Electronic Supplementary Information for Dalton Transactions

Complexation of the triphosphate anion: tuning the structure of cyclen based macrotricycles with 1,2-dimethylbenzene and 2,6-dimethylpyridine linkers. A potentiometric and NMR study.

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Electronic Supplementary Information (ESI)

Recognition constants, log K_{alh}, for the three macrotricycles with PO_4^{3-}, $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$

orthophosphate		***TMC***		***TMPyC***		***TPyC***	
$A+L+2H=ALH_2$		24.43		24.05		24.41	
	$AH+LH=ALH_2$		3.37		2.98		2.95
$A+L+3H=ALH_3$		33.06 *(8.62)*		33.04 *(8.99)*		33.57(9.16)	
	$AH+LH_2=ALH_3$		3.37		3.23		3.05
$A+L+4H=ALH_4$		40.59 *(7.53)*		40.76 *(7.72)*		41.75(8.18)	
	$AH+LH_3=ALH_4$		3.64		3.35		3.25
$A+L+5H=ALH_5$		47.82 *(7.23)*		47.67 *(6.91)*		49.04(7.29)	
	$AH+LH_4=ALH_5$		4.02		3.62		3.94
	$AH_2+LH_3=ALH_5$						
$A+L+6H=ALH_6$		53.92 *(6.10)*		54.13 *(6.46)*		55.37(6.33)	
	$AH_2+LH_4=ALH_6$		3.37		3.33		3.52
$A+L+7H=ALH_7$				56.32 *(2.19)*		58.09(2.72)	
	$AH_2+LH_5=ALH_7$				3.68		4.28

I = 0,1 M (NaCl) ; T = 298 K

pyrophosphate		***TMC***		***TMPyC***		***TPyC***	
A+L+H = ALH		14.33*(9.50)*		13.18		12.83	
	A+LH = ALH	4.66			3.50		2.76
$A+L+2H=ALH_2$		23.24*(8.91)*		22.28(9.1)		22.26(9.43)	
	$A+LH_2=ALH_2$		4.82		3.86		3.13
$A+L+3H=ALH_3$		31.38*(8.14)*		30.27(7.99)		31.07(8.81)	
	$AH+LH_2=ALH_3$		4.73		3.35		3.59
$A+L+4H=ALH_4$		38.9*(7.52)*		37.19(6.12)		38.88(7.81)	
	$AH+LH_3=ALH_4$		4.99		2.67		3.42
$A+L+5H=ALH_5$		45.72*(6.82)*		44.43(7.24)		46.20(7.32)	
	$AH+LH_4=ALH_5$		4.96		3.27		4.14
$A+L+6H=ALH_6$		51.35*(5.63)*		50.55(6.12)		51.89(5.69)	
	$AH_2+LH_4=ALH_6$		4.54		3.49		3.78
$A+L+7H=ALH_7$				53.56(3.01)		55.04(3.15)	
	$AH_2+LH_5=ALH_7$				4.60		4.97

