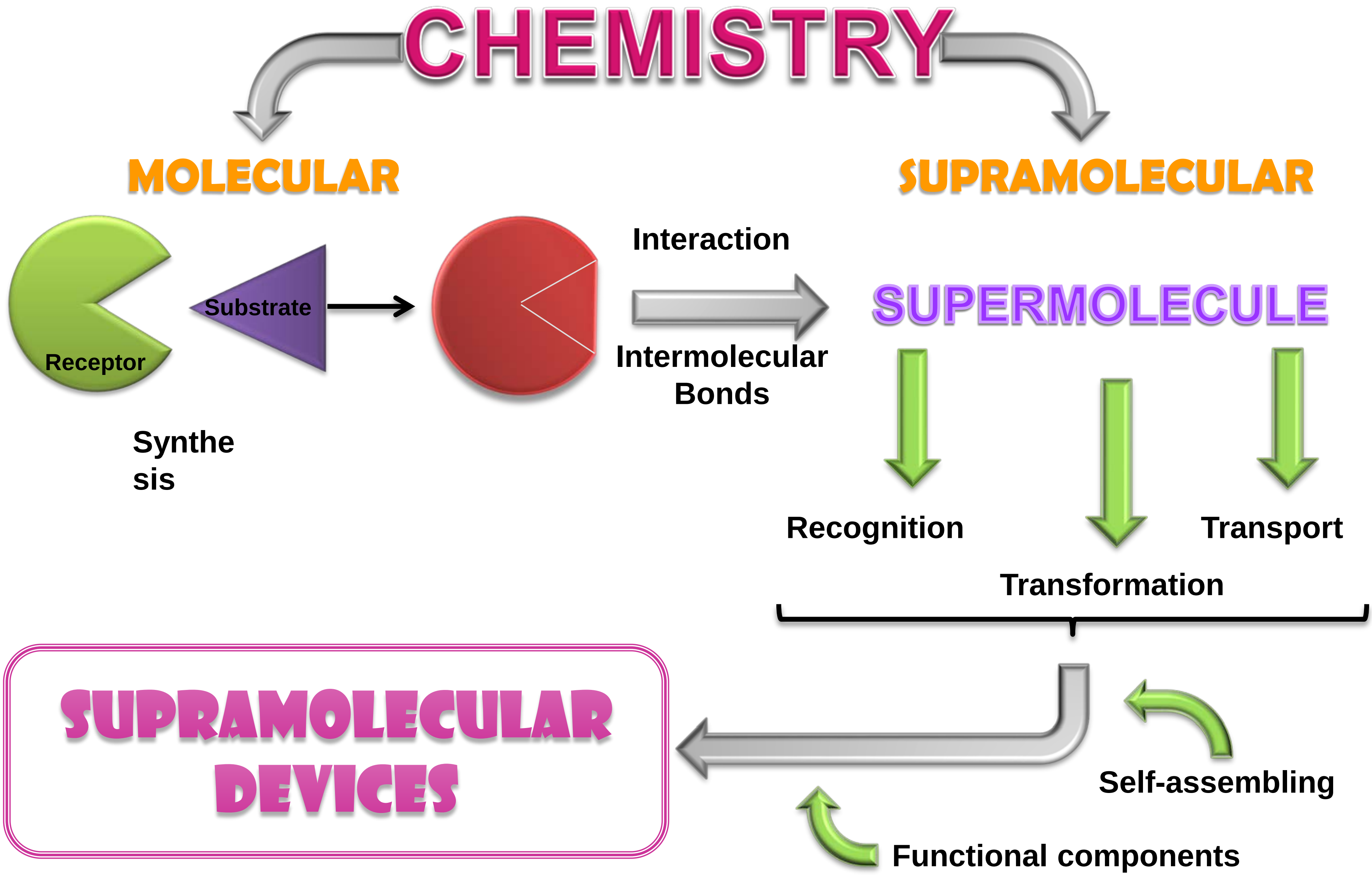
Supramolecular Chemistry:

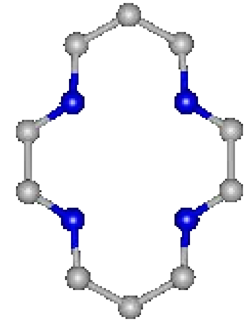
Chemistry Beyond the Molecule.

Instituto de Ciencia Molecular (ICMol)

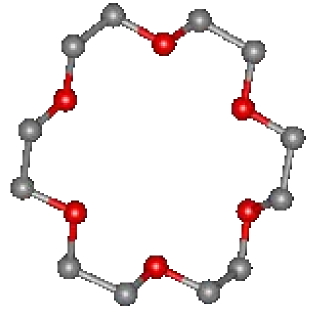
Master "Nanociencia y Nanotecnología Molecular"


CHEMISTRY
MOLECULAR
SUPRAMOLECULAR
Substrate
Receptor
Interaction
Intermolecular
Bonds
SUPERMOLECULE
Synthe
sis
Recognition
Transport
Transformation
SUPRAMOLECULAR
DEVICES
Self-assembling
Functional components

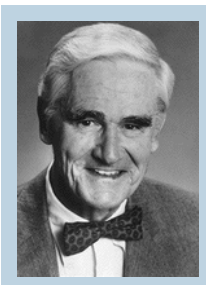
1987 D. J. Cram, J.-M. Lehn, C. J. Pedersen: for the design and properties of supramolecular systems

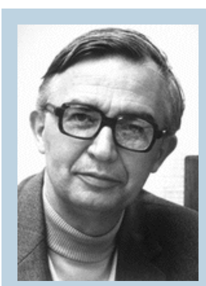


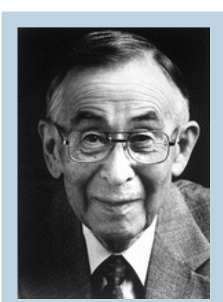
CYCLAM
$[14]aneN_4$

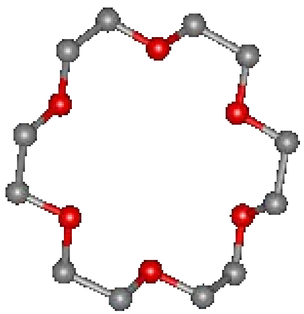


18-crown-6

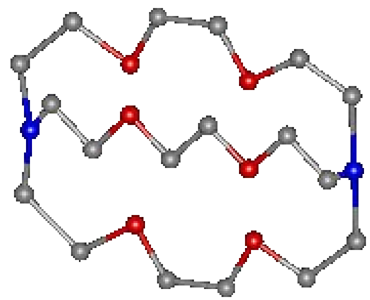




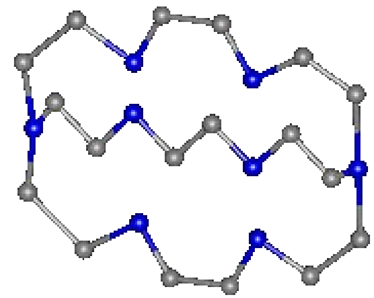




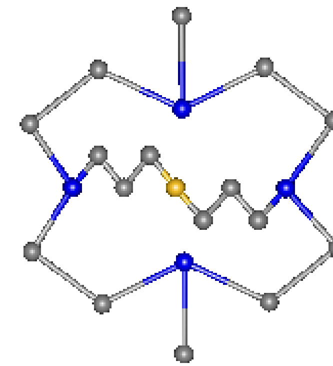
18-crown-6



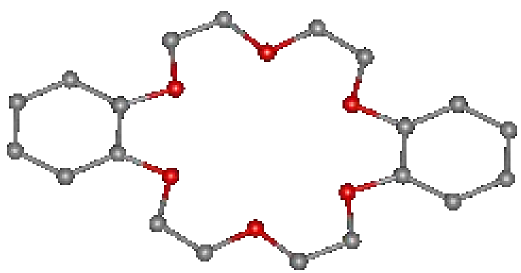
C222



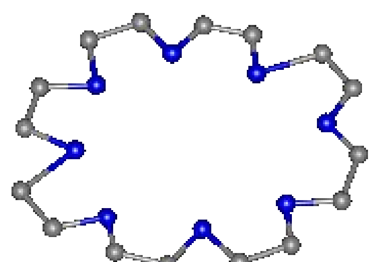
Sepulcrand



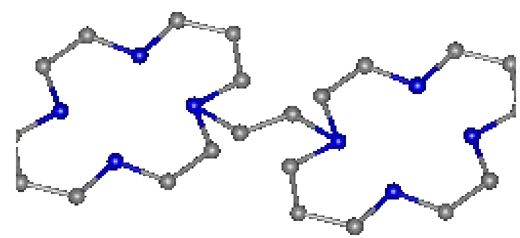
12,17-dimethyl-5-tia-
1,9,12,17-tetraazabiyciclle
[7.5.5]nonadecane



Dibenzo-18-corona-6



$[24]aneN_8$



Bis-cyclam

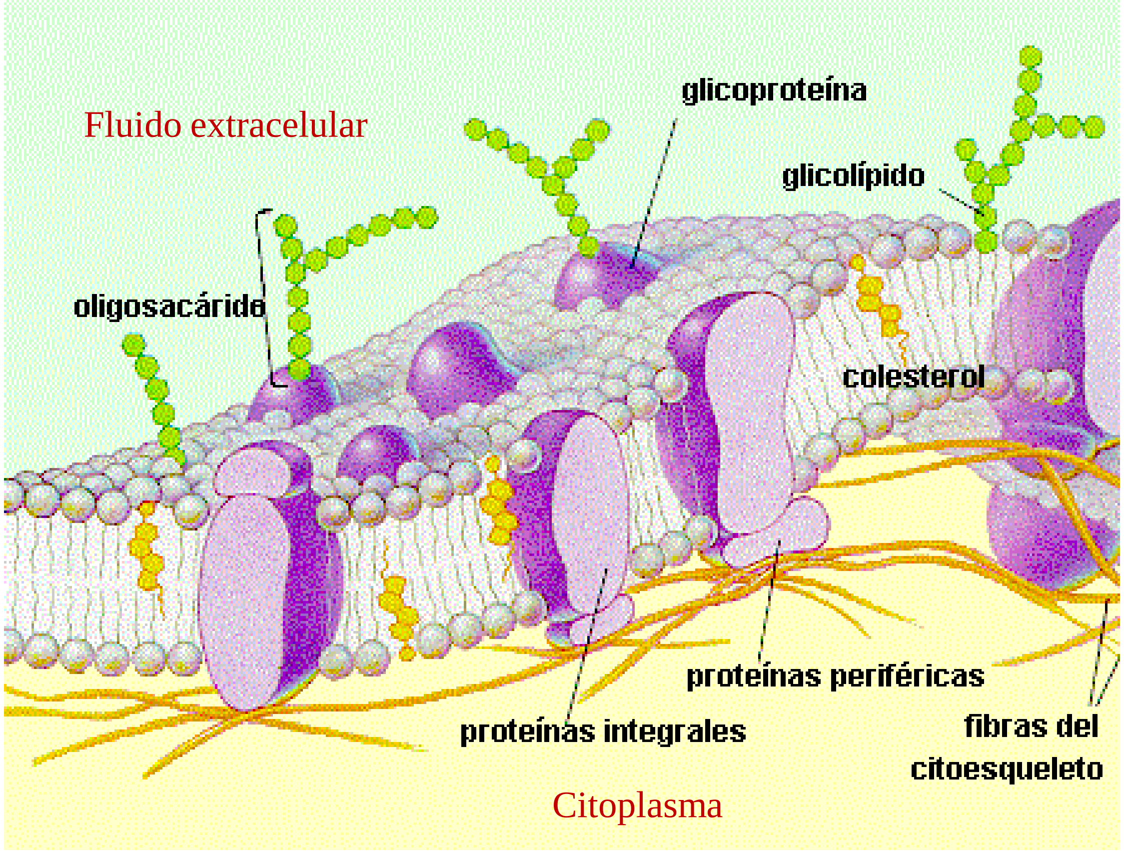
INTERACTION WITH ALKALI METAL IONS

Chemical Features and Distribution of Na^+, K^+, Ca^{2+} y Mg^{2+}.

Property	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Ionic radius (Å)	1,02	1,33	1.00	0.72
Relative value q/r (K^+ = 1)	1.30	1,00	2,66	3,70
Preferred coordination number	6	6-8	6-8	6
Hydration energy (kJ mol^{-1})	412	337	1516	1890
Preferred donor atoms	O	O	O	O, N

Concentration (mM)	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Human Erythrocytes (Intracelular)	11	92	10^{-4}	2,5
Blood Plasma (Extracelular)	152	5	1,5	1,5
Interior of the squid nerve	10	300	$5x10^{-4}$	7
Exterior of the squid nerve	440	22	10	55

Biochemistry of the alkali and alkaline earth metal ions

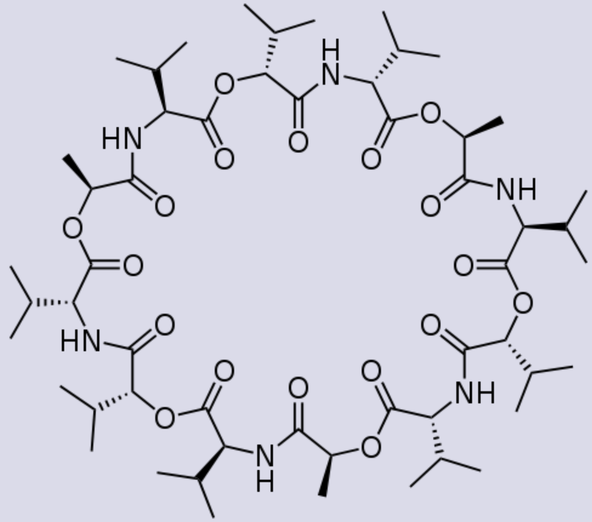


❖The membranes allow the selective flow of certain substrates. The concentration gradient and the flow of substrates between inside and outside is maintained by the performance of pumps and channels.

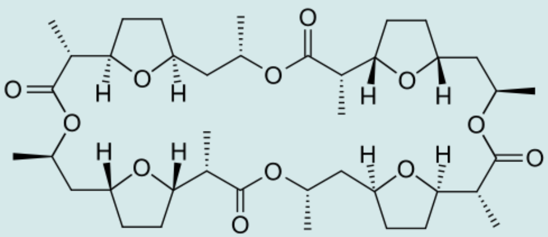
❖Membranes control the flow of information between cells and their environment.

