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Heteroditopic receptors

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Abstract. Data on heteroditopic receptors, an important class of complexing agents, are surveyed. Attention is focused on the synthesis of the ligands and analysis of their binding properties. The influence of structural features on the properties of such systems is investigated. The bibliography includes 49 references.

I. Introduction

Recent years have seen a swift growth in the number of publications devoted to the design of polyfunctional ligands capable of binding both cations and anions. The interest in these compounds, called heteroditopic receptors,[1] is due to their potential use for the recognition of ion pairs, as sensors for the monitoring of biological systems and the environment, as selective extractants, and for the transfer of salts through lipophilic membranes.[2, 3] The heteroditopic ligands incorporate both cation- and anion-binding sites, used for the simultaneous capture of oppositely charged ions with a high degree of selectivity and affinity. This greatly contributes to overcoming the problem of low solubility of salts in organic solvents. This review presents examples of selective complexation of bipolar organic molecules (for example, amino acids).

The idea behind the design of heteroditopic receptors is to synthesise compounds containing several complexing sites of different nature. Fragments capable of either hydrogen bonding with negatively charged species or of ion – dipole interactions are used most often as anion acceptors. These substances include polyamines, urea derivatives and molecules containing amido groups or pyrrole substituents. The complexation with positively charged fragments is accomplished by using compounds that have already proved to be selective cation receptors such as crown ethers, calixarenes and compounds modified by oligopyridyl groups.

The heteroditopic ligands described in the literature can be divided into two large groups:

(1) open-chain compounds containing heterocycles or functional groups [NH_2, NHR, NR^1R^2, (R^1, R^2 = H, Alk), NHCO, C = O, pyridyl];

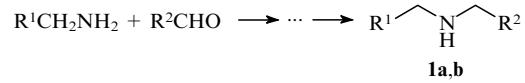
(2) receptors based on macrocycles such as crown ethers (including azacrown compounds), calixarenes and resorcinarenes.

This review surveys the synthetic approaches taken in the development of heteroditopic receptors and data on their complexing properties.

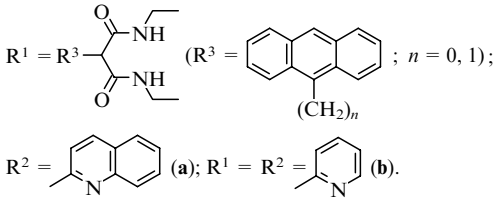
II. Open-chain receptors

Pyridyl fragments are known to exhibit a high binding ability with respect to transition metal cations. Urea residues are very suited for binding of anions owing to the formation of strong hydrogen bonds between the anions and the urea NH groups. Therefore, most of publications devoted to the design of heteroditopic ligands describe the synthesis of this type of compound.

The open-chain ligands **1** contain a pyridyl fragment, which acts as a receptor for transition metal cations, for example, Ni^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+} and Ru^{3+}. The presence of functional groups prone to non-covalent interaction with anions allows one to use them as heteroditopic complexing agents. It is worth noting that some ligands containing amino groups exhibit fluorescence properties.[4, 5]



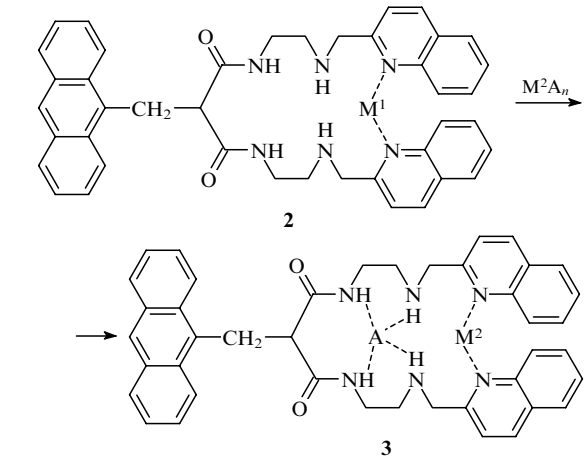
1a,**b**



Complexes of these compounds with transition metal cations **2** can also serve as heteroditopic receptors if they react with ion pairs to give stable complexes **3**.

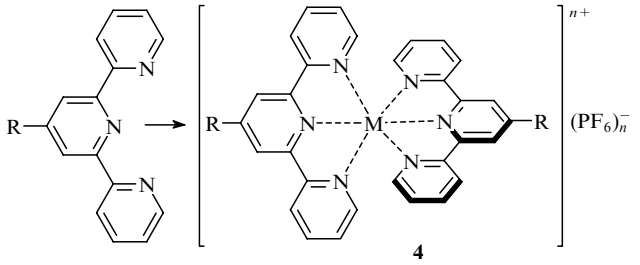
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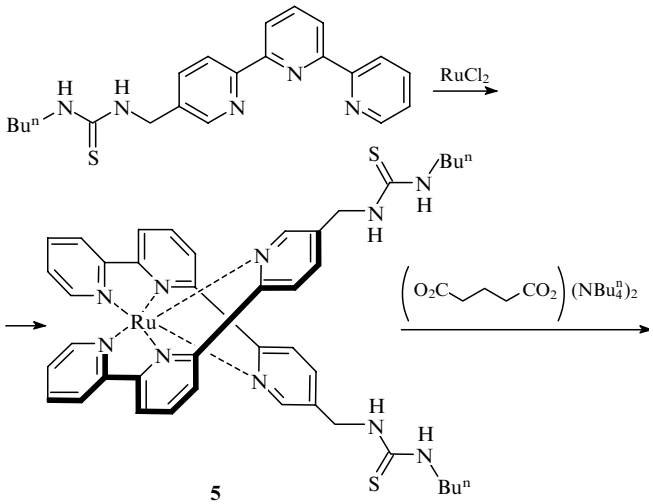
M^1 and M^2 are metal cations, A is an anion.