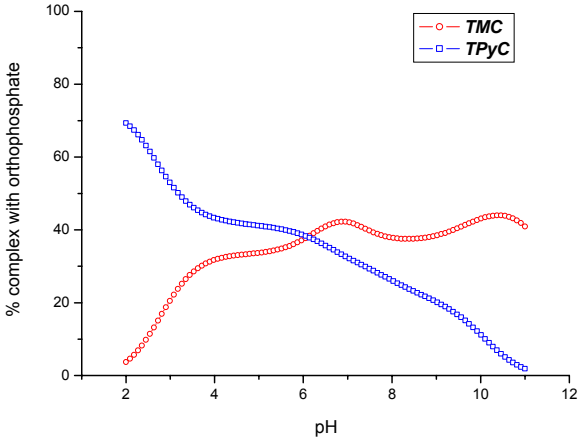
I = 0,1 M (NaCl) ; T = 298 K

triphosphate		***TMC***		***TMPyC***		***TPyC***	
A+L+H = ALH				14.16		13.48	
A+LH = ALH					4.48	3.41	
$A+L+2H=ALH_2$		22.05		24.02(9.86)		23.12(6.64)	
$A+LH_2=ALH_2$			3.75		5.60		3.99
$A+L+3H=ALH_3$		30.46*(8.41)*		32.84(8.82)		31.97(8.85)	
$AH+LH_2=ALH_3$			4.18		6.44		4.49
$A+L+4H=ALH_4$		38.43*(7.97)*		40.90(8.06)		40.19(8.22)	
$AH+LH_3=ALH_4$			4.89		6.90		4.73
$A+L+5H=ALH_5$		45.68*(7.25)*		48.14(7.24)		47.54(7.35)	
$AH+LH_4=ALH_5$			5.29		7.53		5.48
$A+L+6H=ALH_6$		52.28*(6.60)*		54.94(6.80)		54.36(6.82)	
$AH_2+LH_4=ALH_6$			6.15		8.56		6.25
$A+L+7H=ALH_7$		57.49*(5.21)*		60.82(5.88)		60.09(5.73)	
$AH_2+LH_5=ALH_7$			8.29		12.54		10.02
$A+L+8H=ALH_8$				63.51(2.69)		63.13(3.04)	
$A+LH_2=ALH_8$					13.10		11.46

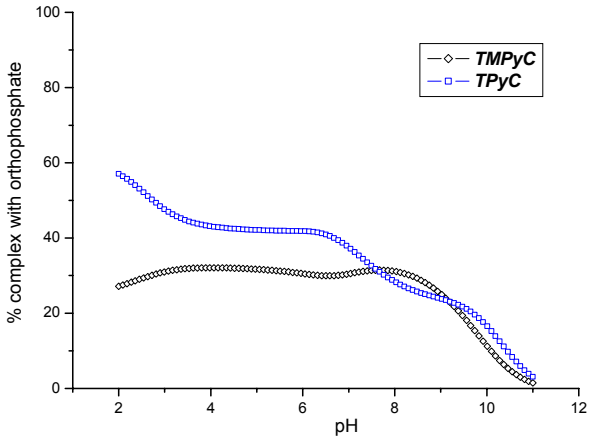
I = 0,1 M (NaCl) ; T = 298 K

Diagrams 1

Competition systems between two ligands for orthophosphate : (a) *TMC* : *TPyC* ; (b) *TMPyC* : *TPyC* (c) *TMC* : *TMPyC*



(a)



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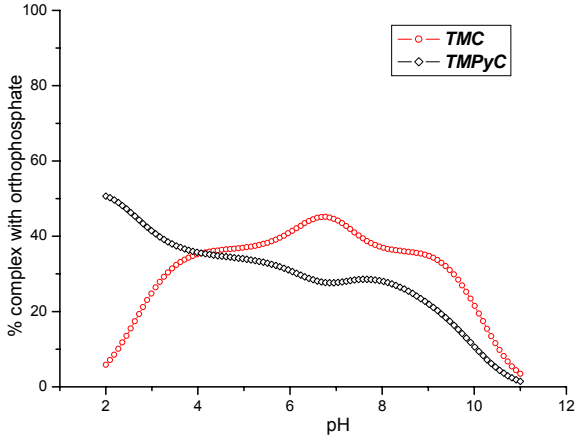
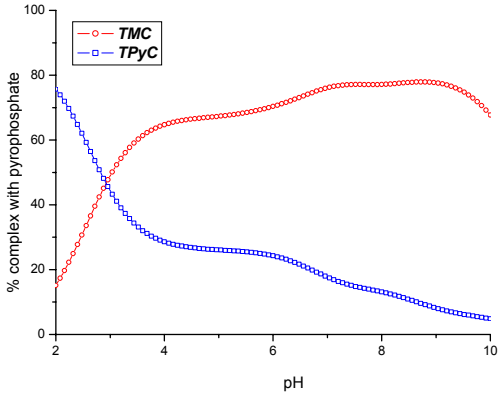