Biologic Ionophores

Valinomycin

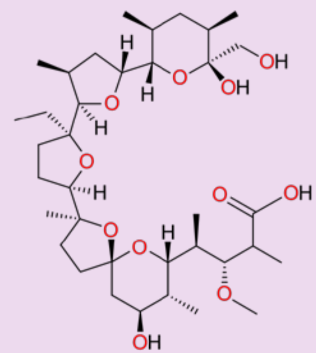


K^+



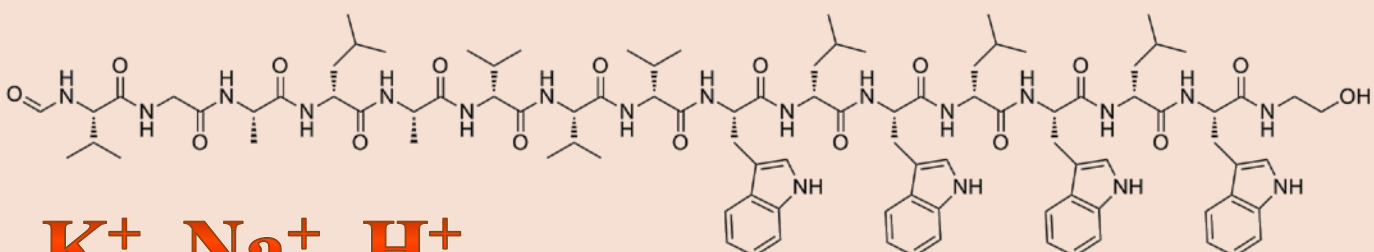
Nonactin

K^+, NH_4^+



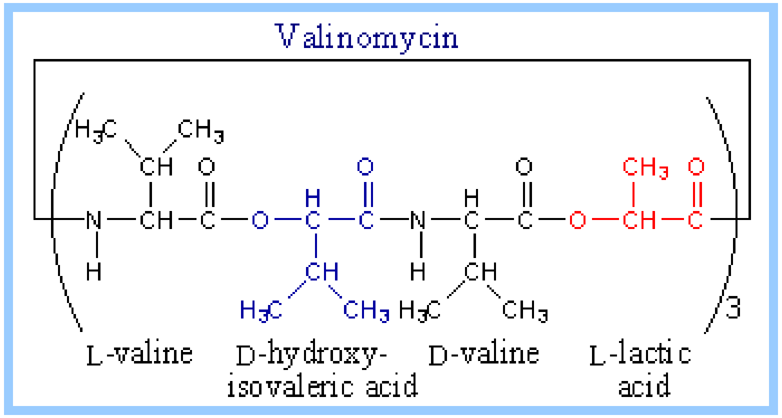
Na^+, H^+

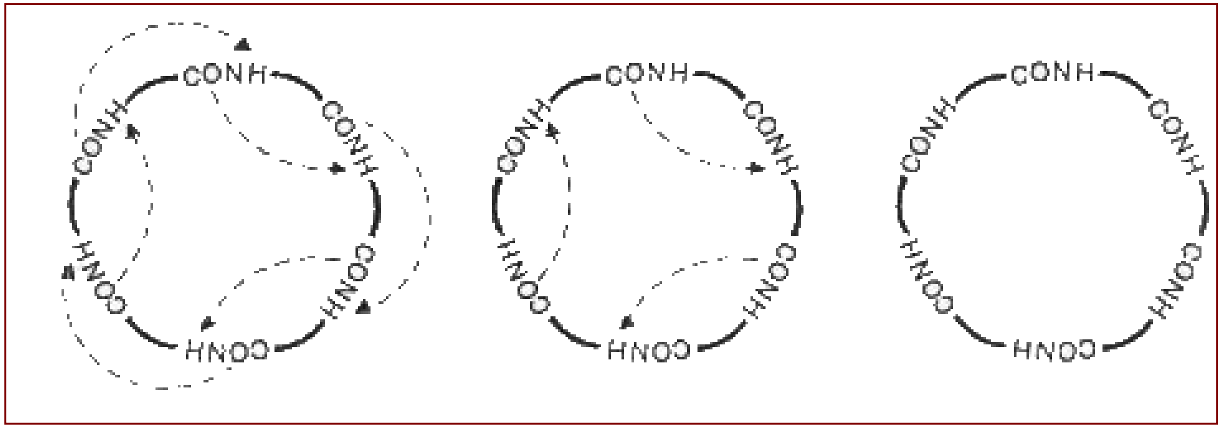
Monensin



K^+, Na^+, H^+

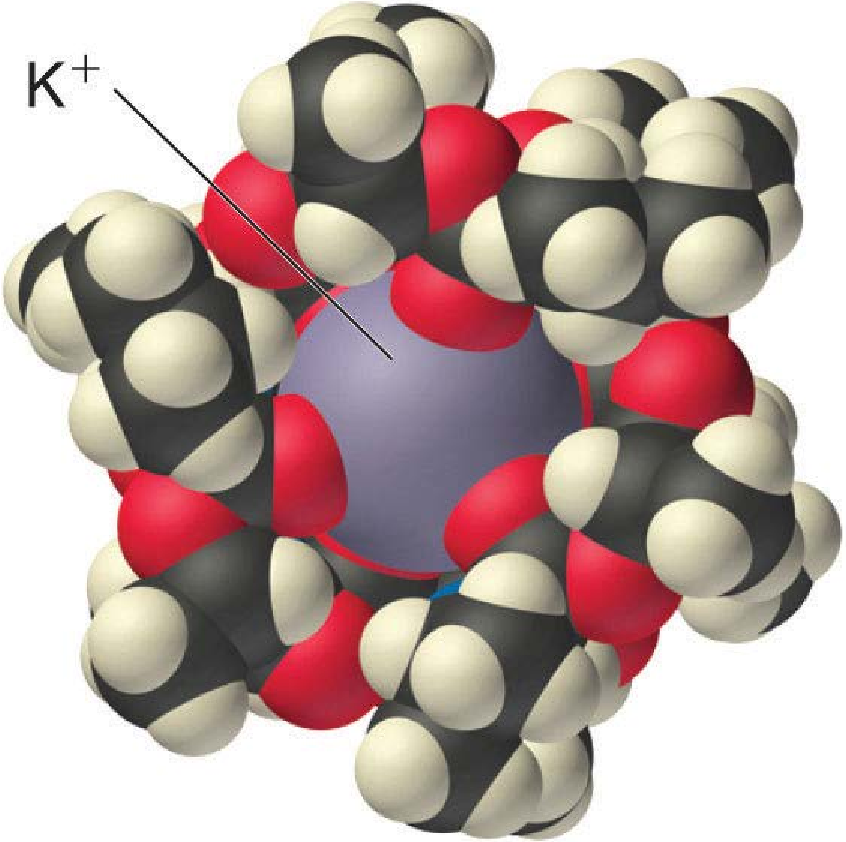
Gramicidin A





Valinomycin conformation in : a) CCl_4, b) ethanol and c) H_2O

K^+-Valinomycin



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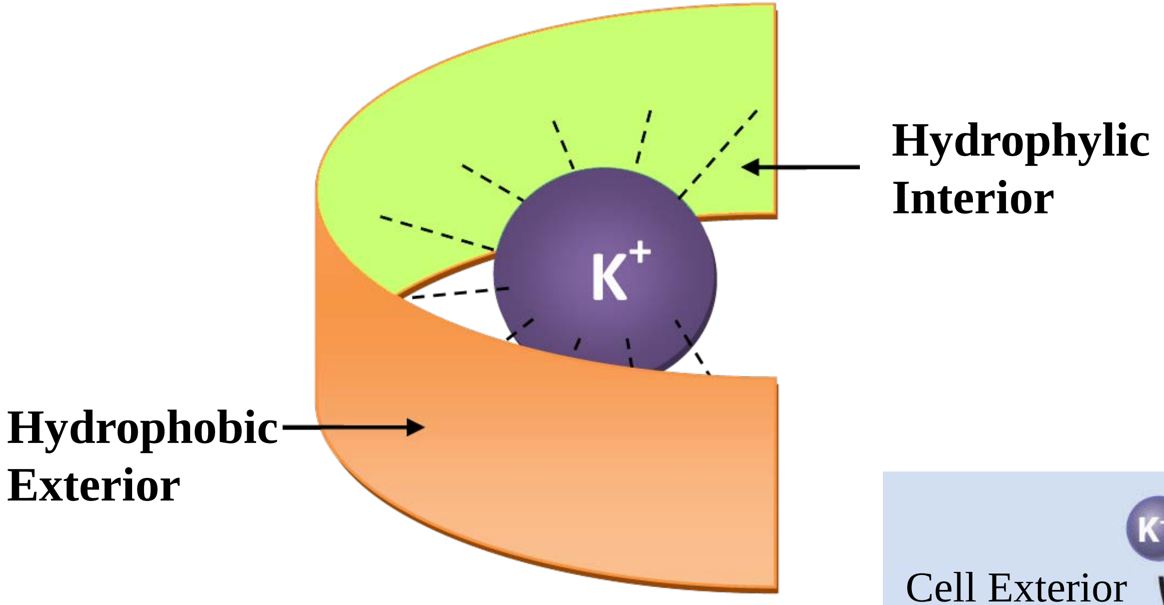
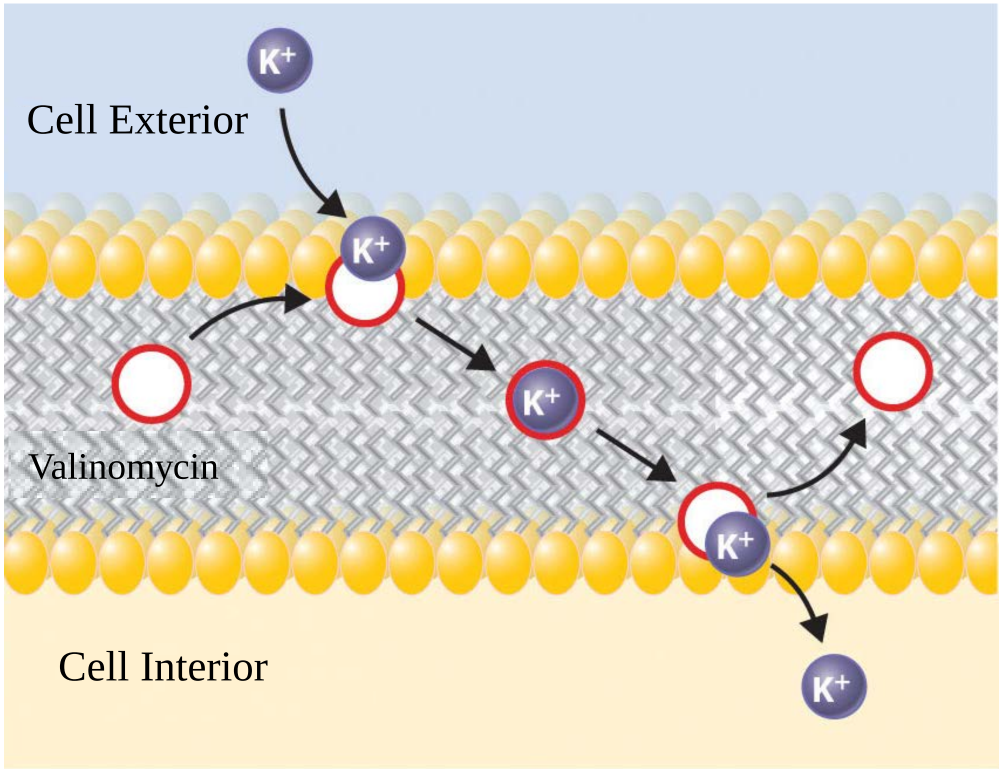
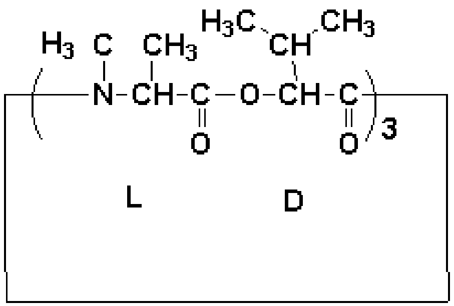
B. G. Cox, H. Schneider, "*Coordination and Transport Properties of Macrocyclic Compounds in Solution*", Elsevier, Amsterdam , 1992.

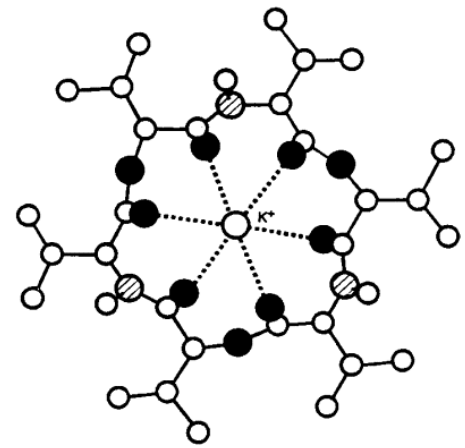
K^+ transport through membrane

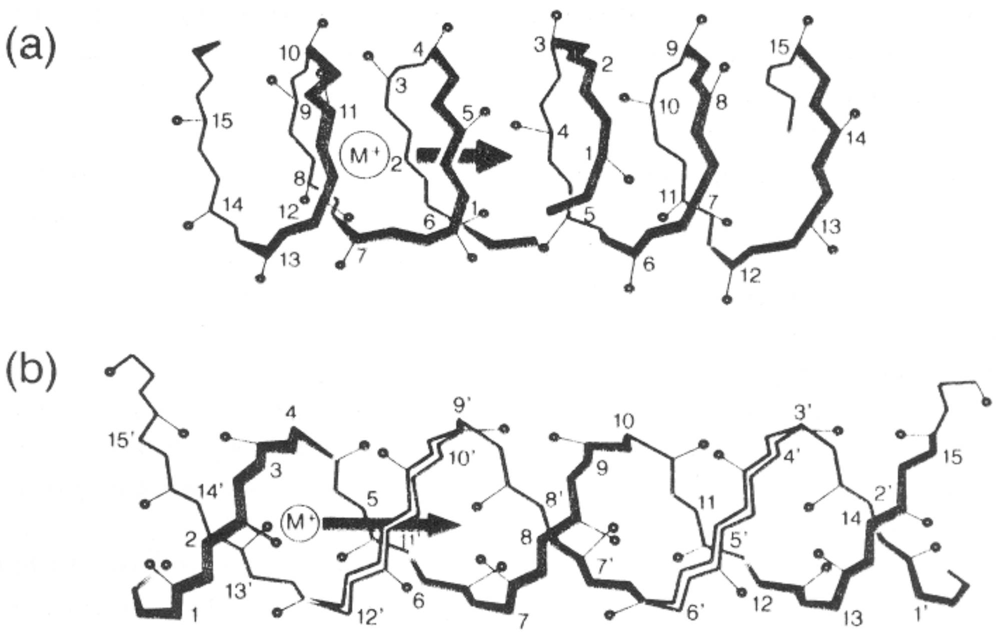




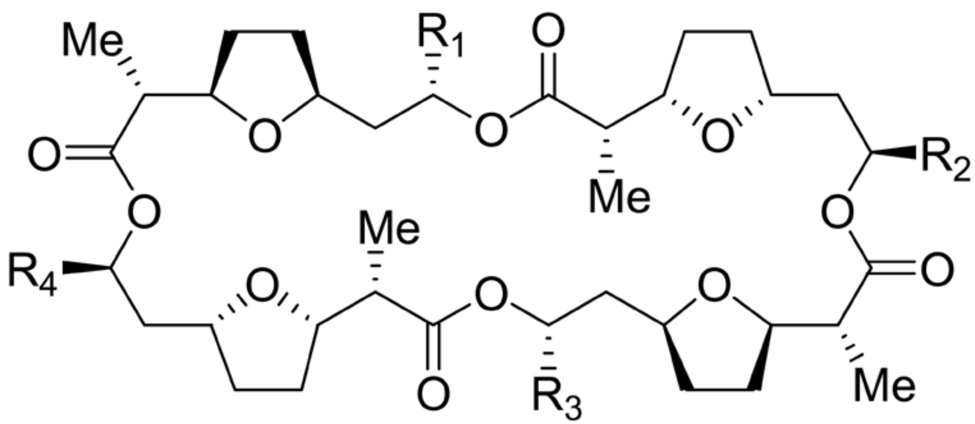


R = bencilo, beauvericina
R = isobutilo, eniantina A
R = isopropilo, Eniantina B

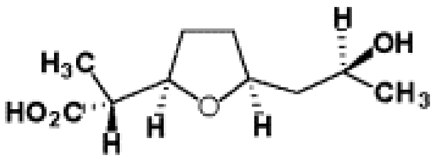




Actins

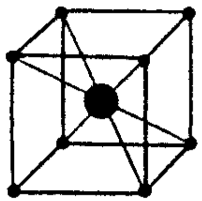


	R_1	R_2	R_3	R_4
Nonactin	CH_3	CH_3	CH_3	CH_3
Monactin	CH_2CH_3	CH_3	CH_2CH_3	CH_3
Dinactin	CH_2CH_3	CH_3	CH_2CH_3	CH_3
Trinactin	CH_2CH_3	CH_2CH_3	CH_2CH_3	CH_3
Tetranactin	CH_2CH_3	CH_2CH_3	CH_2CH_3	CH_2CH_3