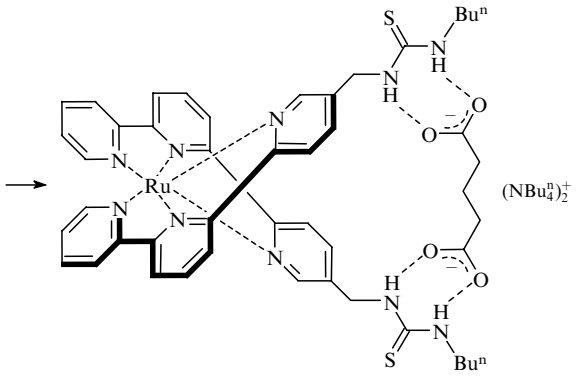
Terpyridyl ligands are involved in the formation of inclusion compounds with transition metal cations and the PF_6^- anion, which occurs in the outer sphere. The reaction of polypyridyl-containing receptors with $FeCl_2$, $RuCl_3$ and $CoAc_2$ in the presence of NH_4PF_6 results in the isolation of stable hexafluorophosphates **4**.[6, 7]



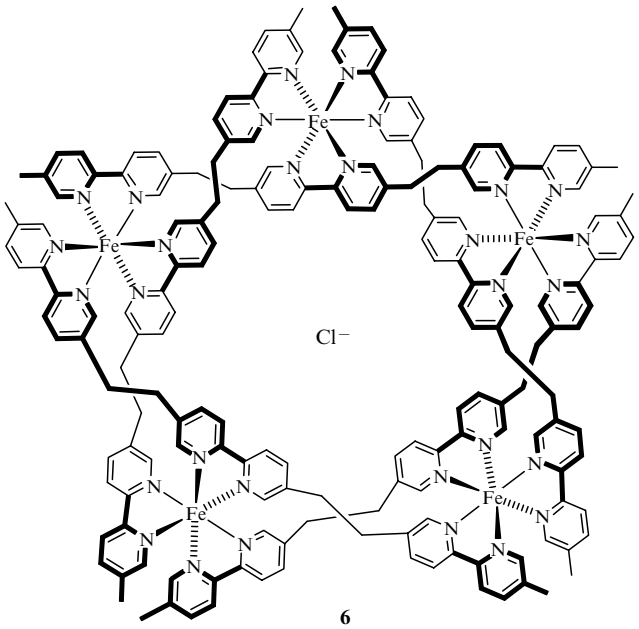
R = Ph_2P, Ph_2PO.

The combination of pyridyl fragments and (thio)urea residues within one molecule enables the use of these compounds for the simultaneous binding of transition metal cations and dicarboxylic acid anions. In particular, upon the formation of a Ru(II) complex with two terpyridyl fragments, the urea residues are arranged in space in such a way that they can interact with dicarboxylic acids. For example, compound **5** (based on terpyridyl-substituted thiourea) selectively extracts the glutarate anion [K_{ass} = 8300 mol litre^{-1} (see†)].





The replacement of the thiourea fragment by the urethane residue results in non-covalent binding of the acetate.[8] An interesting case of the construction of supramolecular structures with simultaneous complexation of Fe^{3+} and Cl^- ions has been discovered.[9] Ensemble **6** was obtained upon the template reaction between five tris(bipyridyl) ligands and $FeCl_3$.



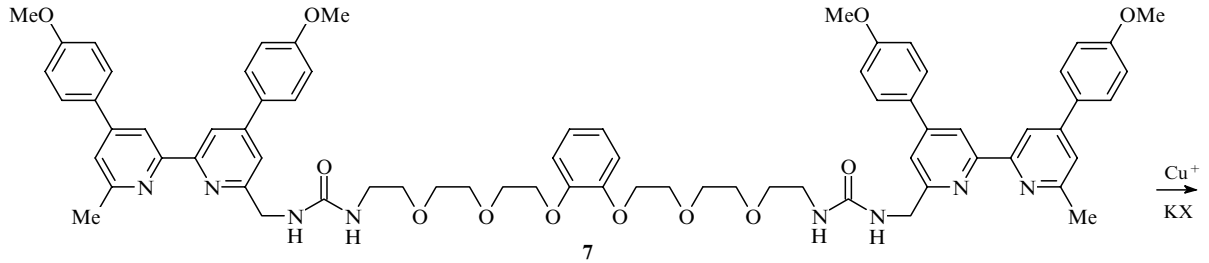
Recently,[10] an ion pair receptor has been prepared on the basis of a pseudocrown ether modified by urea and a bipyridyl fragment. The resulting compound **7** is complexed with Cu(I) through bipyridyl groups to form closed structure **8**, whose cavity is suitable for the complexation of a potassium cation. Due to the presence of anion-binding sites, this compound can be used for the recognition of ion pairs, the receptor ability decreasing in the sequence $Cl^- \gg Br^- > I^-$ (Scheme 1).

A few examples of heteroditopic receptors devoid of pyridyl and ureide fragments have been reported. It was shown that monodendate pyrazole and 3(5)-*tert*-butylpyrazole as solutions in methanol form stable complexes $[ZnX(Het)_3]X$, where X = Cl, Br, I, with zinc halides either in the solid state or as solutions in non-polar solvents.[11]

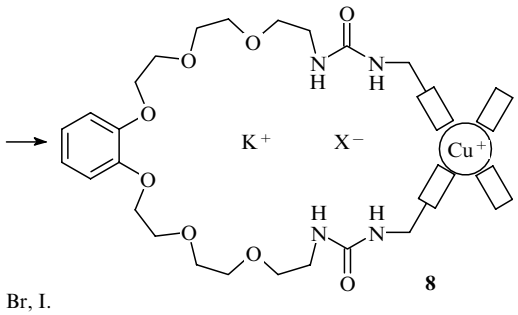
Compound **9** in the zwitter-ionic form is capable of the separate extraction of cations and anions.[12, 13]

† Here and below, the binding constant is given in mol litre^{-1}.