(c)

Diagrams 2

Competition systems between two ligands for pyrophosphate : (a) *TMC* : *TPyC* ; (b) *TMPyC* : *TPyC* (c) *TMC* : *TMPyC*



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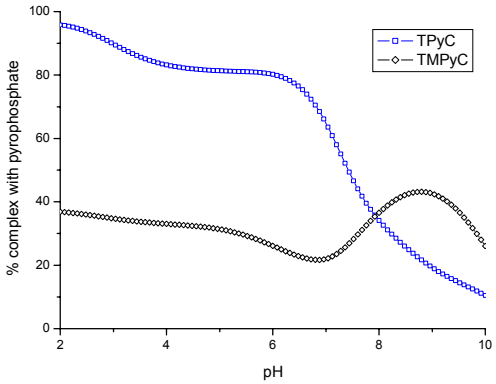

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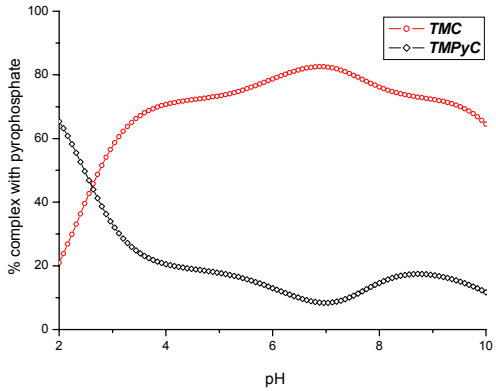
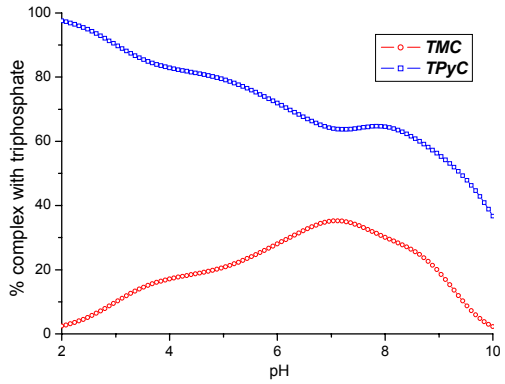


(c)

Diagrams 3

Competition systems between two ligands for triphosphate : (a) *TMC* : *TPyC* ; (b) *TMPyC* : *TPyC* (c) *TMC* : *TMPyC*



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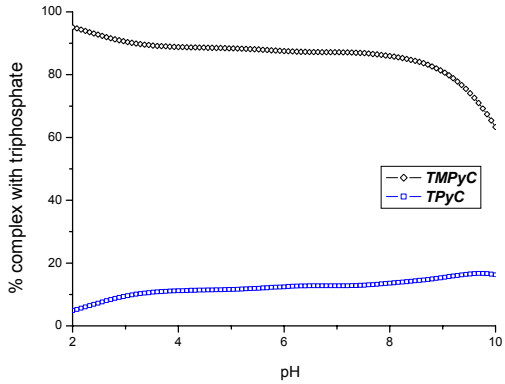

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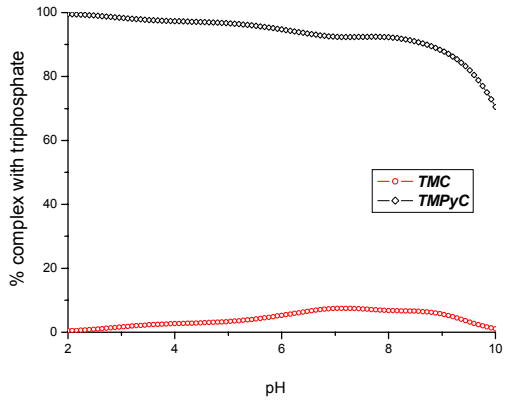