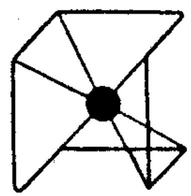


Ácido (-)-nonactico

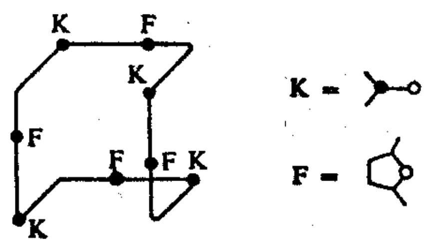
Nonactina

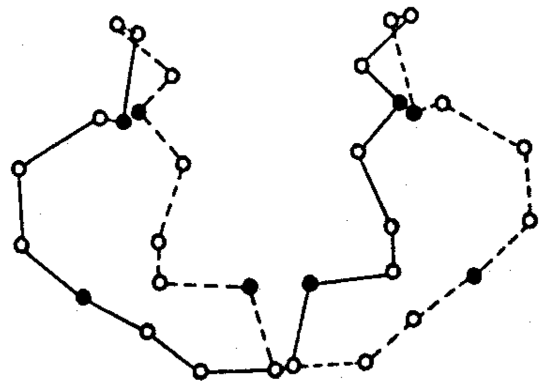


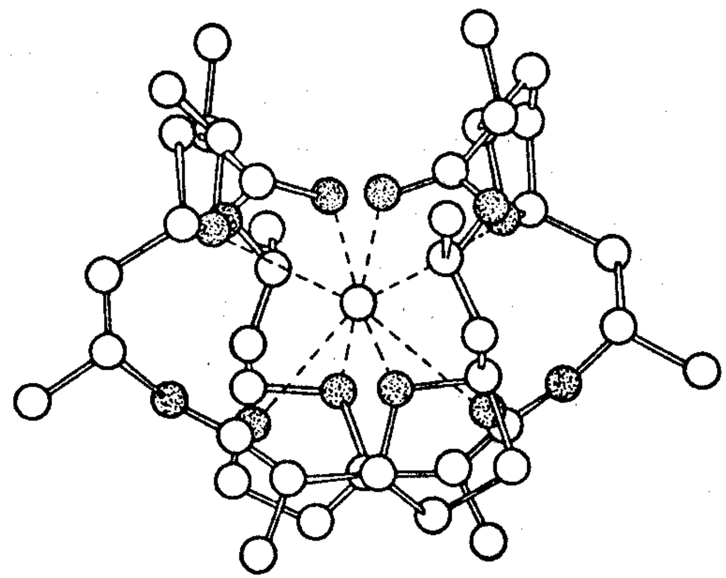
Disposición cúbica

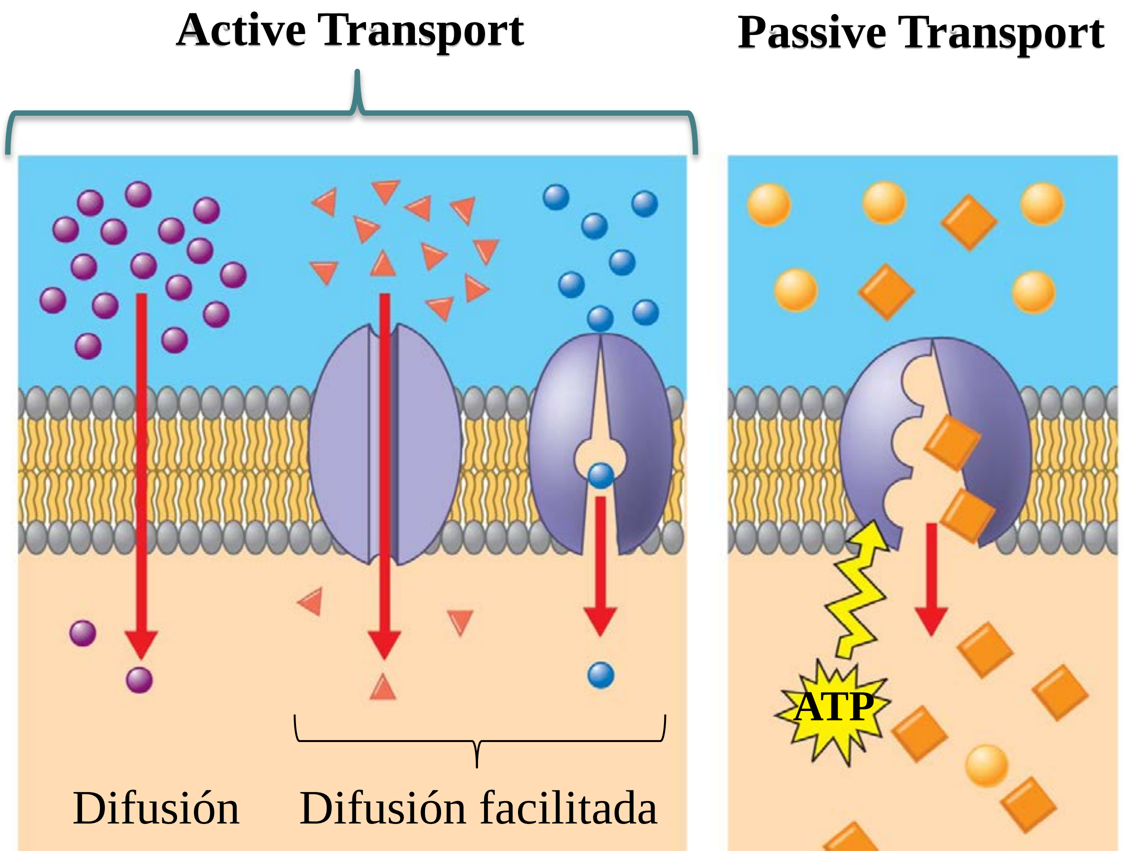


Disposición en forma de costura de pelota de tenis







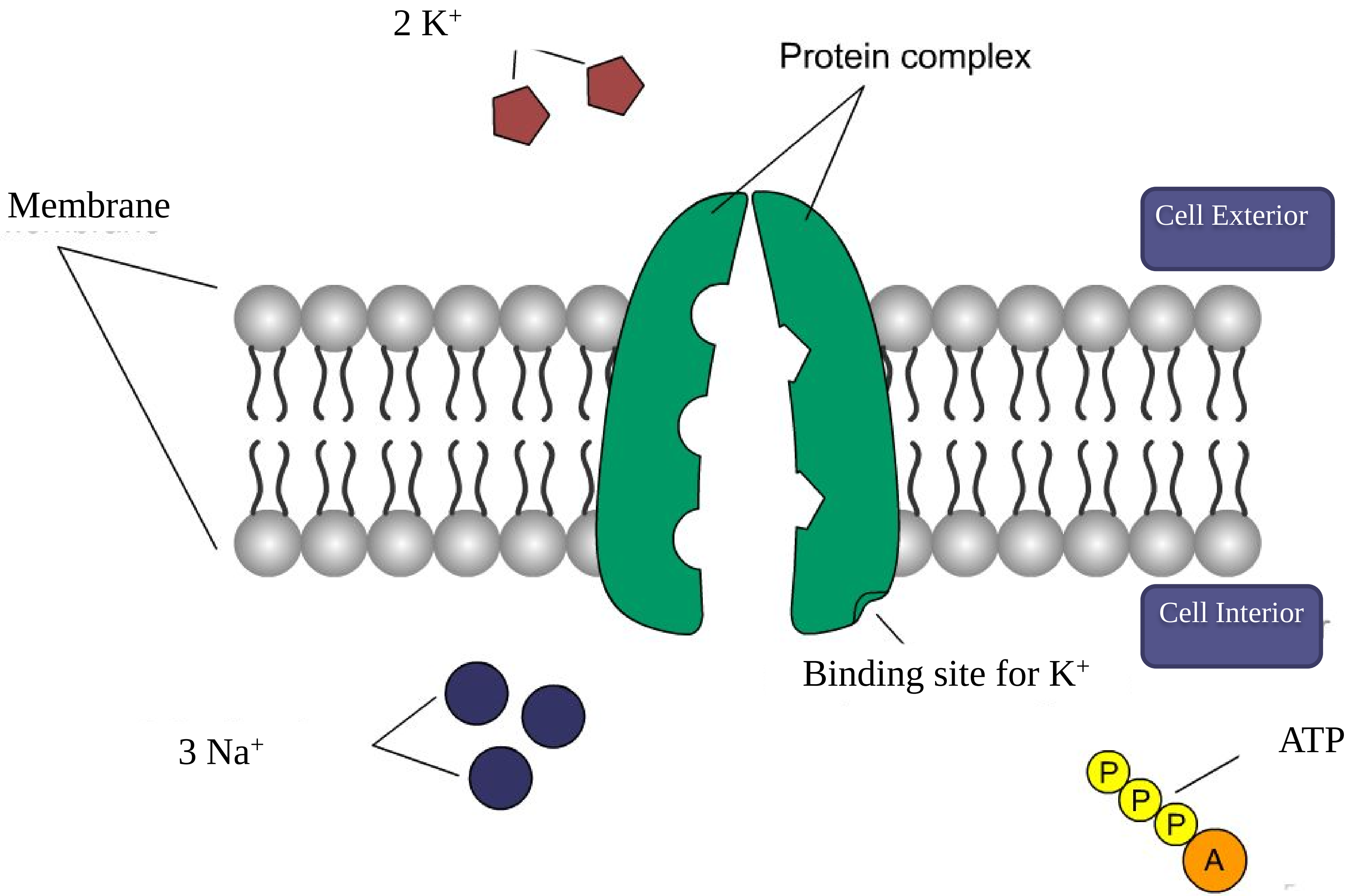


- The transport can be divided into passive and active as it occurs associated with favorable or unfavorable ΔG values, that is, for or against a concentration gradient.

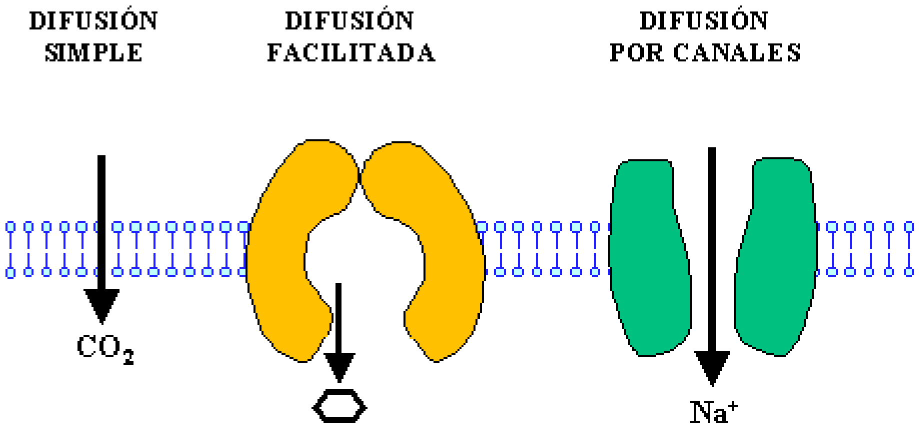
- For a charged species: $\Delta G = 2.303RT\log C_R/C_F + zF\Delta V$

- If we consider concentrations of extra and intracellular Na^+ 152 and 11 mM and T = 310 K ΔV = -70 mV, the energy for the passage of these ions from the inside out is +13.5 kJ mol^{-1}. For [K +] i = 92 mM and $[K^+]_e$ = 0.75 kJ mol^{-1} from inside to outside.

Na^+ / K^+ ATPasa Pump



Passive Transport



- Passive transport describes processes that occur in favor of a concentration gradient.

- This transport is carried out by transmembrane alostéricas proteins called channels that have opening devices based on:

i) electrical stimuli

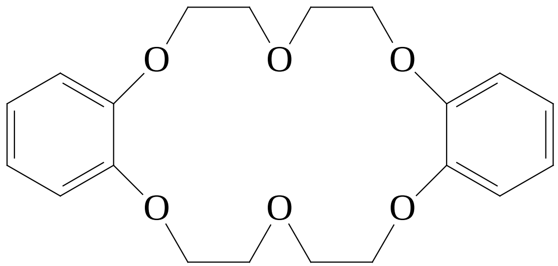
ii) chemical stimuli (effectors)

iii) mechanical stimuli

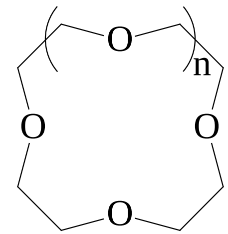
- By compounds of discrete molecular mass included in the organic phase that can act as ionophores..

SYNTHESIS

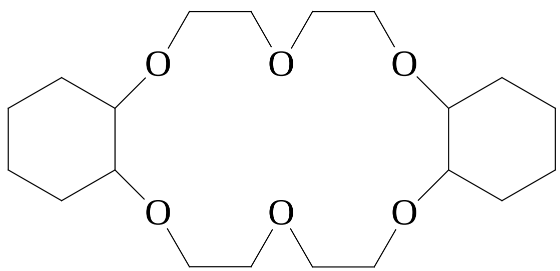
Abiotic Macrocycles



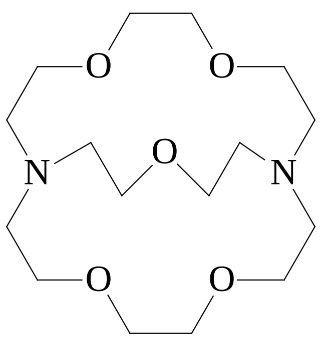
DB18C6



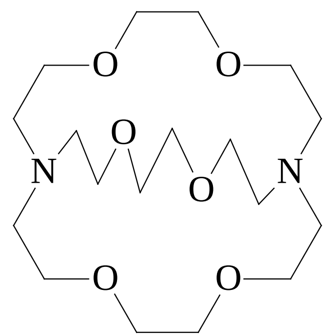
n = 1	**14C4**
n = 2	**15C5**
n = 3	**18C6**



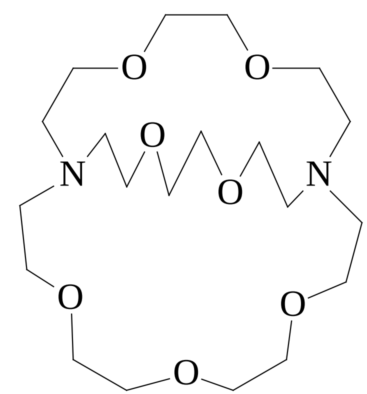
DCH18C6



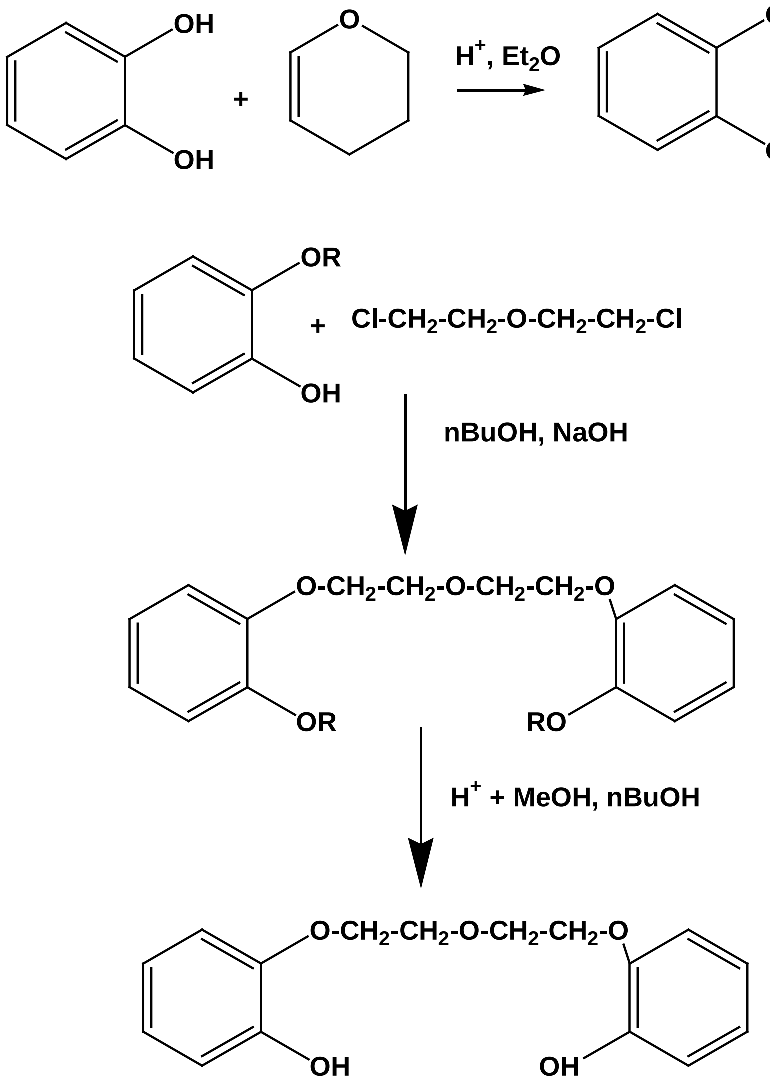
C2.2.1

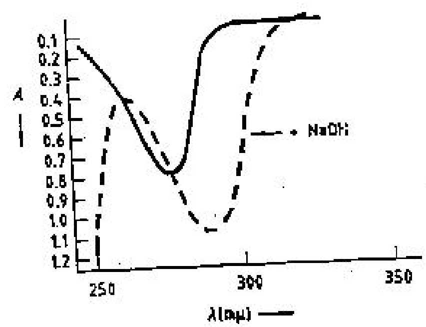


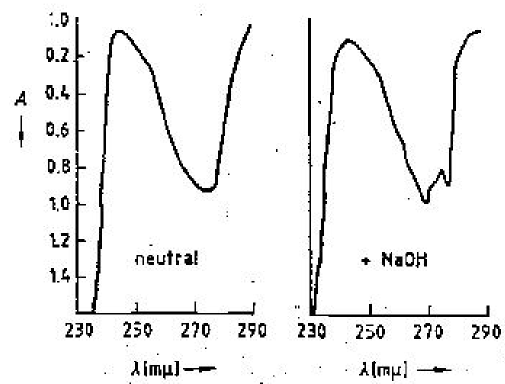
C2.2.2



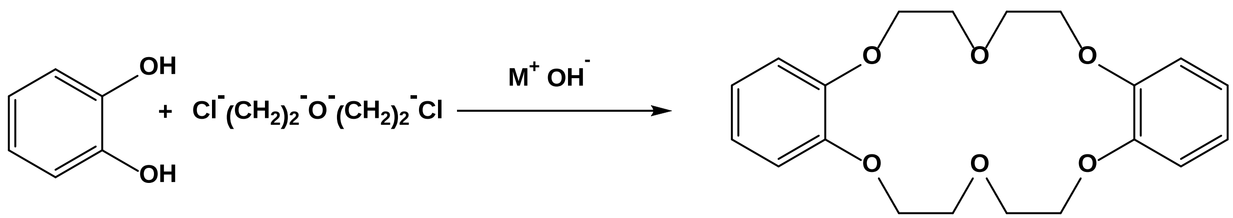
C3.2.2

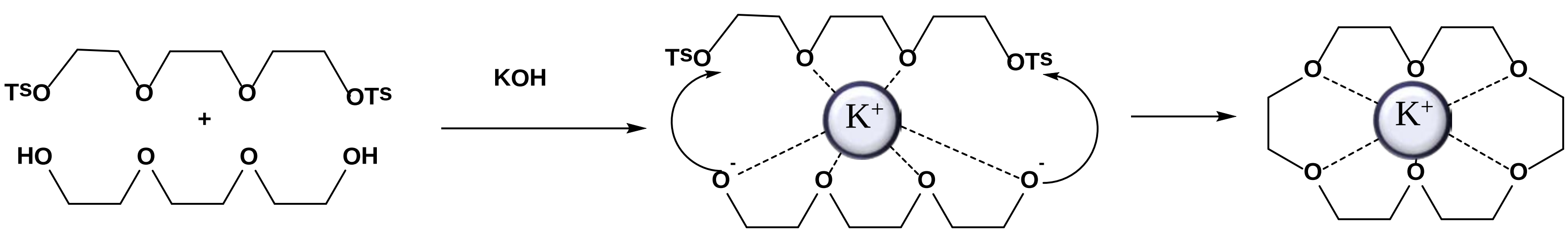

OH
OH
+
O
H+, Et2O
O
O
OH
OR
OH
+
Cl-CH2-CH2-O-CH2-CH2-Cl
nBuOH, NaOH
O-CH2-CH2-O-CH2-CH2-O
OR
RO
H+ + MeOH, nBuOH
O-CH2-CH2-O-CH2-CH2-O
OH
OH


A
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
+ NaOH
250
300
350
λ(mμ)


A
0.2
0.4
0.6
0.8
1.0
1.2
1.4
neutral
+ NaOH
230
250
270
290
λ(mμ)