Scheme 1

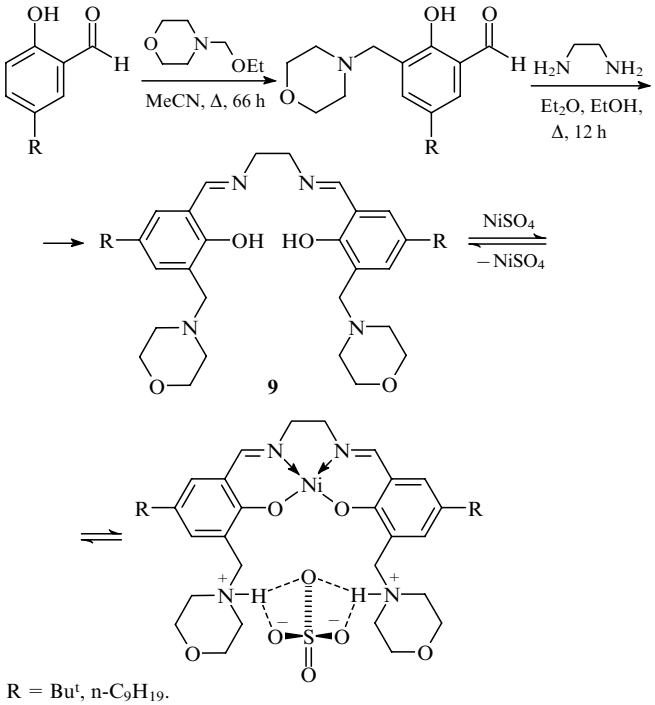


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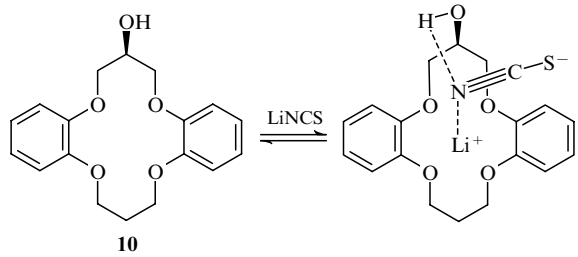
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X = Cl, Br, I.



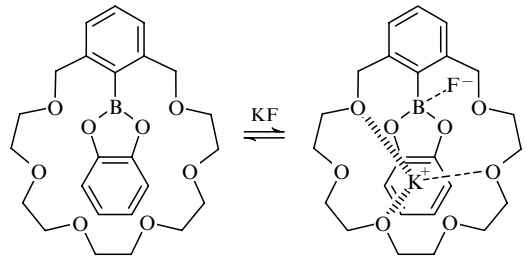
9

R = Bu^t, n-C_9H_{19}.



10

Crown ethers linked with Lewis acid fragments by covalent bonds represent another example of heteroditopic receptors. It was found that the oxygen atoms of the crown ether ring in compound **11** coordinate the potassium cation, the fluoride anion being bound simultaneously by the boron atom.



11

III. The design of heteroditopic receptors based on crown ethers and calixarenes

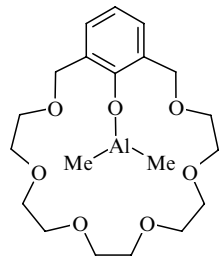
Crown ethers and calixarenes are selective extractants for metals and therefore they are often used for the design of heteroditopic complexing agents as cation-binding sites.

1. Crown-containing ligands

Crown ether **10**, containing a free hydroxy group, is among the first examples of heteroditopic receptors based on a macrocyclic matrix. This compound as a suspension in THF binds simultaneously a Li^+ cation and a thiocyanate anion.[14] The cation is retained by the macrocyclic cavity, while the thiocyanate anion is coordinated to the hydroxy group due to the formation of an intermolecular hydrogen bond.

However, in an attempt to trap KCl or KBr in the same way, compound **11** acts only as a cation acceptor.

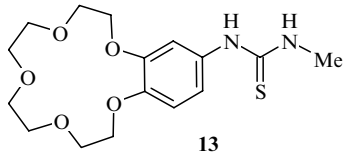
Related compound **12**, prepared by the reaction of the corresponding alcohol with Me_3Al, forms a complex with lithium chloride both in solution and in a suspension in THF.[15–17]



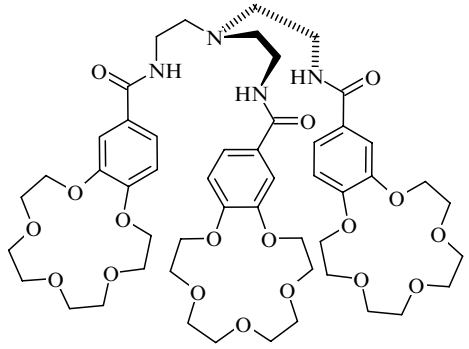
12

The introduction of urea fragments or amide groups, which tend to bind anions, into crown ether molecules allows one to use these compounds as bifunctional receptors.

A study of the binding of benzo-15-crown-5 ether, modified by a thiourea residue, to a series of anions has shown that upon the addition of two equivalents of $NaBPh_4$, ligand **13** captures the NO_3^- ($K_{ass} = 66$) Br^- ($K_{ass} = 260$), and I^- ($K_{ass} = 20$) anions.[18] Compound **14** forms complexes with the Cl^-, I^- and ReO_4^- anions upon the introduction of one equivalent of sodium picrate.[19]

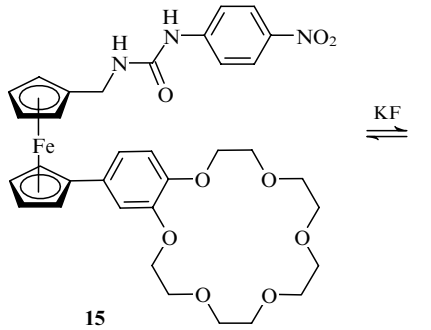


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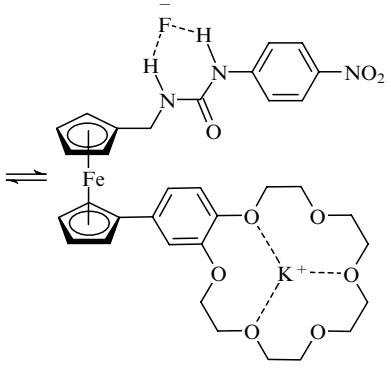