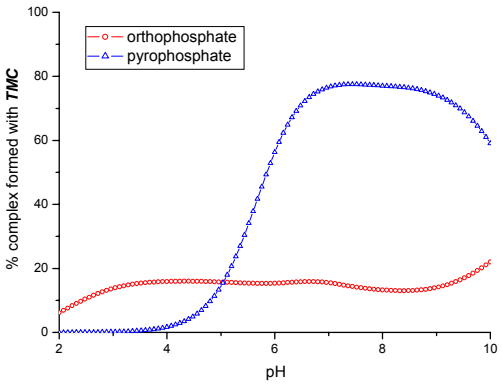
(c)

Diagrams 4

TMC selectivity: (a) orthophosphate : pyrophosphate

(b) orthophosphate : triphosphate

(c) pyrophosphate: triphosphate



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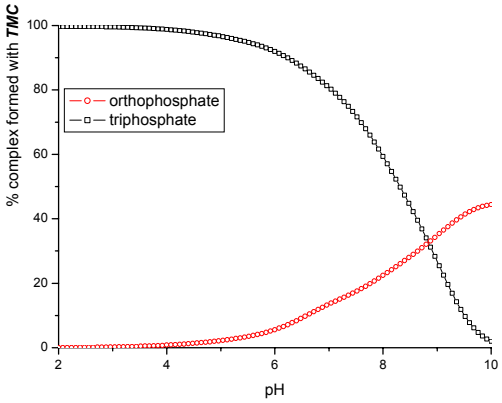

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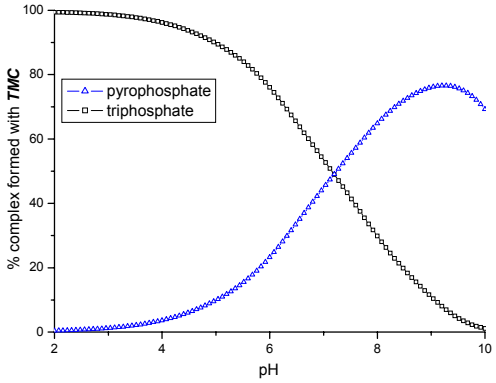


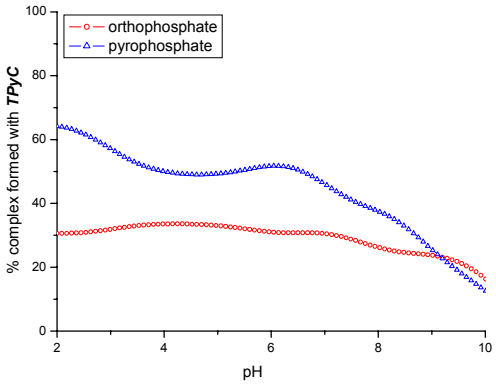
(c)

Diagrams 5

TPyC selectivity: (a) orthophosphate : pyrophosphate

(b) orthophosphate : triphosphate

(c) pyrophosphate: triphosphate



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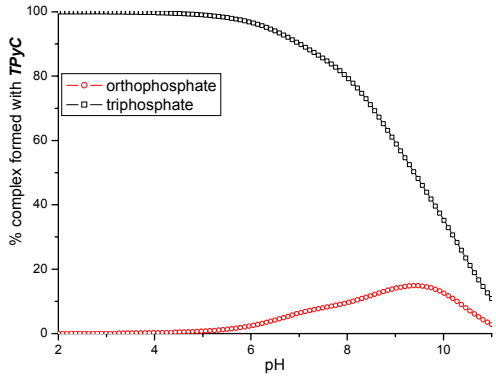

