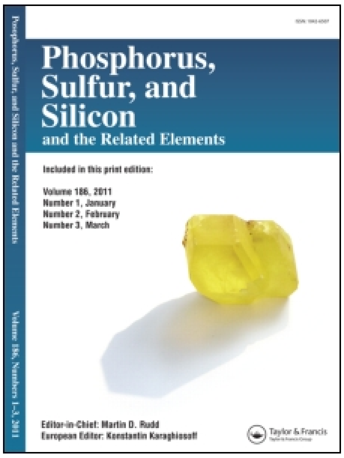

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STRUCTURE AND PROPERTIES OF MONO AND BIS-MACROCYCLIC PHOSPHORUS COMPOUNDS

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Abstract In order to complex cations and neutral molecules, hosts including the phosphoramide group have been designed and studied by nmr and X-ray crystallography. Macrocyclic derivatives containing the phosphoryl group can be easily synthesized from a diamine and an appropriate diaminophosphane. The complexation of alkaline and ammonium cations has been studied. The stability of the complexes is strongly related to the preorganized character of the phosphorus ligands. The formation of bis-macrocyclic compounds, bearing an asymmetric phosphorus atom is also reported.

INTRODUCTION

There exists a large amount of macrocyclic and polymacrocyclic structures designed for specific complexes formation. In this supramolecular chemistry area, polyheteroatomic ligands are still developped and mainly concerned with elements IV-VI of the second and higher raws of the periodic table. In this context phosphorus compounds appear to be of particular importance because of the ability of the phosphorus atom to complex a wide variety of guests (e.g. hard and soft cations with P^{III} and P^{IV} species,[1] neutral guests by means of hydrogen bonding to the phosphoryl group[2]). Furthermore, the phosphate anions, some being of biological relevance, offer potential binding sites for molecular recognition.[3] For more than a decade the design of original host molecules containing phosphorus has been an area of rapidely extending interest, and still continues unabated.[1,4]

The results reported here will briefly describe the design and complexation behavior of different organophosphorus macrocyclic ligands. In order to explore the structural and recognition properties of these compounds we have investigated the solid state characteristics of these molecules.

SYNTHESIS

Earlier reports from our group have documented the viability and synthetic potential of the ring closure reaction of diamines with a diaminophosphane. A general method for the synthesis of macrocyclic receptors containing the phosphonamide or the phosphoramide group included in a crown ether like structure (**A**) has appeared.[5] This reaction was applied to various diamines and phosphorus reagents leading to the macrocycles **A** in yields up to 80%. Rigidification of **A** can be accomplished by an appropriate substitution on the nitrogen atoms to give the original preorganized structures **B** (Figure 1).[6] A set of different sized receptors of this kind was prepared and their complexing properties towards alkaline and ammonium cations were explored.

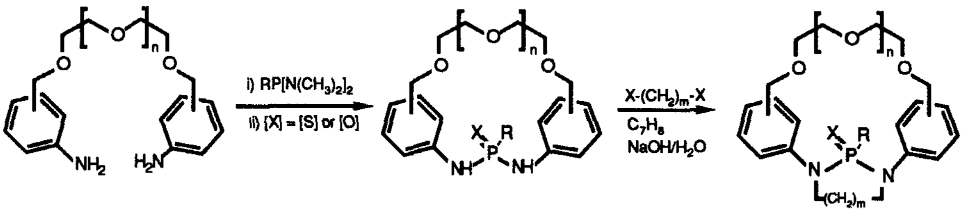
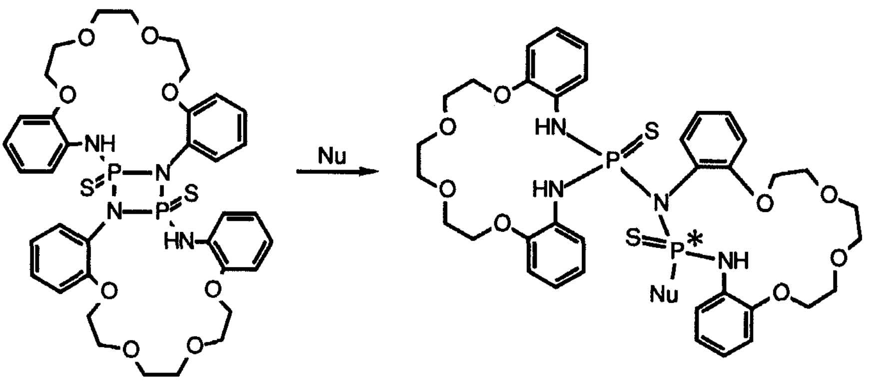


FIGURE 1 **A** **B**

More recently we reported the preparation and characterization of novel ditopic receptors formed of a P_2N_2 basic building block with two annelated macrocycles (**C**).[7] Molecule **C**, when subjected to nucleophilic substrates (alcohol, amines), gives rise to a new family of bis-macrocyclic compounds **D**, containing an asymmetric phosphorus atom as depicted on the scheme below.