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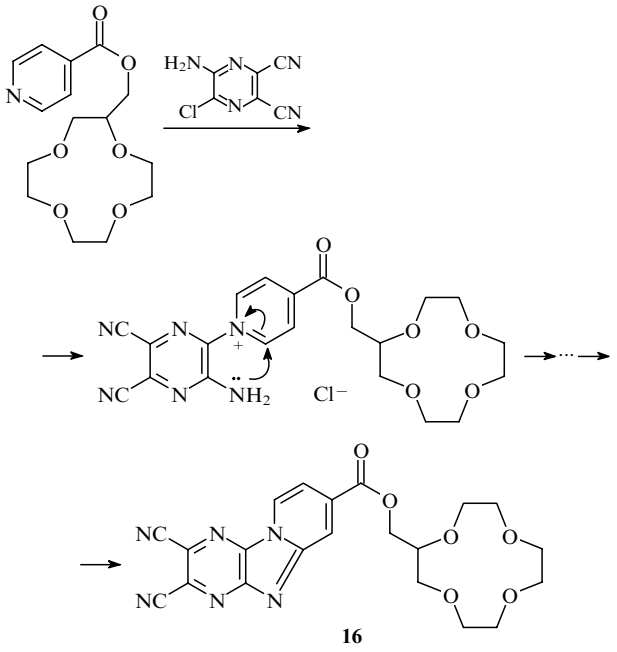
Nitrophenyl-substituted ureas are known to extract anions. Hence, one can expect that the introduction of such a residue into a benzocrown ether molecule would afford a heteroditopic receptor. However, it was found that for simultaneous binding of a cation and an anion, the molecule requires an additional modification with a fragment that would fix the complexation sites in space in an effective manner. Ferrocene proved to be the most appropriate spacer; this was used to synthesise the selective receptor for potassium fluoride **15**.[20]



15

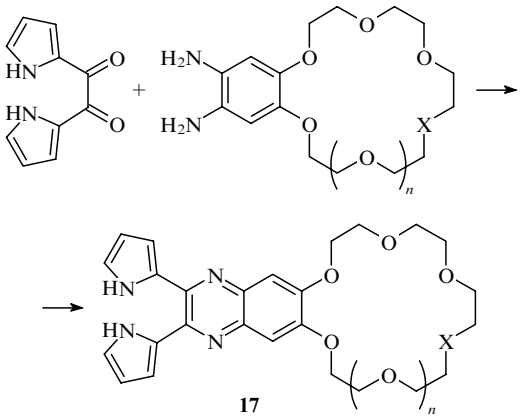


Subsequently, examples of using hetaryl derivatives of crown ethers as bifunctional complexing agents have appeared in the literature. For example, a crown ether containing diaminopyridyl residues has been synthesised.[21] This molecule is capable of recognising monopotassium salts of dicarboxylic acids due to the formation of a hydrogen bond between the carboxyl group and the diaminopyridyl fragment, and the coordination of the potassium cation by the crown-ether oxygen atoms. 12-Crown-4 ether **16** modified with pyrido[1′,2′:1,2]imidazo[4,5-*b*]pyrazine exhibits complexing properties unusual for a compound with this size of molecular cavity. It was found by UV spectroscopy that compound **16** effectively reacts with $Ba(SCN)_2$ giving rise to a stable complex ($\log K_{ass} = 3.98$).[22]



16

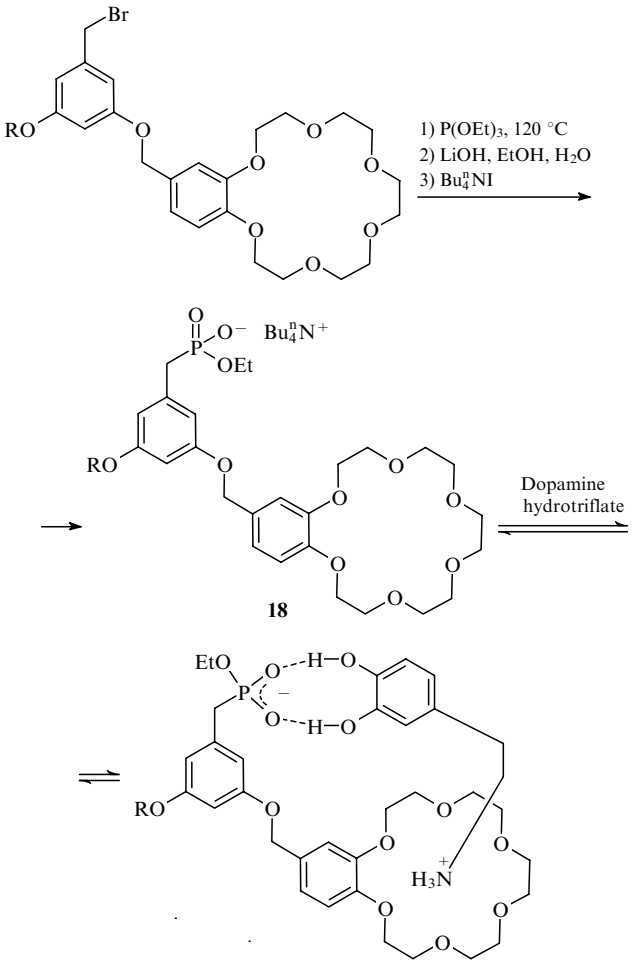
Recently, ditopic receptors **17** of a new class based on dipyrrolylquinoxaline have been prepared by the reaction of 1,2-diaminobenzocrown ethers with 1,2-dipyrrolylethane-1,2-dione.[23] Using NMR spectroscopy, it was shown that these compounds form complexes with the sodium cation and the fluoride anion.



17

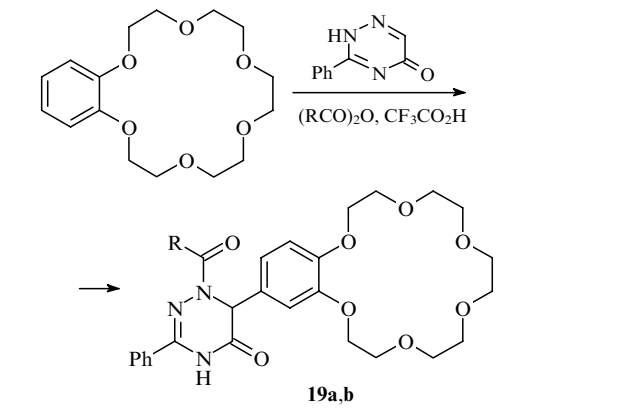
X = O, NH; $n = 0, 1$.

Heteroditopic receptors are used not only for binding inorganic ions but also for complex formation with bipolar organic molecules. The combination, within one crown-ether host molecule, of a fragment capable of forming complexes with the NH_3^+ group and an organophosphorus residue able to capture anions accounts for the use of compound **18** for dopamine transport.[24]



R = n-$C_{18}H_{37}$.