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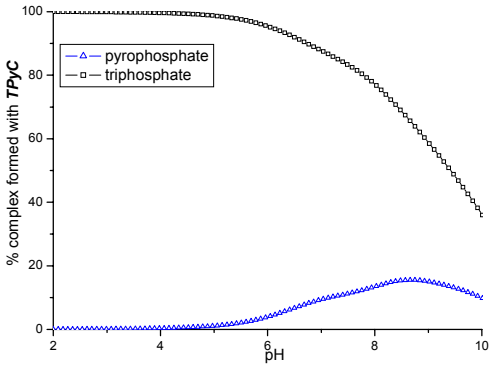


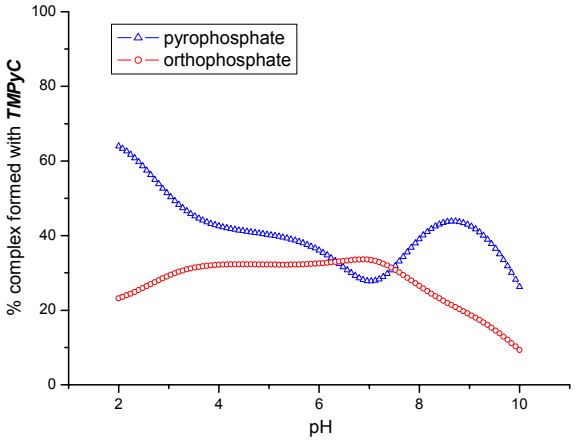
(c)

Diagrams 6

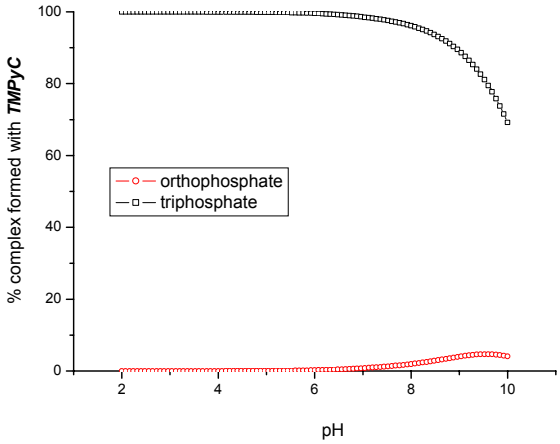
TMPyC selectivity: (a) orthophosphate : pyrophosphate

(b) orthophosphate : triphosphate

(c) pyrophosphate: triphosphate



(a)



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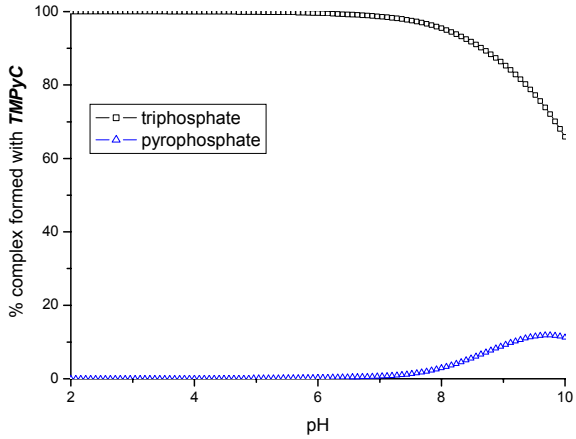


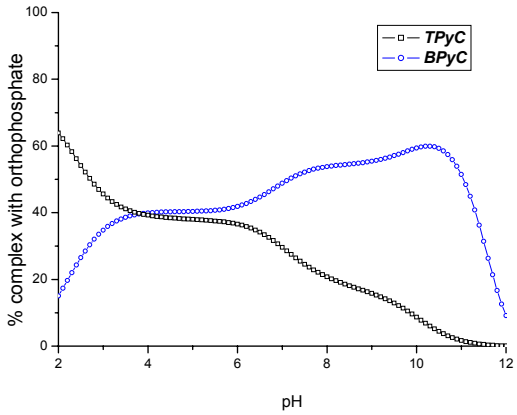
(c)