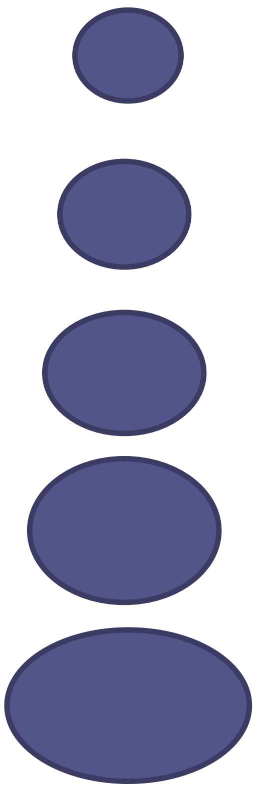
Crown Ether Synthesis





Akali metal ions (Spheric Ions)

$$M^+ (aq) + L (aq) \rightarrow ML^+ + nH_2O$$



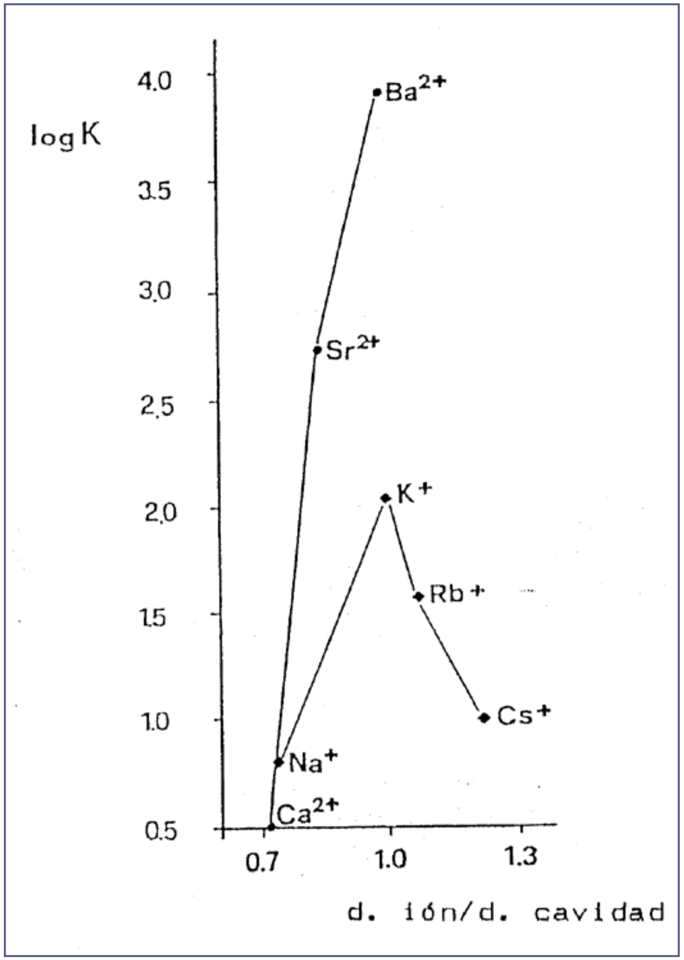
	R (Å)	-ΔGº (KJ mol⁻¹)
Li^+	0.60	511
Na^+	0.90	411
K^+	1.33	337
Rb^+	1.48	316
Cs^+	1.69	284

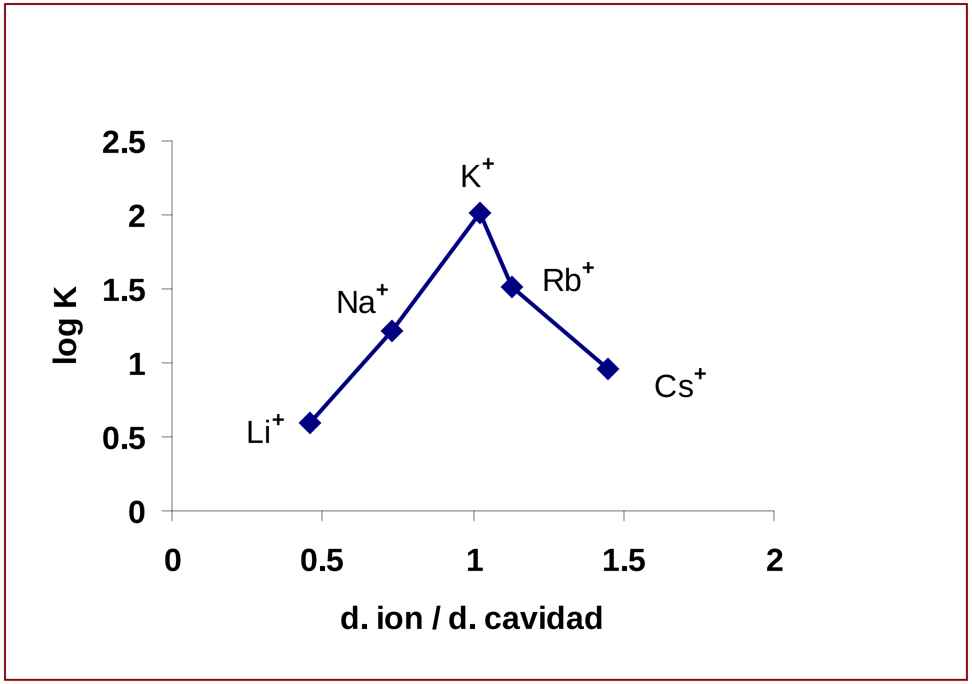
- Hard acids
- Preference for O versus N
- Competition with the solvent
- Weak interactions
- Non-directional bonds

Factors that affect stability

- Relationship between the size of the cavity and the metal ion
- Number and type of donor atoms
- Solvent
- Number and type of chains. Molecular topology

Selectivity





$$[M(H_2O)]^{n+} + L \leftrightarrows [ML]^{n+} + nH_2O$$

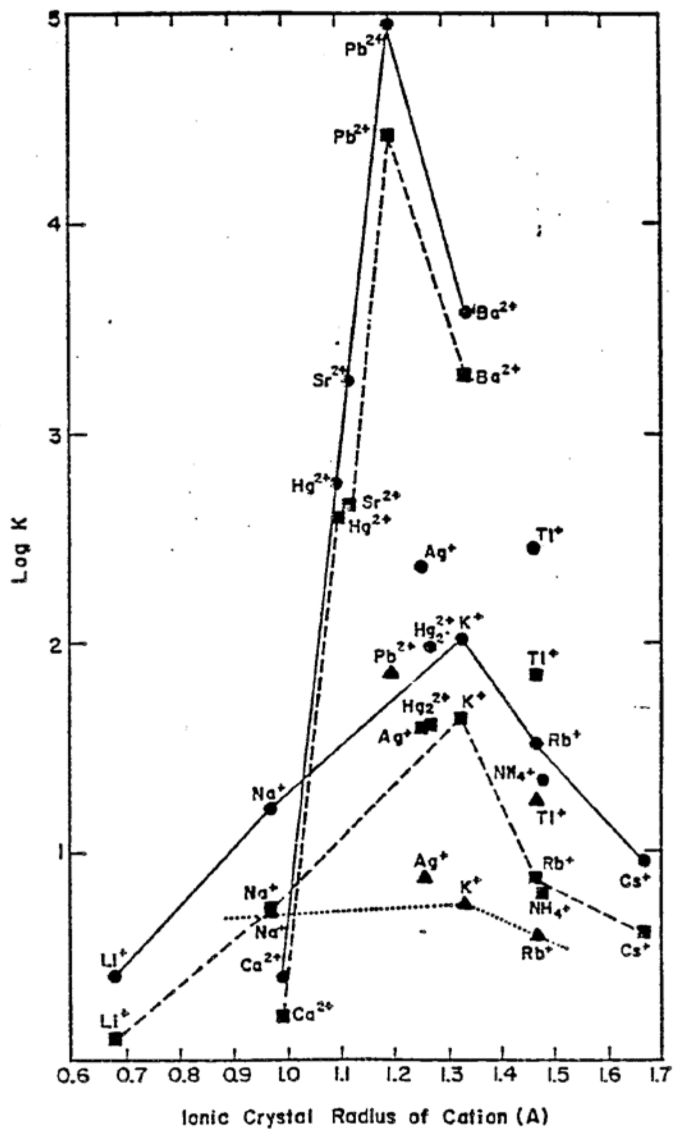
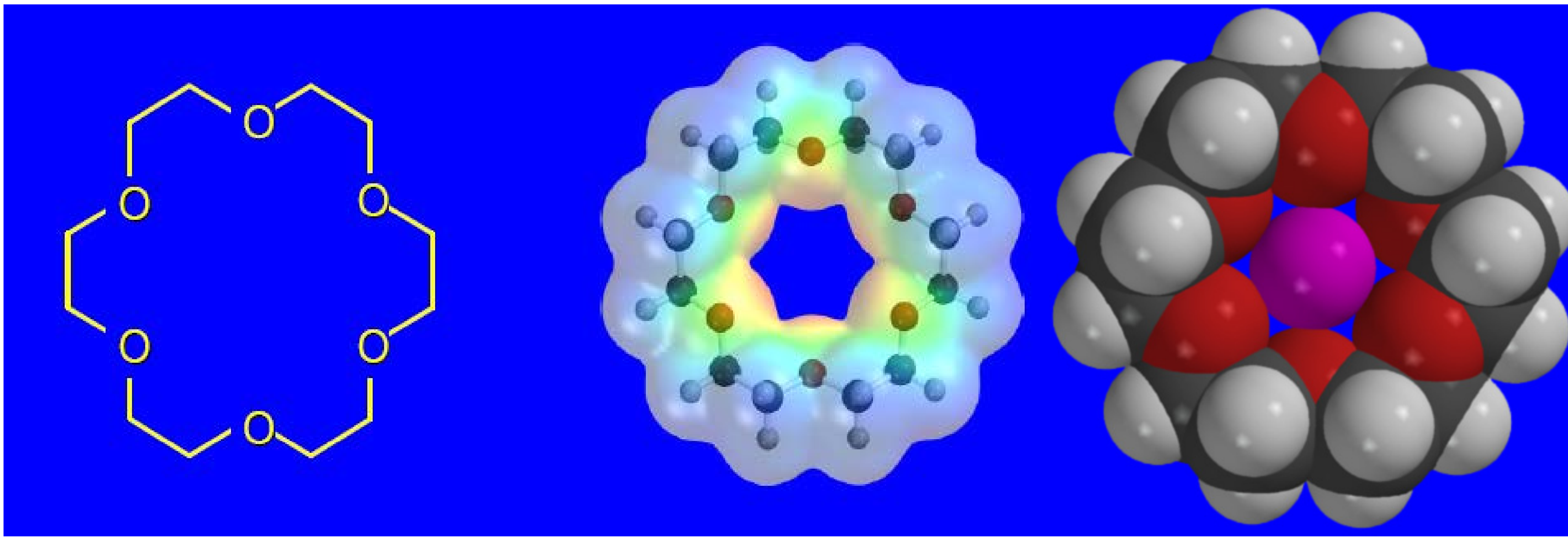


Fig. 1. Plot of log K *vs* cation radius for the reaction in aqueous solution, $M^{n+} + L = ML^{n+}$ where L = dicyclohexyl-18-crown-6, isomer A (●), dicyclohexyl-18-crown-6 isomer B (■), or 15-crown-5 (▲). T = 25°. (*4, 14*)

18-crown-6



[18]corona-6

$[K([18]corona\text{-}6)]^{+}$

KF is soluble in benzene in the presence of 18-crown-6

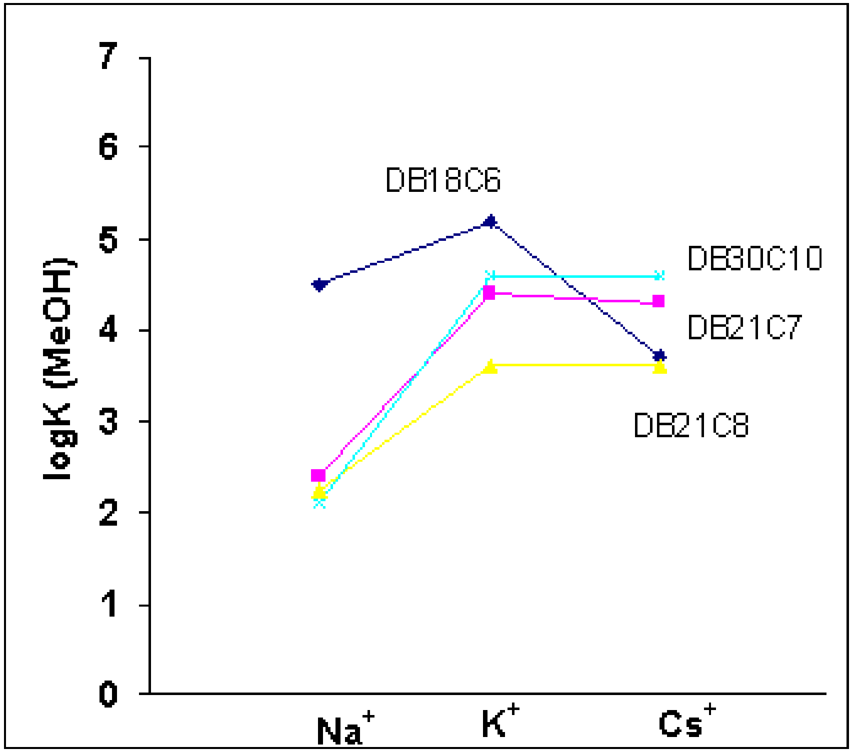
Size of crown ther vs crystallographic radius alkali ions

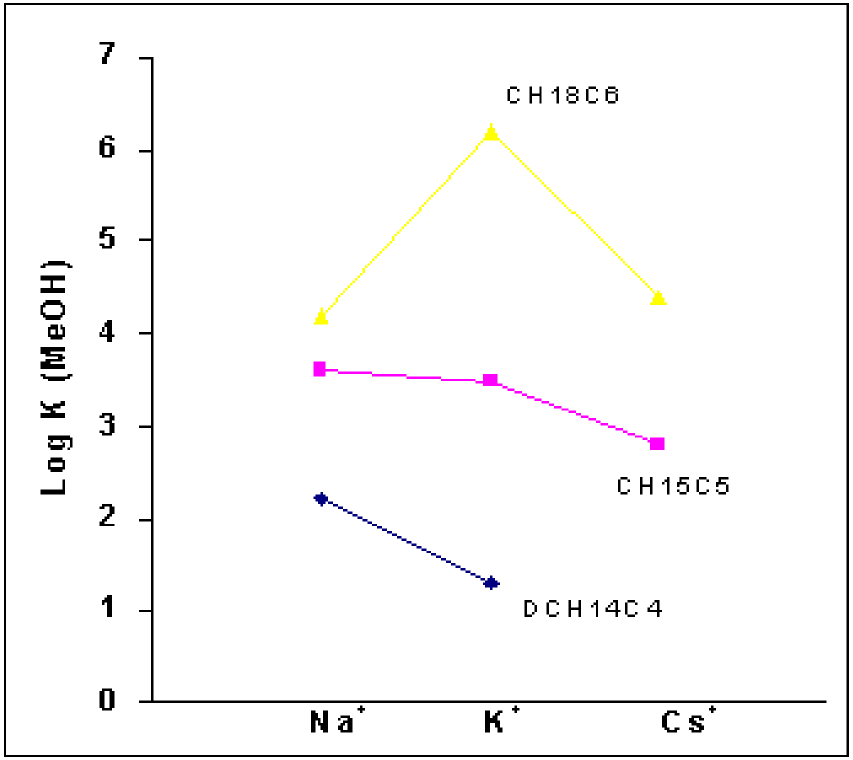
Ion	Diameter (pm)	Cyclic Polyether	Cavity Diameter (pm)*
		14-corona-5	120-150
Na^+	190	15-corona-5	170-220
K^+	266	18-corona-6	260-320

- * Obtained from models and crystallographic data.

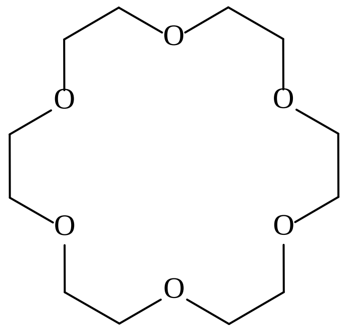
Ligand	**Na^+**	**K^+**	**Ag^+**
18-crown-6	0.3	2.1	1.6
15-crown-5	0.7	0.7	0.9