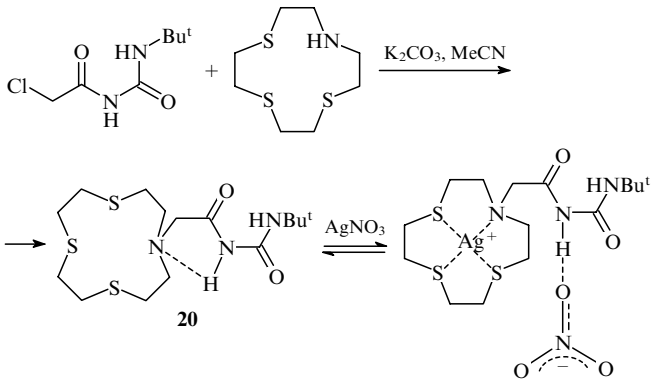
Direct, metal-noncatalysed C–C coupling of 1,2,4-triazin-5-one and benzo-18-crown-6 ether has furnished triazine-containing benzocrown ethers **19a**,**b**,[25] which form complexes with amino acids. According to ^{1}H NMR spectroscopy, compound **19b** selectively extracts β-phenylalanine due to binding of the NH_3^+ group by the crown ether fragment and hydrogen bonding between the NH group of the triazine ring and the carboxyl group of the amino acid.



R = Me (**a**), CF_3 (**b**).

The formation of the complex is indicated by the upfield shift (by 0.07 ppm) of the ^{1}H NMR signals of the methylene groups of the crown ether ring.[26]

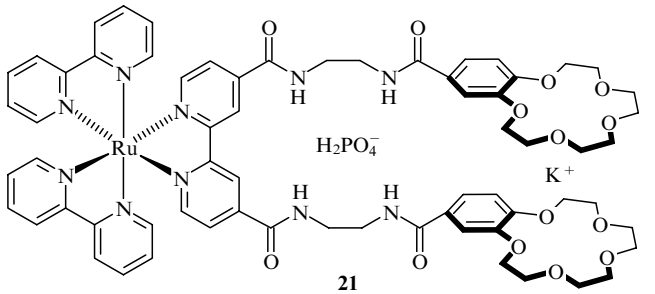
Thiaazacrown compounds are the most vivid representatives of heteroditopic receptors. They are used most often to capture ion pairs formed from transition metal cations and anions of various natures. Compounds such as macrocycle **20** selectively bind $PdCl_2$, $CuCl_2$ and $AgNO_3$.

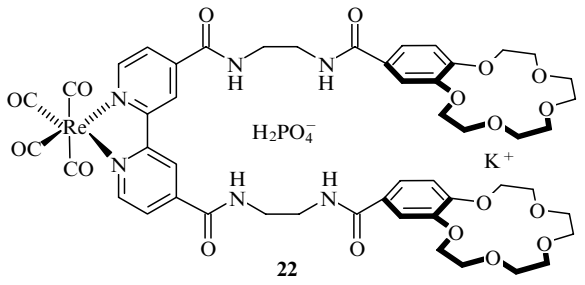


When $AgNO_3$ is added to a solution of ligand **20** in acetonitrile, the signals for the NH protons in the ^{1}H NMR spectrum shift upfield by 0.4 ppm. This shift is due to rupturing of the intramolecular hydrogen bonds upon the complex formation with Ag(I). Further addition of silver nitrate induces the formation of an intermolecular hydrogen bond with the nitrate anion, which is manifested as a downfield shift of the NH-proton signals. Thus, binding of the anion can take place only after the initial interaction of the ligand with the silver cation, resulting in cleavage of the intramolecular hydrogen bond.[27]

When cryptands are used as heteroditopic ligands, their interaction with anionic substrates such as 1- and 2-naphthalenemonosulfonates and 1,5-, 2,6- and 2,7-naphthalenedisulfonates can be observed.[28]

The introduction of pyridyl fragments into an azacrown ether, both as additional ligand groups and as binding sites, results in new complexing centres in azacrown ether molecules, *i.e.*, the binding properties of the molecule change. Heteroditopic ruthenium(II)- and rhenium(I)-bipyridylbis(benzocrown ether) receptors **21** and **22** (see Ref. 29) selectively bind KH_2PO_4 (K_{ass} = 205) in the presence of chloride anions (K_{ass} = 55).



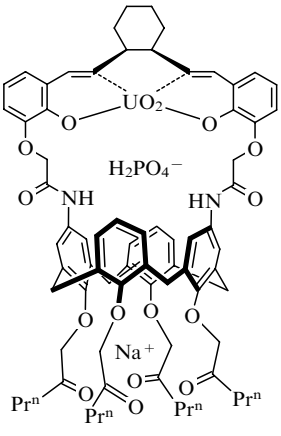


2. Heteroditopic receptors on a calixarene matrix

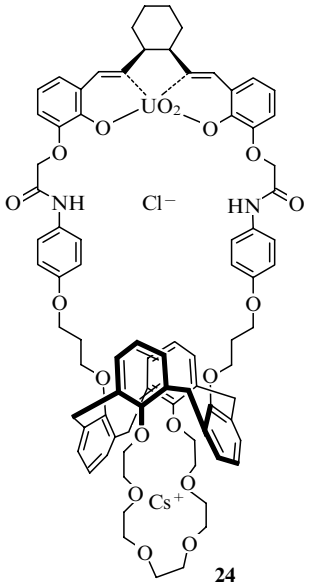
The cation-binding properties of calixarenes are well-known. For the design of a heteroditopic ligand, it is necessary to introduce anion receptors into the calixarene structure.

Binding of NaH_2PO_4 and CsCl by calixarene complexes containing UO_2 has been described.[30, 31] In these cases, the cation

interacts either with the functional groups grafted to the lower rim (compound **23**) or with the crown-ether fragment which cross-links the lower rim of the calixarene matrix (compound **24**). In both examples, the anions are bound by the amide groups immobilised on the calixarene matrix.