Diagrams 7

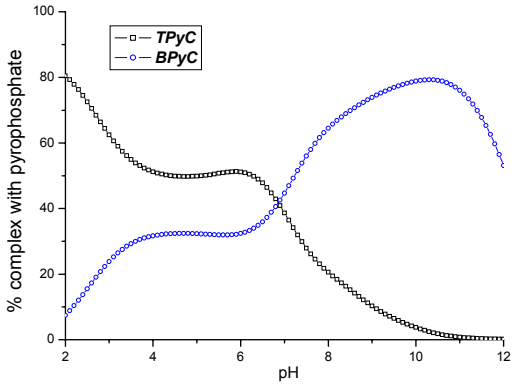
Competition systems between 2 ligands for 1 anion: bis-macrocycles / macrotricycles

BPyC* : *TPyC (a) orthophosphate ; (b) pyrophosphate ; (c) triphosphate

BPyC* : *TMPyC (a) orthophosphate ; (b) pyrophosphate **;** (c) triphosphate



(a)



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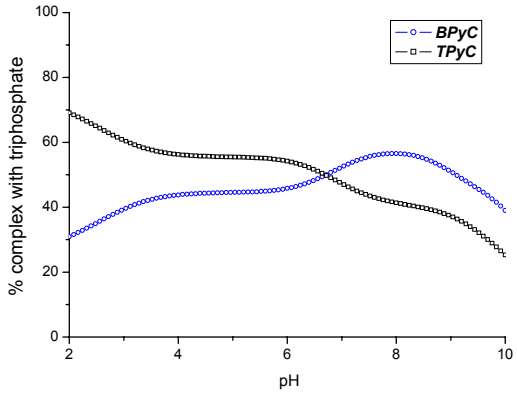

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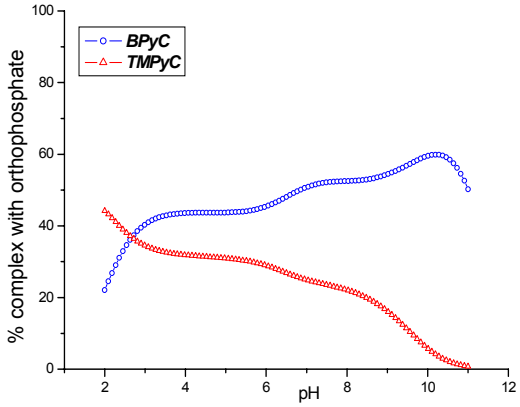

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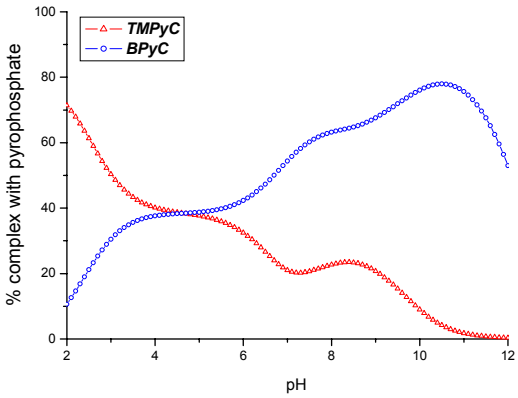
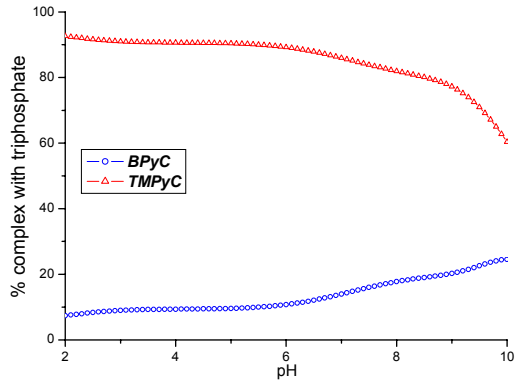