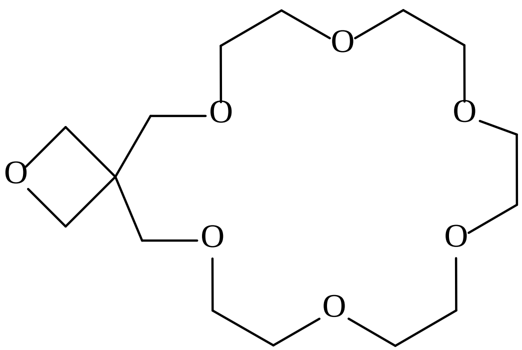
Size of the cavity and solvent

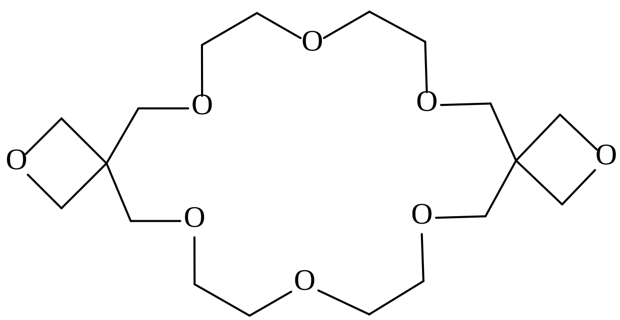




Size of the cavity and solvent



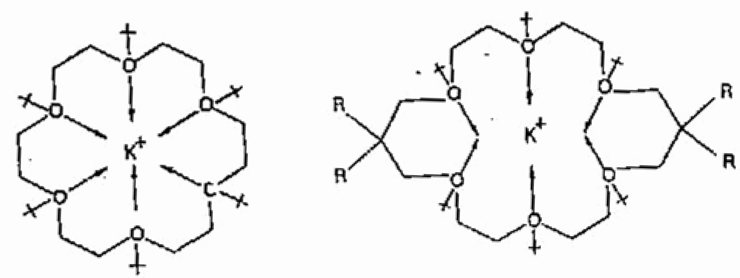


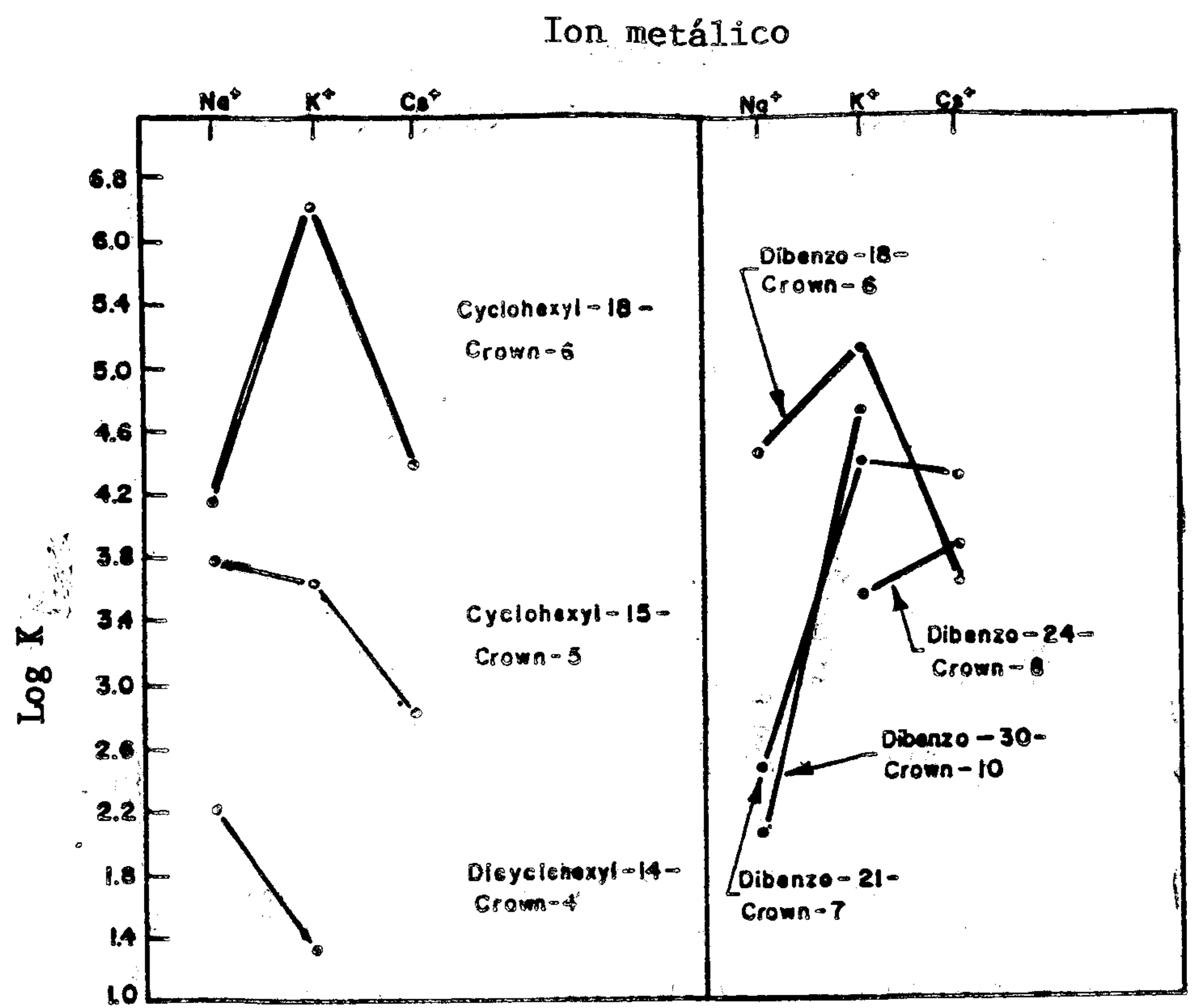


Logarithm of the stability constant of the metal complexes with 18-crown-6 and with the 19-crown-6 and 20-crown-6 derivatives determined in methanol at 25 ° C.

Na^+	K^+	Rb^+	Cs^+
4.36	6.10	5.35	4.61
	3.81		
<0.8	1.8;1.65	1.4	0.8

Rappresentazione schematica della orientazione dei dipoli degli atomi donatori nei complessi di K^+ con 18-corona-6 e con un 20-corona-6 sostituito.



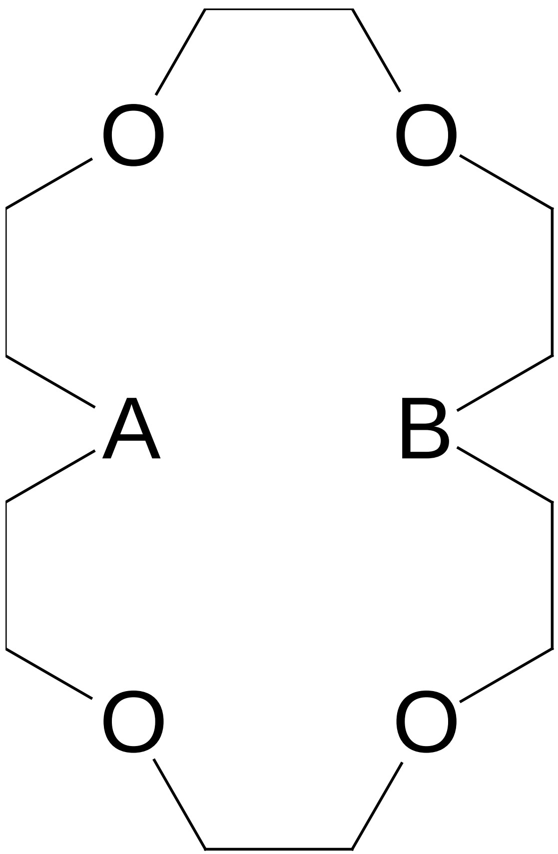


Ion metálico
Na+
K+
Cs+
Na+
K+
Cs+
Log K
6.8
6.0
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
Cyclohexyl-18-
Crown-6
Cyclohexyl-15-
Crown-5
Dicyclohexyl-14-
Crown-4
Dibenzo-18-
Crown-6
Dibenzo-24-
Crown-8
Dibenzo-30-
Crown-10
Dibenzo-21-
Crown-7

. log K values for
M + L = ML (L = 18-crown-6).

A	B	K^{+} [a]
O	O	6,10
NH	O	3,90
NH	NH	2,04
S	S	1,15

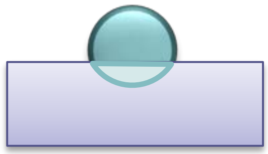
a) Data in methanol.



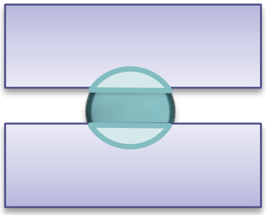
MOST COMMON STOICHIOMETRIES AND PROBABLE STRUCTURES OF CROWN ETHER COMPLEXES WITH ALKALI IONS.

L / M **L / M**

1:1

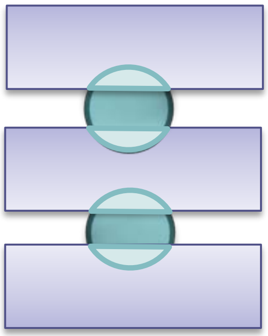


2:1



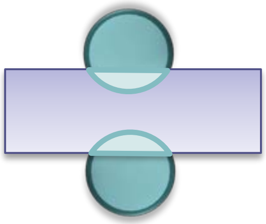
sandwich

3:2



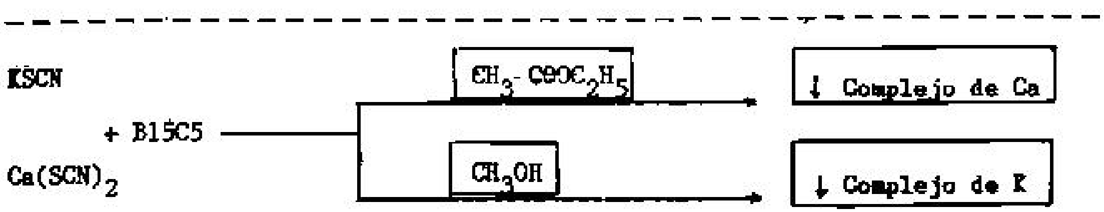
club sandwich

1:2



sandwich invertido

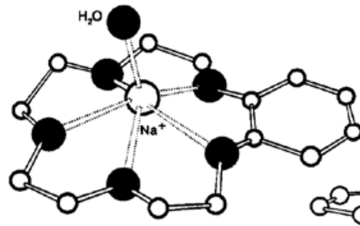
The synthesis of these compounds consists of hot dissolving the salt of the metal ion and the ligand in an appropriate non-aqueous solvent; when allowed to cool, the precipitation of the appropriate complex occurs