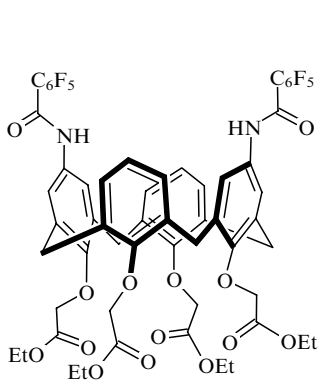
23



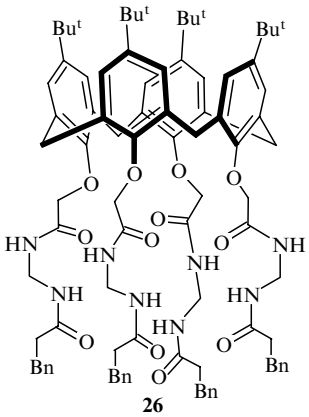
24

Heteroditopic receptors based on calixarenes containing amide functional groups in both the upper and lower rims are known. In the former case (compound **25**), the anion and the cation are separated in space, *i.e.*, they are bound at the upper and lower rims, respectively. The latter case (compound **26**) is of interest for the fact that both the cation- and anion-binding sites are located in the lower rim of the calixarene matrix. A study of the receptor ability of these ligands was carried out by NMR titration. It was found that compound **25** in CD_3COCD_3 is suitable for the selective binding of NaBr to give a complex with the stoichiometric ratio ligand : anion = 1 : 2 (K_{ass} = 738). Compound **26** can selectivity bind $NaHSO_4$ (K_{ass} = 1197).

Potassium acetate selectively reacts with the heteroditopic calixarene receptor **27**, existing in the 1,3-alternate conformation and containing two pentafluorophenylamide groups (for complex formation with the anion) and a crown-ether fragment (to capture the cation) (Scheme 2).[32]



25



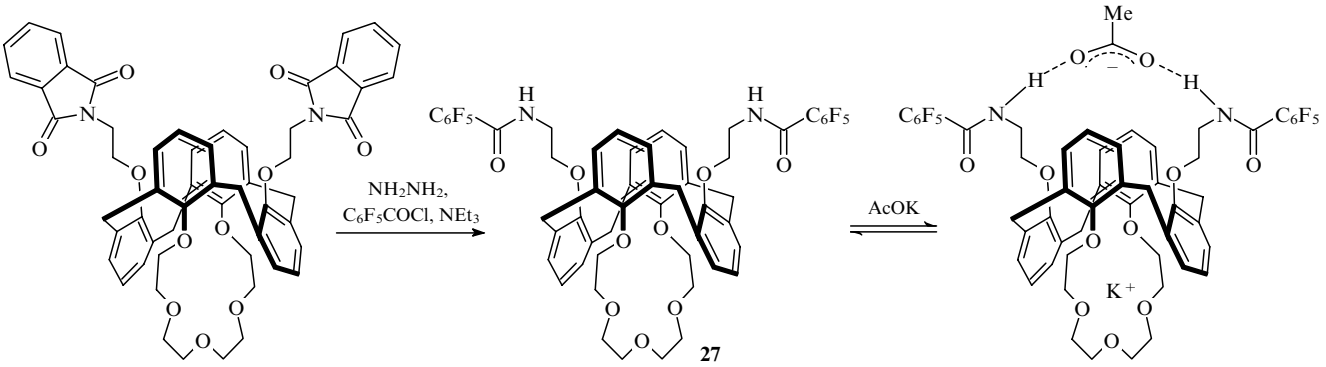
26

Apart from compound **27**, rhenium and ruthenium complexes **28a**,**b** may be applicable for the simultaneous transfer of cations and anions through the membrane (Scheme 3).[33] These heteroditopic ligands, containing Re(I)- and Ru(III)-bipyridylamide fragments connected by a flexible spacer to the calixarene lower rim, proved to be specific for ion pairs containing Li^+, Na^+, Br^- and I^- ions. NMR titration showed selective binding of lithium bromide (K_{ass} = 1260).[34]

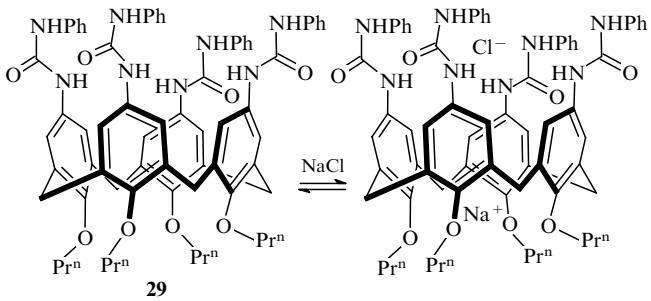
The introduction of Re(I)-bipyridyl fragments into the upper rim gives rise to selective receptor behaviour with respect to sodium iodide (K_{ass} = 392),[35] while the calixarene modified with a Ru(II)-bipyridyl fragment at the upper rim can be used for binding NaH_2PO_4.[36]

It was found that the combination of urea fragments (as anion-binding sites) and ester groups grafted to the lower rim within the same calixarene molecule results in the formation of selective extractants for alkali metal halides.[37–39] This was confirmed by NMR data obtained for mixtures of the bifunctional ligands and alkali metal halides. The extraction of sodium halides with biureide-substituted calixarene involves non-selective binding of the cations and the anions. The attempt to prepare an inclusion compound with caesium salts did not lead to the desired outcome, which may be due to the mismatch between the size of the complexing cavity and the radius of the metal cation. However, this compound can be used for the selective binding of potassium iodide.[40,41] The introduction of four urea fragments into the upper rim (compound **29**) brings about complexing properties with respect to sodium chloride. This is due to a higher affinity of urea for chloride anions (compared to other halide anions) as a result of the formation of strong hydrogen bonds.[42]