C **D**

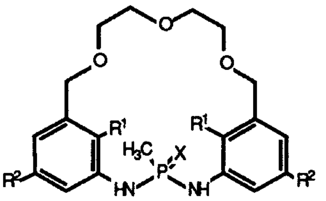
Molecule **D** (Nu = C_2H_5OH) exists in the solid state as a conglomerate.[6] We have thus access to a chiral compound which is spontaneously resolved.

CATION BINDING PROPERTIES

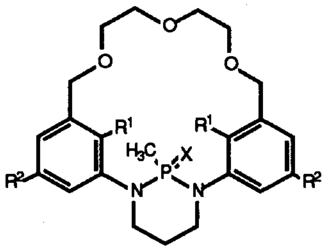
Ligands of type **A** and **B** were subjected to complexation experiments with alkaline and ammonium picrate salts using an extractive method. We report in Table 1 some significant K_a values (M^{-1}) and binding free energies ($-\Delta G°$, $kcal.mol^{-1}$) at 298K.

TABLE 1 Association constants and free energies of macrocyclic compounds **A** and **B** for alkaline and ammonium cations

Host



A



B

	host		guest cation							
			Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	$MeNH_3^+$	$t\text{-}BuNH_3^+$
	R^1=OMe	$-\Delta G°$	7.49	6.31	6.45	6.16	6.44	6.07	5.29	5.09
A	R^2=Me	*Ka*	31.5	4.20	5.40	3.30	5.27	2.84	0.76	0.54
	X=O	x(10^{-4})								
	R^1=H	$-\Delta G°$	6.08	5.06	4.94	5.82	5.22	5.64	5.05	4.70
A	R^2=H	*Ka*	2.90	0.52	0.42	1.85	0.67	1.38	0.51	0.28
	X=O	x(10^{-4})								
	R^1=H	$-\Delta G°$	6.98	6.39	6.18	6.23	6.21	6.29	5.23	3.79
B	R^2=H	*Ka*	13.2	4.87	3.42	3.70	3.57	4.08	0.69	0.06
	X=O	x(10^{-4})								

CORRELATIONS BETWEEN STRUCTURE AND BINDING

The stereochemical problems which arise from the particular structure of the macrocyclic molecules were examined in solution and in the solid state by nmr and X-ray diffraction. Depending on size, configuration and substituents, the different molecules exhibit different behaviors which are of main importance for the complexes formation, their stability and selectivity.

The preorganization concept is useful in the design of specific ligands for the complexation of various substrates.[8] Preorganized molecules **B** (an example is given in figure 2), which impose the inward orientation of the phosphorus moieties into the macrocyclic cavity, are better ligands for alkaline cations as compared to the non rigidified hosts **A**.

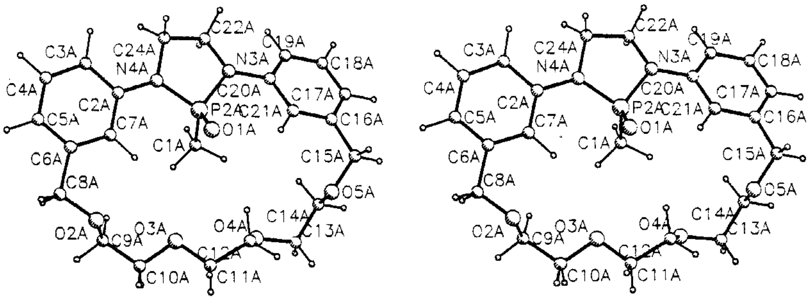


FIGURE 2

As expected the larger the number of binding sites the better the complex, and the P(O) phosphoryl group is a better binding site for hard cations than its P(S) counterpart.

Two main configurations are observed in the crystal structures of compounds **A**, mainly due to hydrogen-bond formation involving the NH groups. The presence of a molecule of water located inside the cavity of the macrocycle leads to an extended planar conformation of the macrocycle. Otherwise the molecules adopt a folded conformation where methylene groups turn inward, partially filling the cavity of the macrocycle.[6] The hydrogen bonding ability of the phosphoramide group could be used to form complexes with complementary guests. On the other hand the structural reorganization of such a conformation for complexation to occur, will probably be associated with an increasing energy cost. Such a situation can be avoided with the partially preorganized hosts (**B**).

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