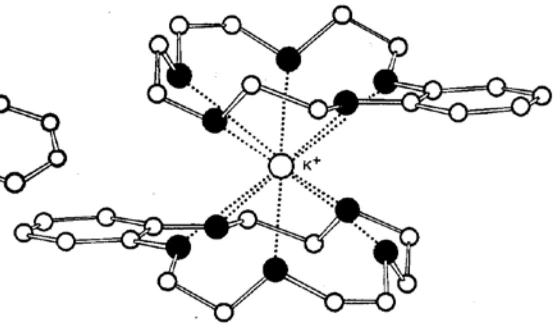


-Sandwich

-Inverted Sandwich

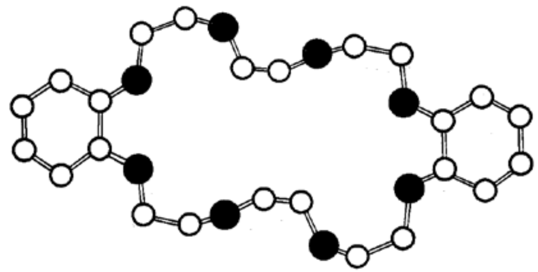
-Club Sandwich



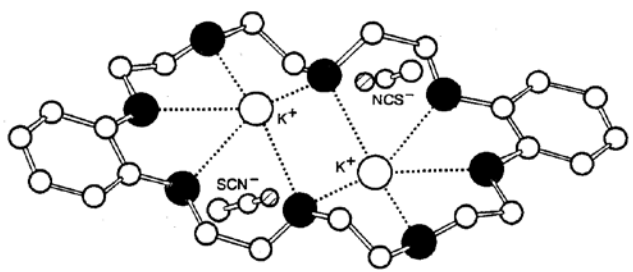


44 Na^+– B15-crown-5

45 K^+– (B15-crown-5 $)_2$

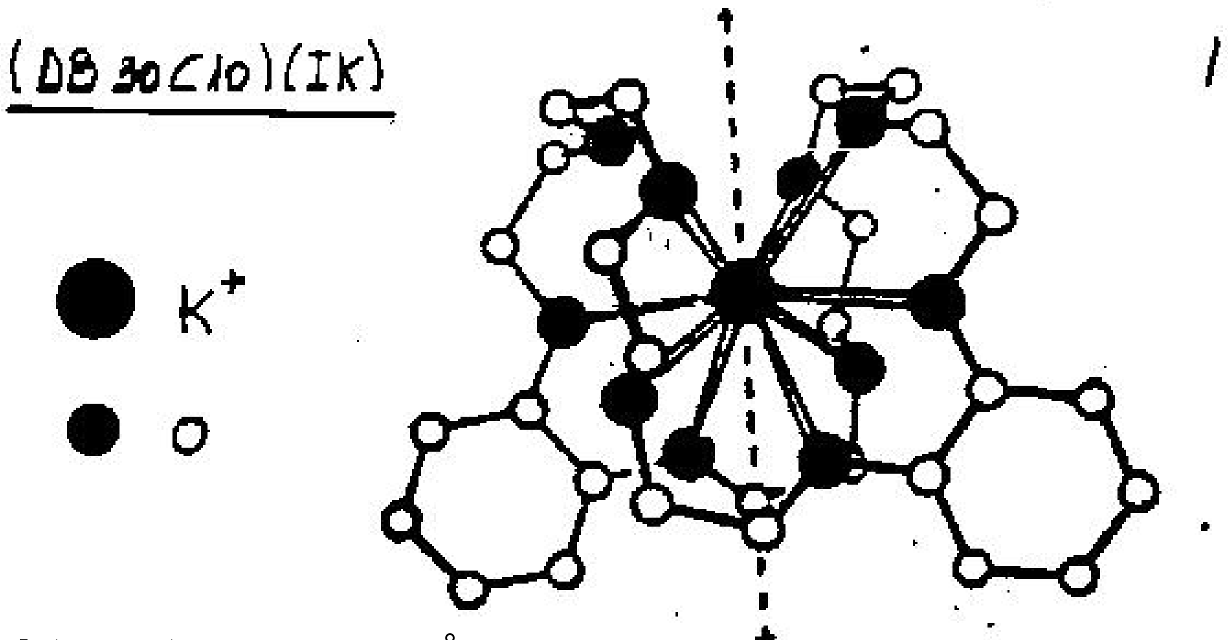


46 B_2 24-crown-8



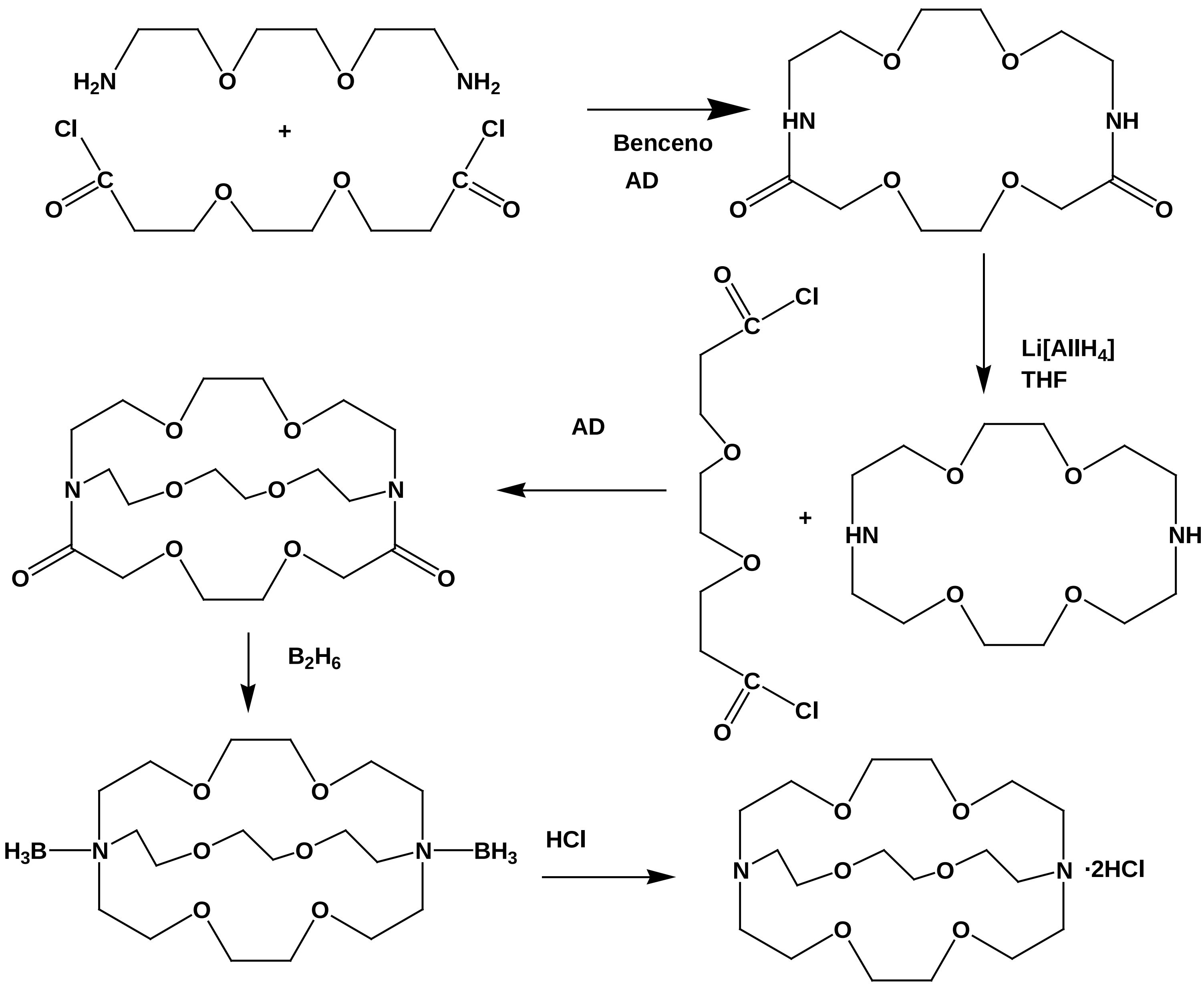
47 (K NCS $)_2$. B_2 24-crown-8

STRUCTURE OF COMPLEXES WITH 1: 1 M/L STOICHIOMETRY



d (K^+_O) = 2.85-2.93 Å

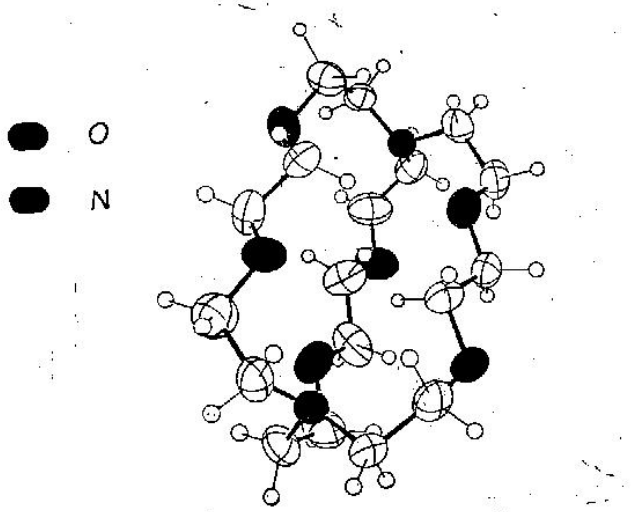
Cryptand Synthesis

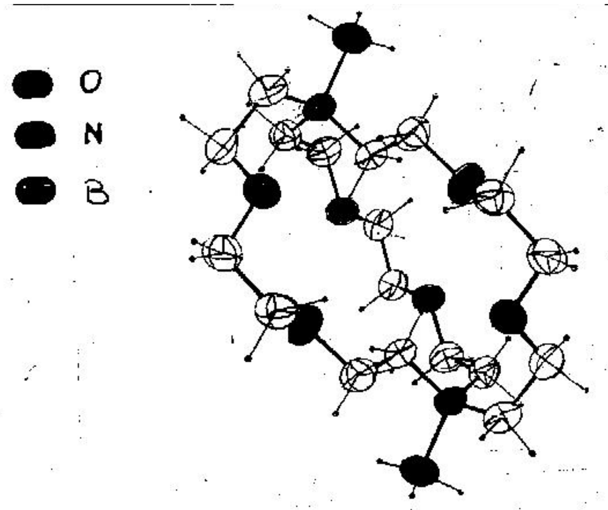


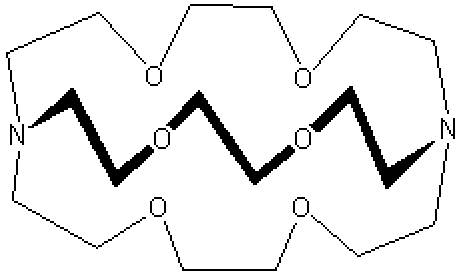
[2] CRYPTAND CONFORMATION

Structure of cryptand 222

Structure of bisborohydride derivative C 222



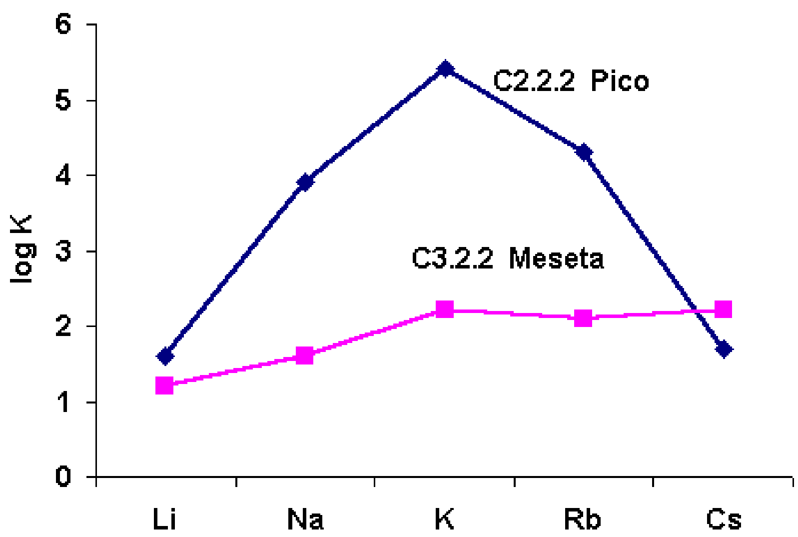


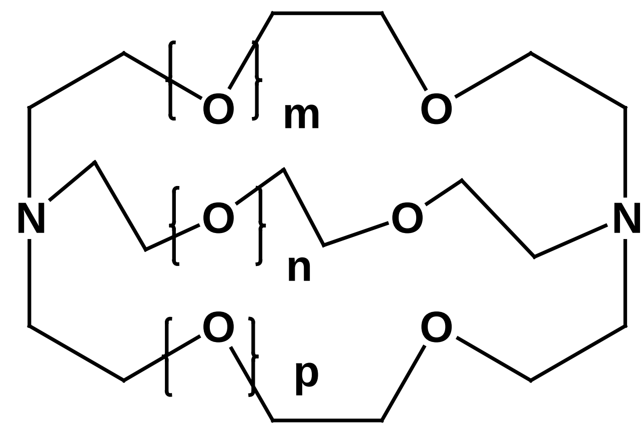


Cryptand Stability

Ligando	Cavidad (Å)	Li^{+} (0,60 Å)	Na^{+} (0,95 Å)	K^{+} (1,33 Å)	Rb^{+} (1,48 Å)
		$LogK_{ML+}$			
2.1.1	0,8	4,30	2,80	<2	<2
2.2.1	1,15	2,50	5,49	3,95	2,55
2.2.2	1,4	<2	3,90	5,40	4,35
3.2.2	1,8	<2	<2	2,2	2,05

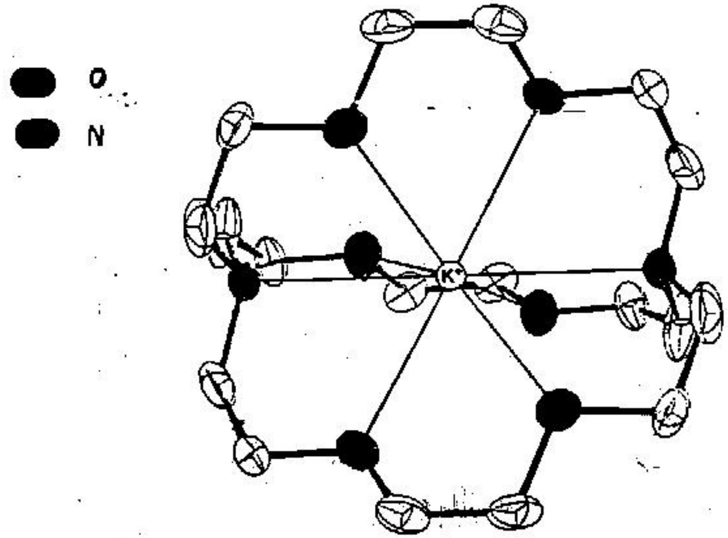
logK values for the formation of cryptand complexes determined in aqueous medium.





Estructura de los complejos del criptando 222 con K^+ y Rb^+

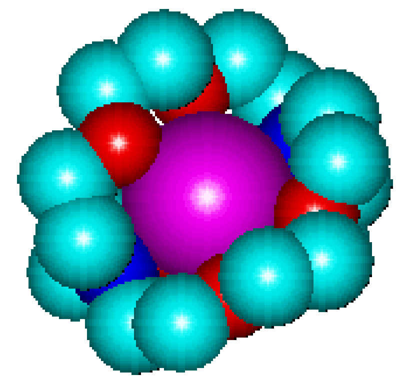
Cryptate Structure

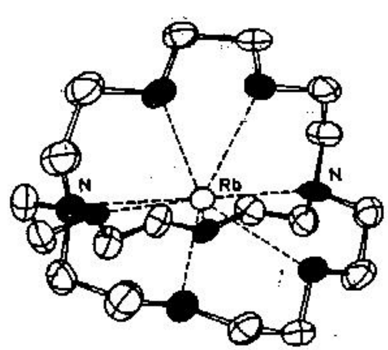


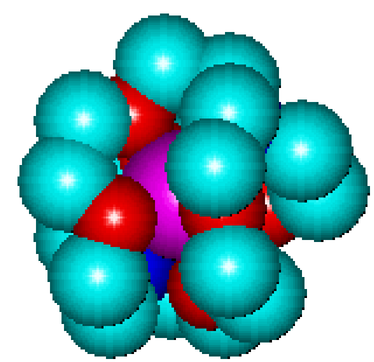
angulo de torsión (N-C-C-O) = 54°

$d(K^+ - N) = 287$ pm

$d(K^+ - O) = 278$ pm



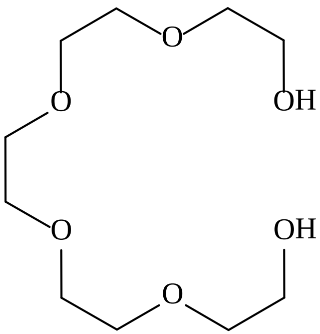


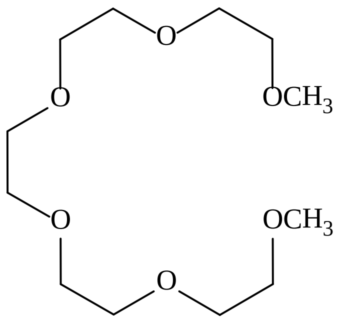


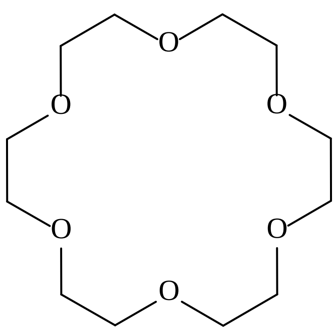
Distances between bridgrhead nitrogen atoms and torsion anglesNC-CO in $[M(2.2.2)]^+$ cryptates

d (pm)	**$[Na(2.2.2)]^+$**	**$[K(2.2.2)]^+$**	**$[Rb(2.2.2)]^+$**	**$[Cs(2.2.2)]^+$**
d (N-N)	550	575	600	607
d (M-O)	257	287	288	296
d (M-N)	272	287	299	302
Mean angle NC-CO	44.8	54.3	57.0	71.2

Thermodynamics of the formation of metal complexes of cyclic and non-cyclic polyethers at 25 ° C in 99 wt,% methanol.





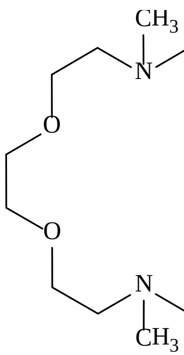


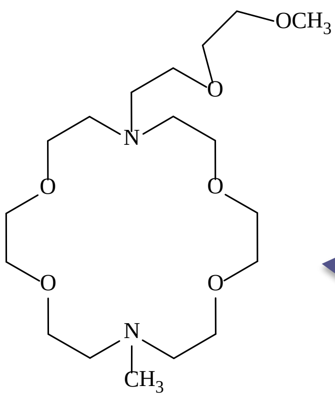
Cation	Log K	ΔH (Kcal mol^{-1})	TΔS (Kcal mol^{-1})
K^+	2.05	-6.37	-3.57
Ba^{2+}	3.96	-6.71	-1.31
Na^+	1.0	-9.14	-7.7
K^+	2.27	-8.16	-5.06
Ba^{2+}	2.51	-5.64	-2.22
Na^+	4.33	-8.11	-2.20
K^+	6.05	-13.2	-4.96
Ba^{2+}	7.0	-10.18	-0.83

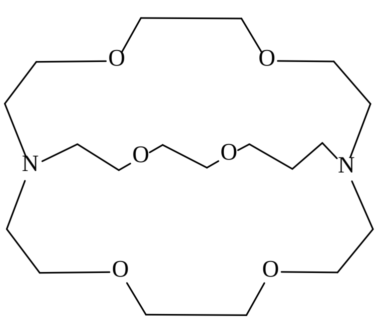
ML acyclic + L cyclic ⇆ ML cyclic + L acyclic

ΔG^o ⇆ $-RT\ln K < 0$

Equilibrium constants (in 95 Vol. 7% Methanol at 25 ° C) of the reaction of metal ions with macrocyclic and macrobicyclic ligands of similar structure.



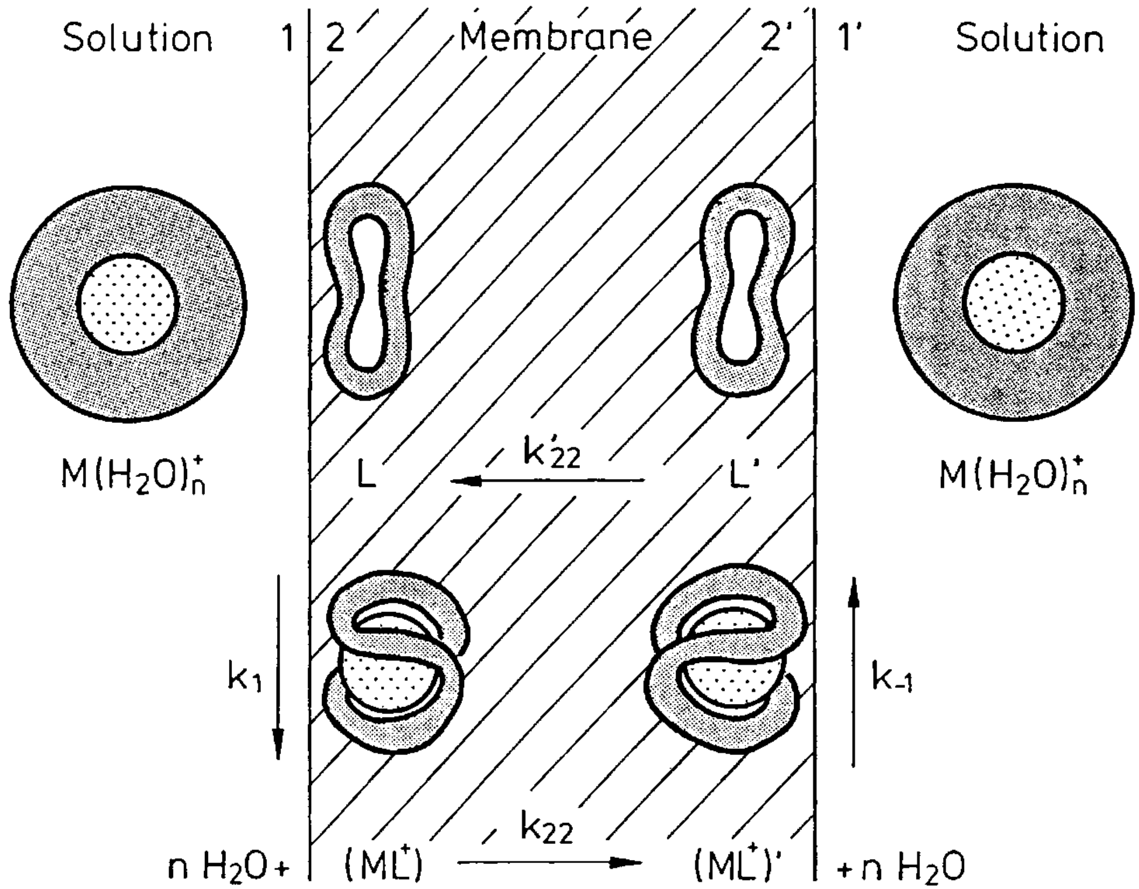




Log K

Na^{+}	K^{+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
3.26	4.38	4.4	6.1	6.7
3.35	4.80			
7.21	9.75	7.60	31.5	12

Transport



Solution
1
2
Membrane
2'
1'
Solution
M(H2O)n+
L
k'22
L'
M(H2O)n+
k1
k-1
n H2O +
(ML+)
k22
(ML+)'
+ n H2O

Transport through liquid membranes

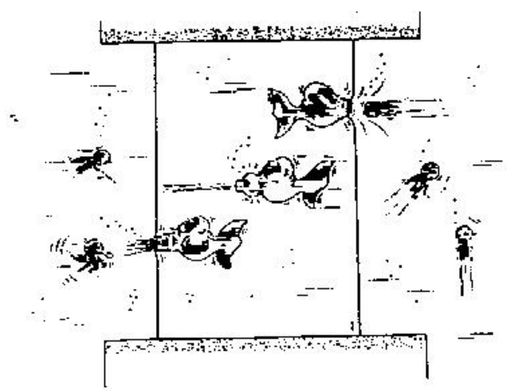
4-step cyclic process

i) Association of the transported species and the transporter (carrier).

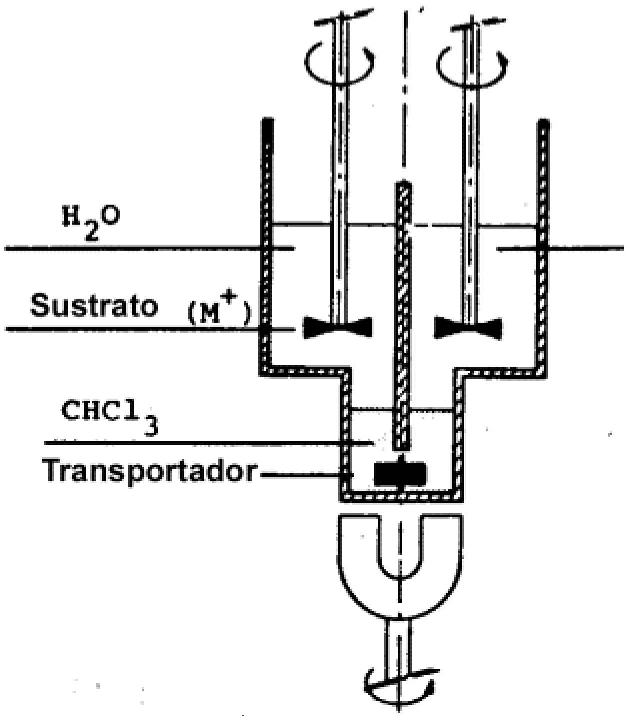
ii) Diffusion of the complex towards the receiving phase.

iii) Dissociation of the complex.