Scheme 2



27

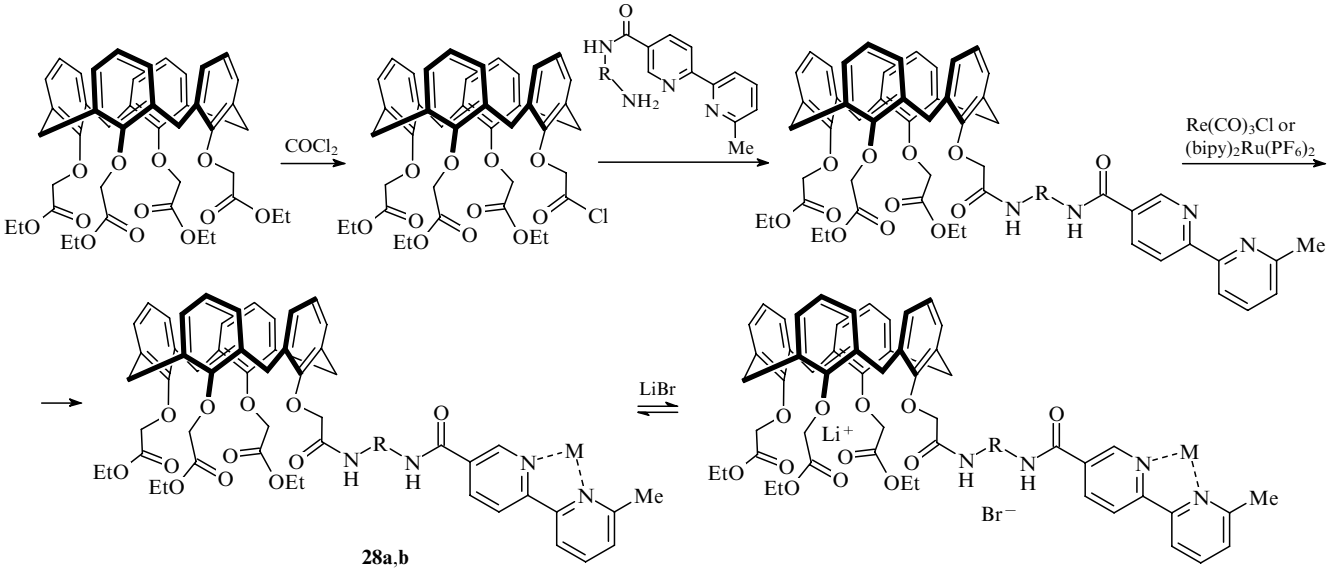


29

NMR titration has shown that calixarenes containing a crown ether substituent in the lower rim [43, 44] and urea residues in the upper rim can be employed as heteroditopic receptors. The binding constant of the anion decreases in the order $H_2PO_4^- \gg Cl^- > Br^- > NO_3^-$. The complexation with NaH_2PO_4 affords an ion pair.[44] Asymmetric thioureidocalixarenes **30** can be used for selective binding of sodium acetate (K_{ass} = 1200) (Scheme 4).[45]

Linking two calixarenes by an ethylene bridge produces a molecular cavity suitable for the formation of complexes with cations. The modification of these calixarenes by urea fragments results in receptor **31**, which forms a complex with potassium