(e)



(f)

Comments: Competitive diagrams and selectivity

Distribution diagrams for systems with equimolar amounts of macrotricyclic ligand, orthophosphate, pyrophosphate and triphosphate present a view of the selectivity of each ligand for different couple of substrates as a function of p[H] (diagrams 4, 5 and 6)
In the selectivity diagrams of a ligand ***L*** for one anion **A** versus a second one **A'** as a function of p[H], the selectivity at a given [pH] for the formation of H_h:***L***:**A** species over H_h:***L***:**A'** is defined here respectively as ([(% H_h:***L***:**A**) / ((% H_h:***L***:**A**) + (% H_h:***L***:**A'**))].100)).
The important feature is the high selectivity of the ***TMPyC*** and ***TPyC*** ligand in favor of triphosphate complexation against orthophosphate and diphosphate in the p[H] range 2-7: indeed, at p[H] 2 the selectivity values obtained exceed 99.99 % and > 90 % until p[H] 7. ***TMC*** show lower selectivity than these both ligands.

Competitive diagrams between two ligands for one anion as a function of p[H] are displayed in Diagrams 1 to 3 and 7 and are available in supplementary material. Diagrams for monophosphate show that the smallest anion as no affinity for the three kind of ligands. Competitions for pyro- and tri-phosphate are the most interesting. For the first one, the competition between ***TMC*** and ***TMPyC*** or ***TMC*** and ***TPyC*** ligands unambiguously show that above p[H] 3, the affinity is better with the ***TMC*** than for the pyridinyl linked ligands. In other words, pyrophosphate complexation is efficient with ***TMPyC*** and ***TPyC*** only when the pyridinyl linker is protonated. When the two pyridinyl derivatives are compared, one can see that pyrophosphate presents curiously a better affinity for ***TPyC*** until p[H] 7.
Competitions for tri-phosphate between ***TMC*** and ***TMPyC*** or ***TMC*** and ***TPyC*** ligands clearly point up the preponderant role of the pyridinyl linker. The anionic guest presents a better fit with the pyridinyl derivative all along pH range. However, the best affinity is obtained for the ***TMPyC***. This fact is corroborated by the competition diagram between ***TMPyC*** and ***TPyC***, which shows again that only one pyridinyl linker is better than two.

In comparison to the open bismacrocycles, we previously show that the stability of the phosphate ternary complexes with macrotricycle is largely higher, and that the rigidity of the host structure due to the introduction of the second linker brings an additional benefit: the selectivity of the host-guest recognition.

In addition, our previously presented results with open bismacrocycles with one pyridinyl linker ***BPyC*** evidence the effect of the supplementary anchoring point represented by the protonated nitrogen atom of the linker on the triphosphate complexation.

Competitive diagrams between bismacrocycle and the corresponding macrotricycle of the pyridinyl family (***BPyC***, ***TMPyC***, ***TPyC***) for the three anions as a function of p[H] are available in Electronic Supplementary Information (ESI). Two of them are of course the most interesting: the competition between (e) ***BPyC*** and ***TPyC*** and (f) between **BPyC** and ***TMPyC*** for triphosphate (diagrams 7e-f). The first one (diagram 7e) shows that the affinity of triphosphate for ***TPyC*** in acidic medium (80% at p[H] 2) rapidly decreased to be inexistent at p[H] 12. It is interesting to note the selectivity of triphosphate in favour of ***TPyC*** against ***BPyC*** is also inverted in basic medium (diagram 7f), the rigidity effect induced by the macrotricyclic cavity is lost by the presence of two pyridinyl linkers.

The competition diagram between ***BPyC*** and ***TMPyC*** incontestably confirms this fact showing a selectivity of triophsophate species between 70 and 93 % all along the p[H] range.