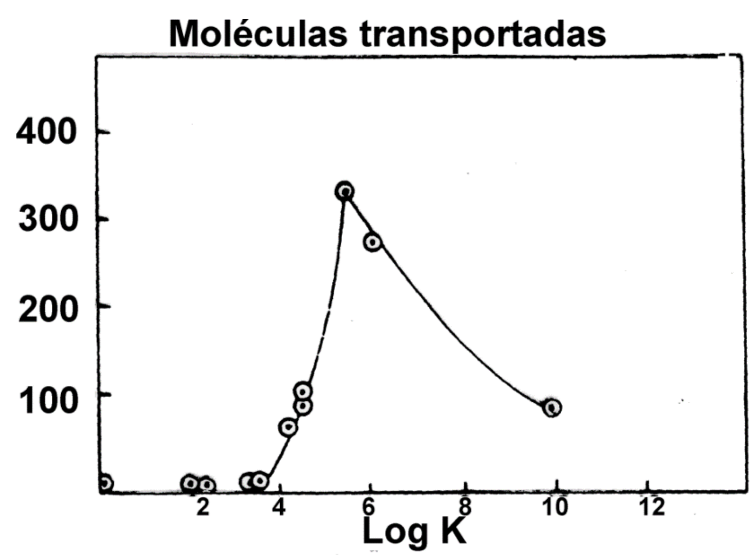
iv) Back-diffusion of the transporter to the source phase.



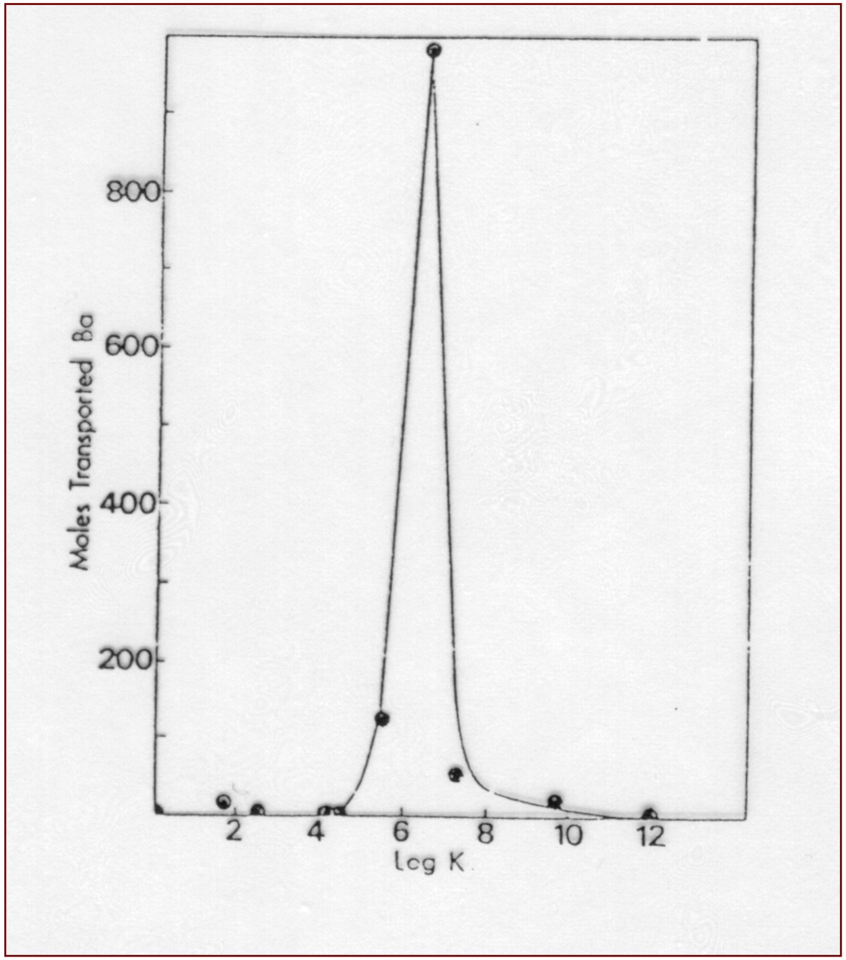
This process represents a mechanism of physical catalysis that effects the transfer of a substrate analogously to the chemical catalysis that effects the transformation of a substrate into products. The "carrier" is the transport catalyst and the complex the active species.

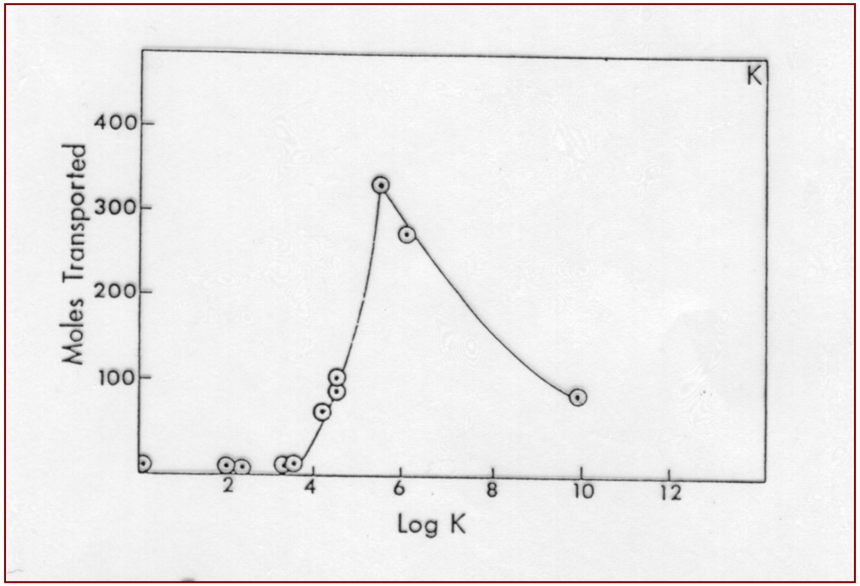


i) Solubility of the carrier and the complex
ii) Stability of the complex in the organic phase
iii) Conveyor concentration
iv) Counters used
v) Diffusion
vi) Contact surface between phases
vii) Concentration gradient between the source and receiver phases



Dependence with the stability constants





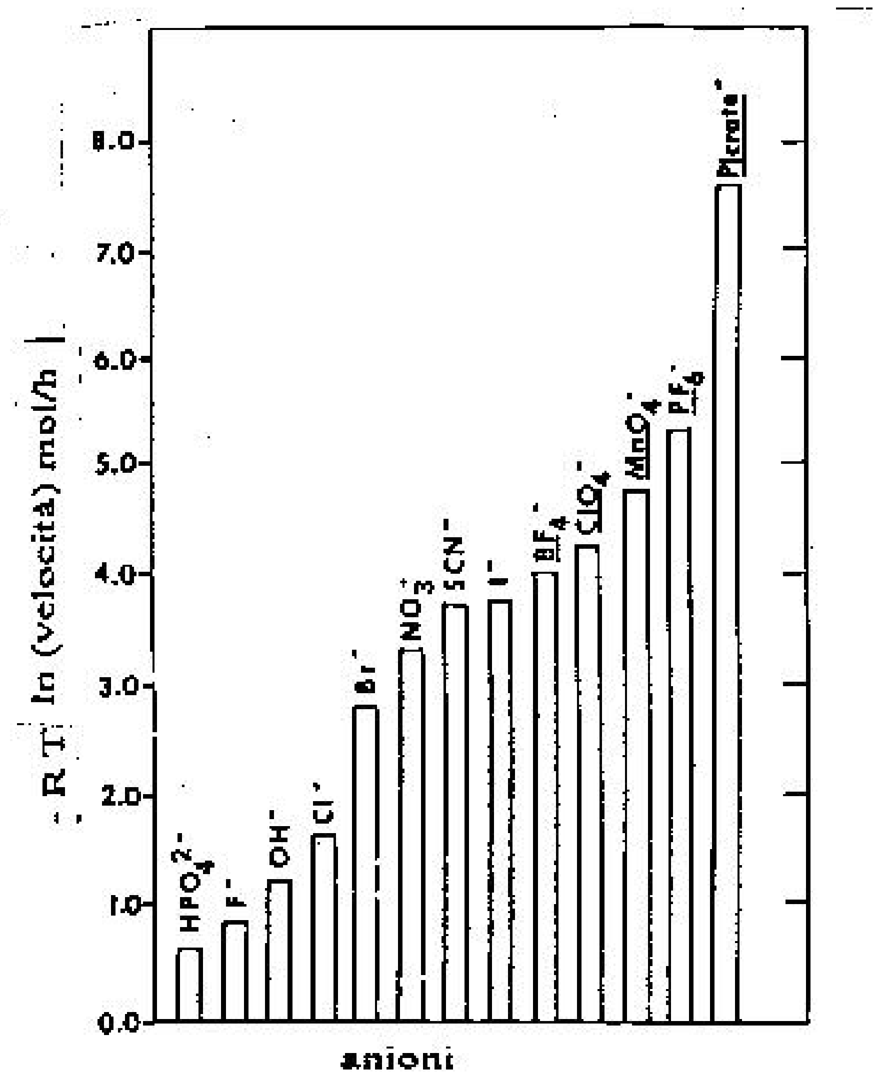
sale Tipo	Conc mol/l	Velocità di trasferimento 10^7 (mol/h) Dibenzo 18 crown-6	t-butilbenzo 15-crown-5
LiCl	1.0	0	0
LiBr	1.0	0	0
LiI	1.0	0.33	0
NaCl	1.0	0.31	0
NaBr	1.0	1.6	0
NaI	1.0	15	0
KF	1.0	0.85	
KCl	1.0	6.1	0.17
KI	1.0	620	36
KI	0.50	370	
KI	0.10	34	
KI	0.010	0.46	
KNO_3	1.0	250	1.9
KOH	1.0	2.1	
$KClO_4$	0.10	123	2.0
K-acetato	1.0	1.4	
K-benzoato	1.0	110	
K-picrato	0.0020	510	2.1
K_3PO_4	1.0	<1	
K_2HPO_4	1.0	<1	
KH_2PO_4	1.0	290	1.3
KBF_4	0.020	3.1	0
KPF_6	0.020	66	0.78
$BaCl_2$	1.0	<1	
$BaBr_2$	1.0	<1	
BaI_2	1.0	280	

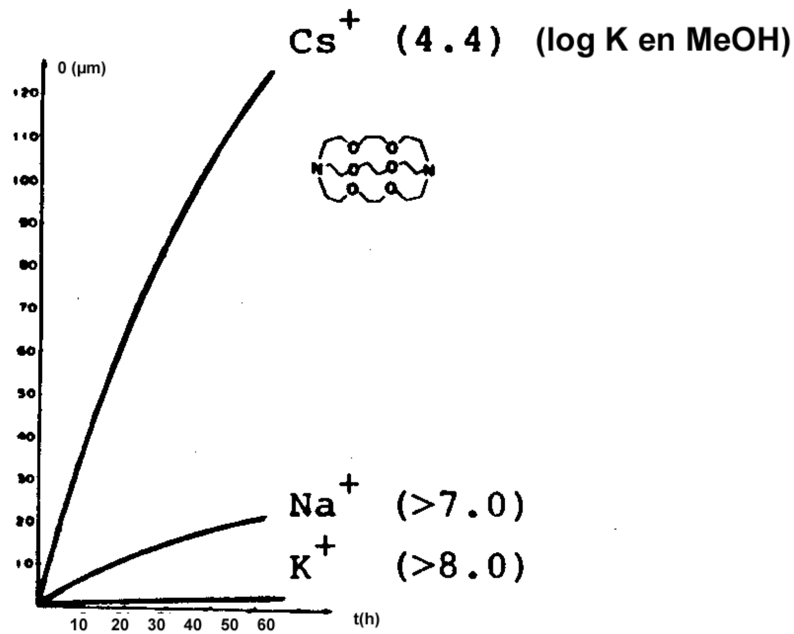
TABLA: Velocidad de transferencia para algunas sales de Li^+, Na^+, y K^+ con el DB18C6 y el TBUTILB15C5.

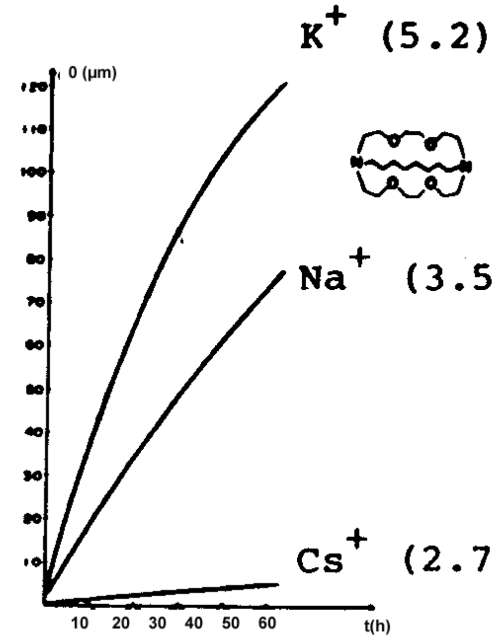
-The transport speed is maximum for any cation in the presence of the anion I^- followed by Br^-, Cl^-, and F^-.

- The transfer rate is higher in the presence of large anions than small anions. The explanation is in the differences of hydration energies in the aqueous phase.

Variation of the transport rate of K^+ through a $CHCl_3$ membrane containing DB18C6 as a function of the anions present

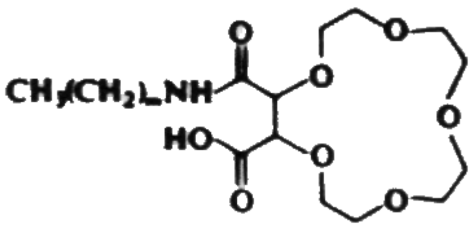




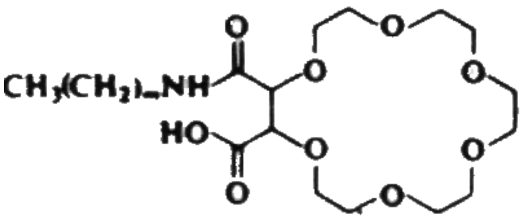


	A	B
Selectividad termodinámica	$K^+ > Na^+ \gg Cs^+$	$K^+ > Na^+ > Cs^+$
Selectividad en el transporte	$Cs^+ \gg Na^+ > K^+$	$K^+ > Na^+ > Cs^+$