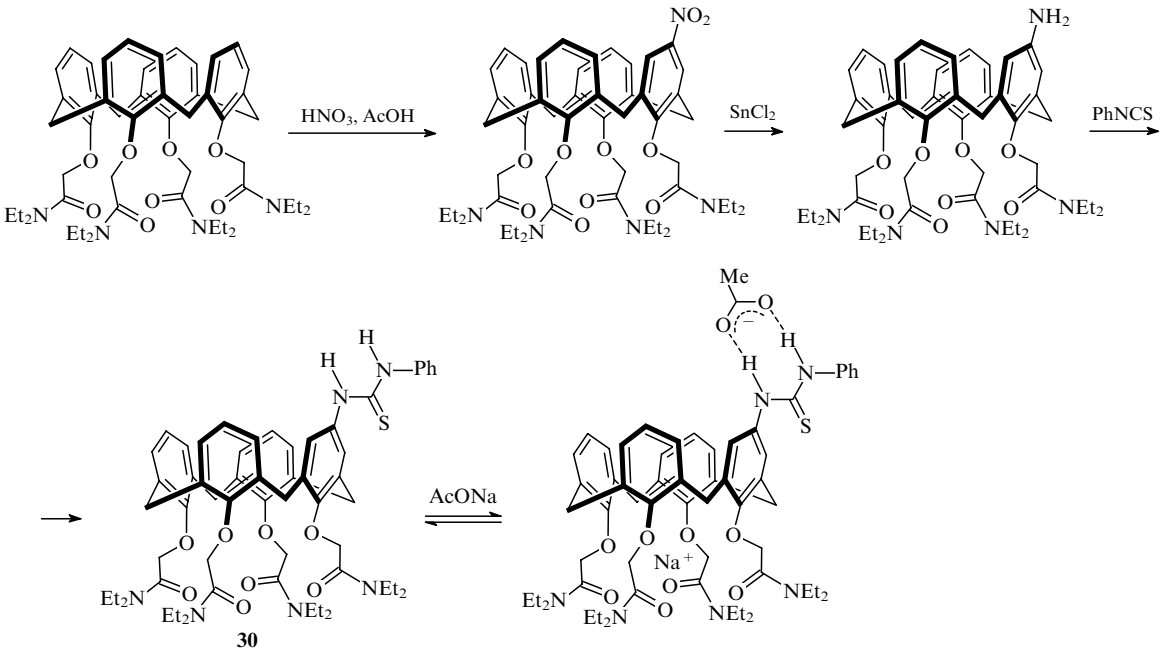
Scheme 3



28a,**b**

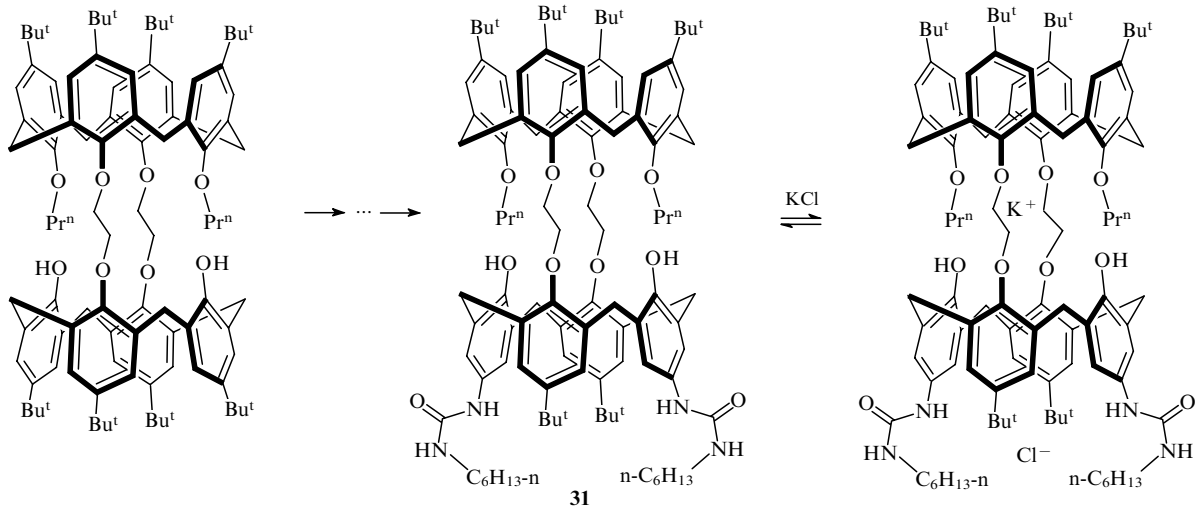
R = $(CH_2)_n$ (n = 2–4),  ; M = $Re(CO)_3Cl$ (**a**), $(bipy)_2Ru^{2+}(PF_6^-)_2$ (**b**).

Scheme 4



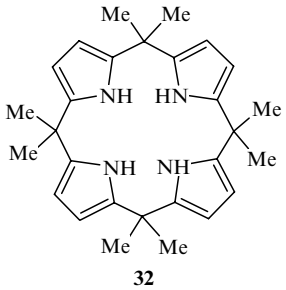
30

Scheme 5

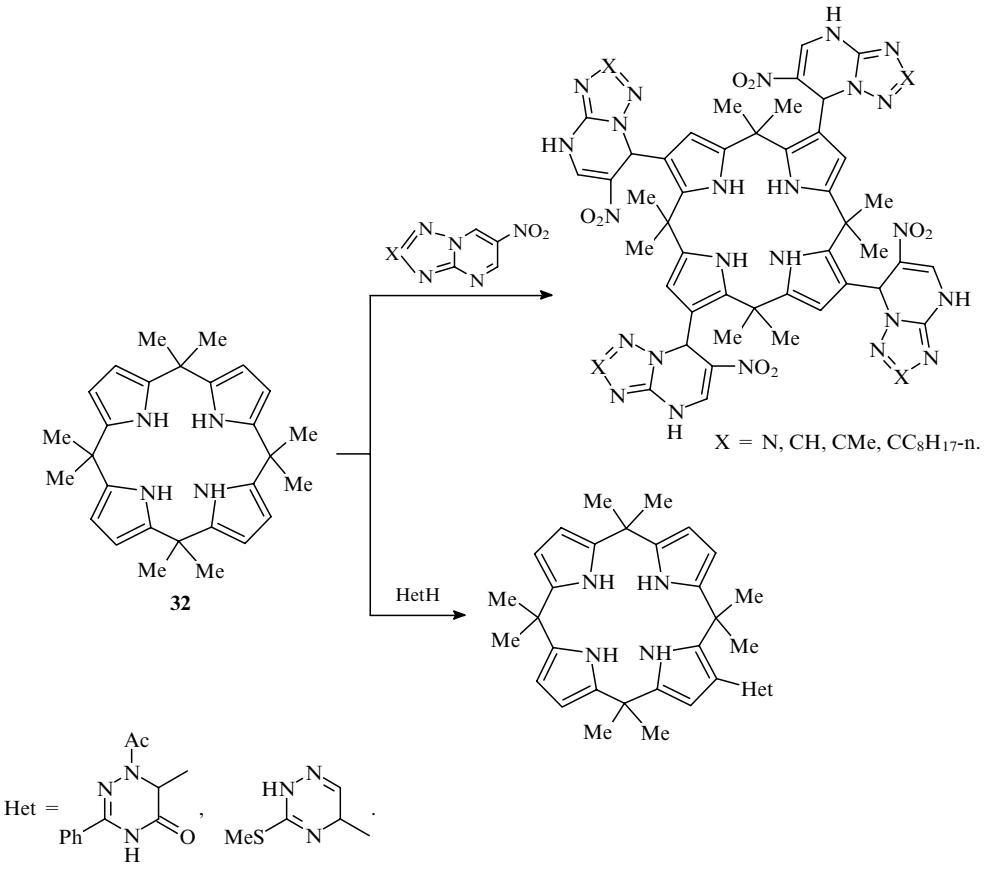


chloride (K_{ass} > 730), as confirmed by NMR titration data (Scheme 5).[46]

The heteroanalogue of calixarene, calixpyrrole **32**, is a promising heteroditopic ligand. In combination with benzocrown ether, this compound can selectively bind fluoride anions and metal cations.[47] Development of direct methods for the modification of calixpyrrole **32** by azine fragments [48] would pave the way to ligands of a heteroditopic nature (Scheme 6).



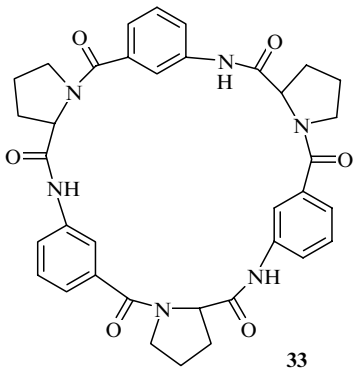
Scheme 6



3. Heteroditopic complexing agents based on other macrocycles

A method for the development of heteroditopic receptors based on cyclic peptides **33** has been proposed.[49]

These compounds can be used to bind ammonium iodide. In this case, the ligand adopts a conformation similar to the conical calixarene conformation and, similarly, it binds the cation through the interaction of the π-electrons of the carbonyl function, whereas the iodide anion is bound by hydrogen bonding with the NH groups of the peptide.



33

IV. Conclusion

The review summarises the data on the synthesis of bifunctional ligands and their complexing properties. The publications devoted to the design of heteroditopic receptors for the recognition of ion pairs on the basis of known cation and anion acceptors are analysed. All the described syntheses have a strategy in common which implies the design of a host molecule containing complexing sites of different nature. The resulting systems can be used not only for simultaneous binding of cations and anions but also for the selective complexation of bipolar organic molecules (for example, amino acids).

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