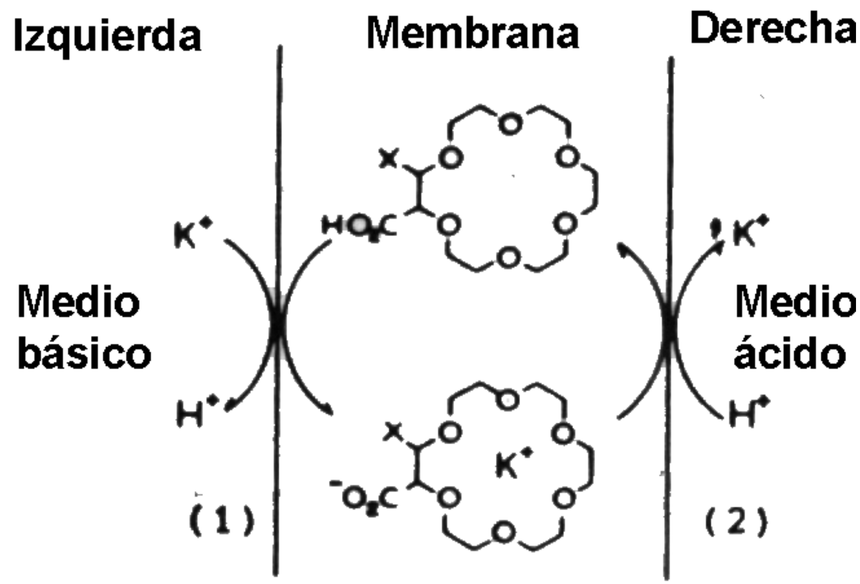
A **B**

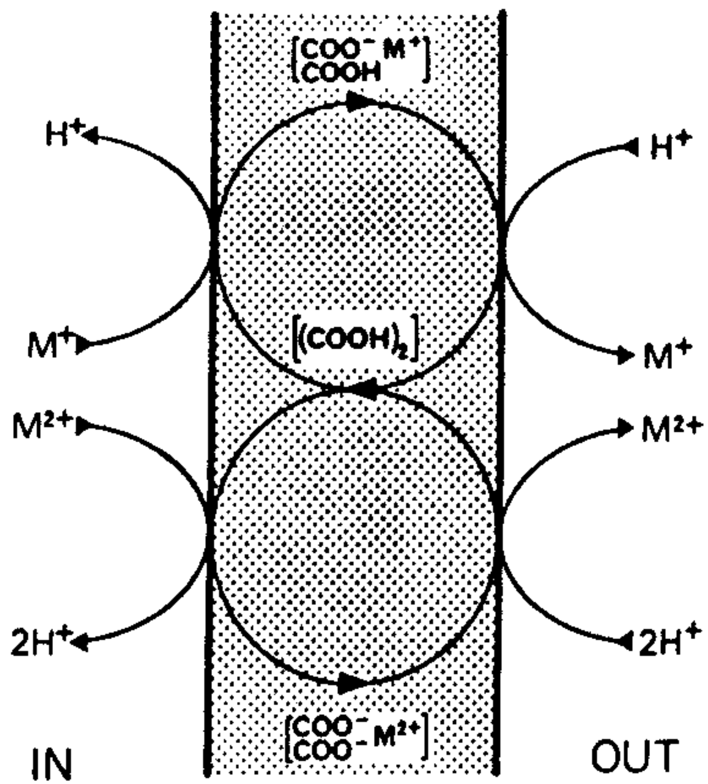


$m = 7$
$m = 13$
$m = 17$

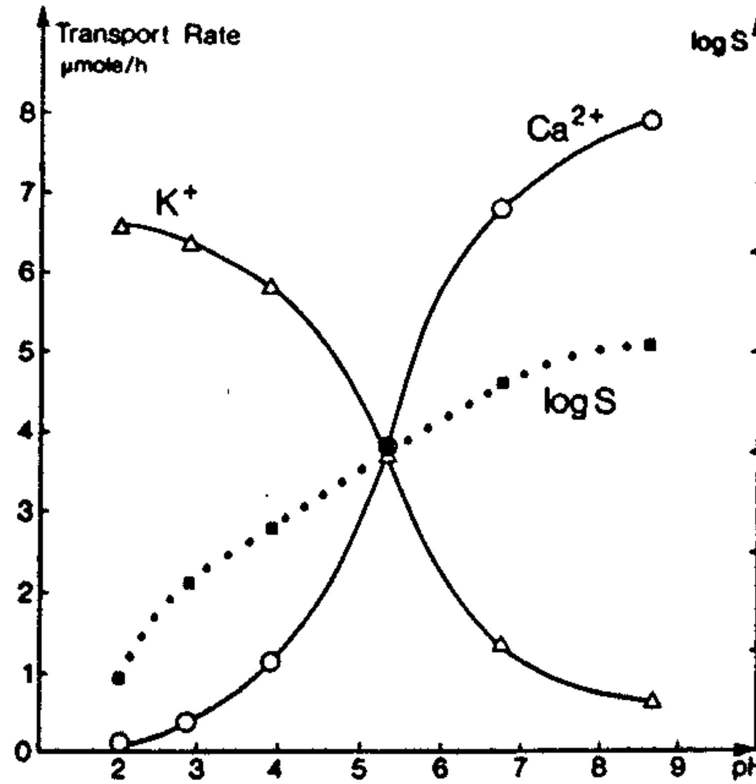


$m = 7$
$m = 13$
$m = 17$



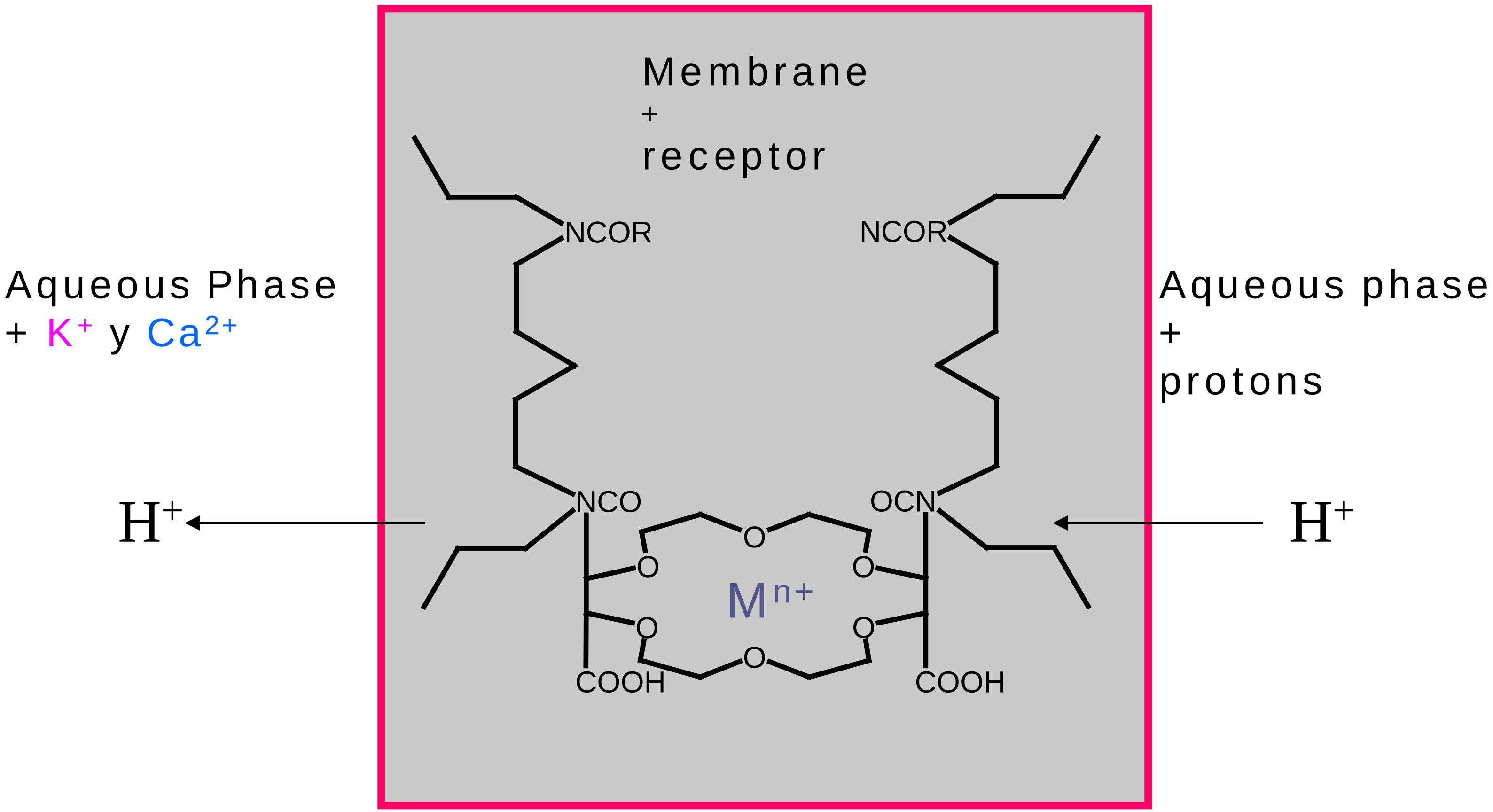


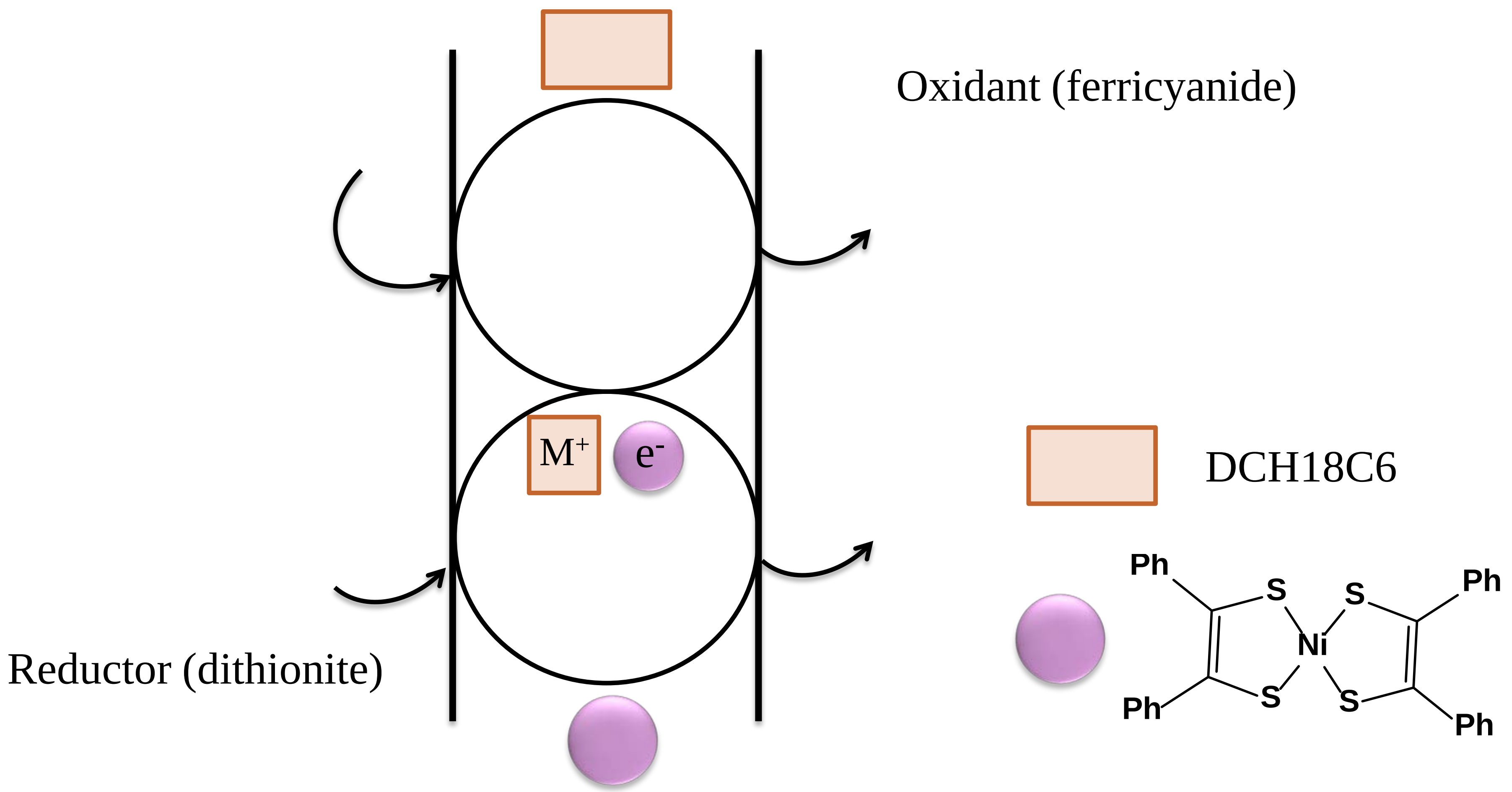
COO⁻ M⁺
COOH
H⁺
M⁺
(COOH)₂
M²⁺
2H⁺
COO⁻
COO⁻ M²⁺
IN
OUT



Transport Rate
μmole/h
log S
Ca²⁺
K⁺
log S
pH
0
1
2
3
4
5
6
7
8
9
+2
+1
0
-1
-2

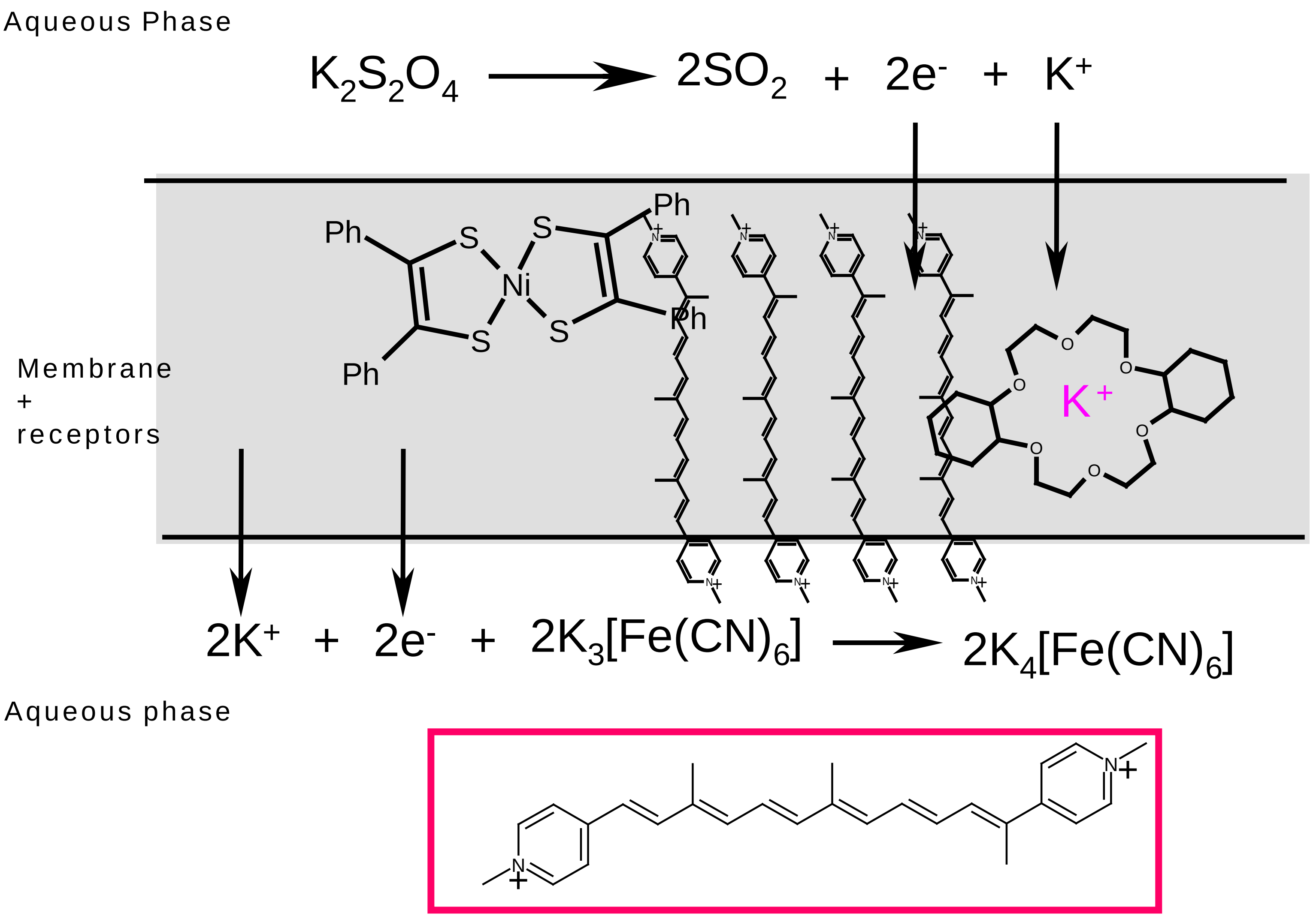
Selective assisted transport of K^+ and Ca^{2+} through a membrane by a functionalized crown ether, coupled to a proton transport and pH gradient.

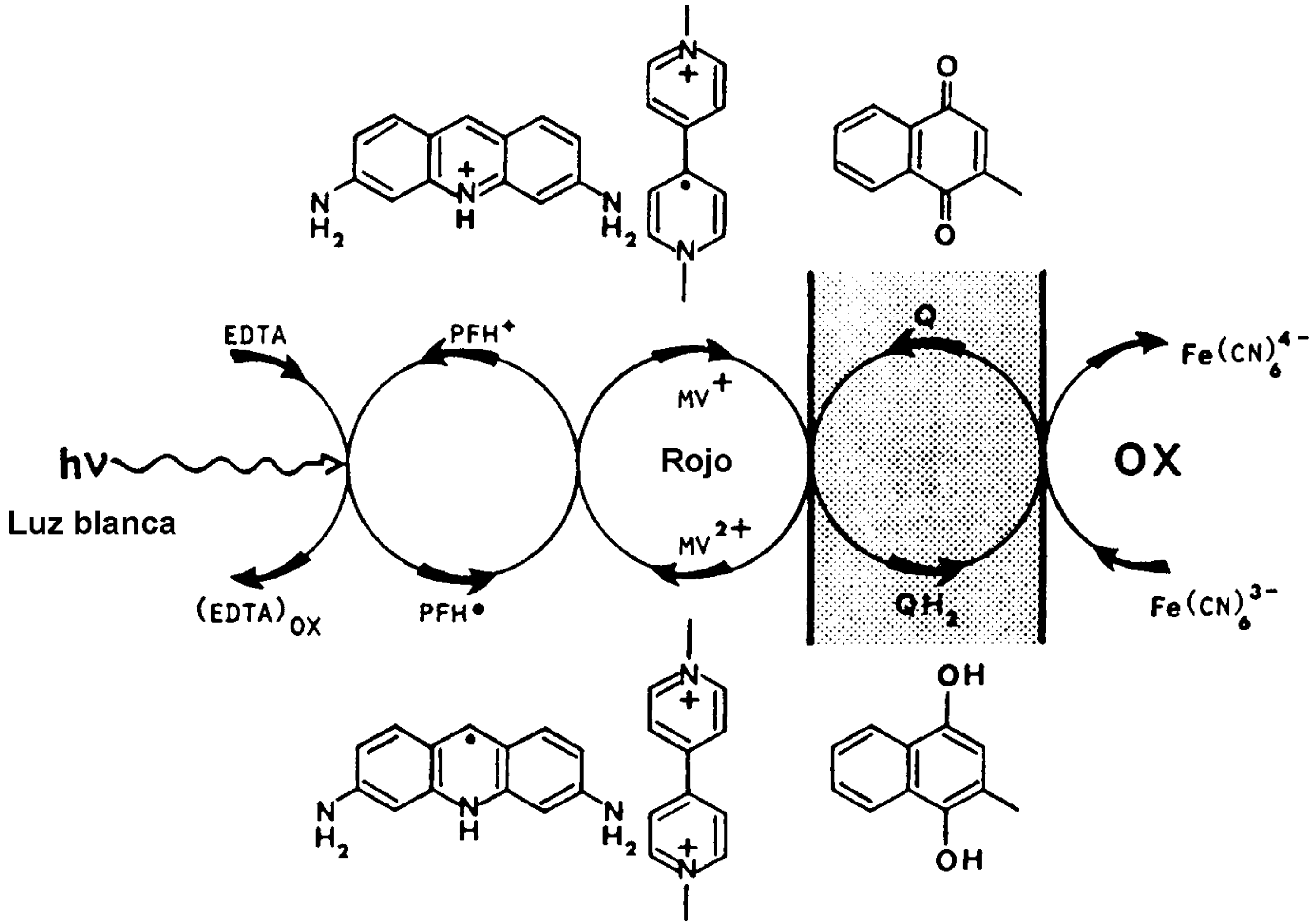




Oxidant (ferricyanide)
M+
e-
DCH18C6
Reductor (dithionite)
Ph
S
Ni
Ph

Assisted transport of K^+ through a membrane by a crown ether, coupled to an electron transport and a redox potential gradient.





EDTA
(EDTA)OX
hν
Luz blanca
PFH+
PFH•
MV+
MV2+
Rojo
Q
QH2
Fe(CN)6 4-
Fe(CN)6 3-
OX

Este material docente ha sido elaborado en el marco de una convocatoria de ayudas para el desarrollo de proyectos de innovación educativa y mejora de la calidad docente (convocado por el Vicerectorat de Polítiques de Formació i Qualitat Educativa de la Universitat de València, en el curso 2017-2018). Código: UV-SFPIE_RMD17-725369

Estas diapositivas forman una parte del contenido docente de la asignatura "Química Inorgánica Avanzada" del Máster Universitario en Química.