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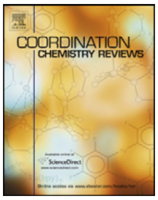

Review

Tetraimine macrocyclic transition metal complexes as building blocks for molecular devices

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This review article is dedicated to Professor Daryle H. Busch on the occasion of his 80th birthday.

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ABSTRACT

The synthetic strategy initiated by Busch and further developed in recent years resulted in an impressive variety of new azamacrocyclic ligand superstructures. In this contribution, we have reviewed papers containing general synthetic strategies, structural and electronic properties and results of electrochemical studies for a long series of neutral and charged macrocyclic tetraimine complexes of transition metals leading to a new type of homo- and heteronuclear[2]catenanes as examples of switchable molecular machines. The whole series consists of neutral and charged mono-, bis- and trismacrocycles and appropriate reference neutral molecules and many of their derivatives. The bismacrocyclic moieties are constructed from simpler tetraazamacrocyclic fragments. When two of them are linked through polymethylene chains, they form face-to-face biscyclidenes—rectangular box-like moieties. They can host some small guest molecules (water, π-electron-donating compounds) and are stabilized by hydrogen bonds with solvent molecules or a shell of neighboring counterions. Neutral thiol derivatives are used as recognition sites of monolayers self-assembled on electrode surfaces to be employed in devices based on donor–acceptor interactions.

Our catenanes consist of bismacrocyclic transition metal complexes linked by aliphatic chains and interlocked with a substituted crown ether. We have proved that under external stimuli – electrochemical pulses – the heteronuclear catenane exhibits controlled intramolecular relocation of the crown ether between two positions. The relocation is possible due to $\pi\cdots\pi$ interactions between the aromatic fragments of the crown ether and the transition metal (Ni, Cu) coordinating macrocyclic rings.

Our model tetraimine complexes of transition metals can also be used to solve the problem of controlling directional relative movement of molecular fragments present in complex supramolecules. On the way to this aim we have synthesized trismacrocyclic derivatives which are now appropriately modified to serve as components of complex catenanes.

1. Introduction

The field of synthesis and physicochemical properties of dynamic molecular or supramolecular systems designed to perform

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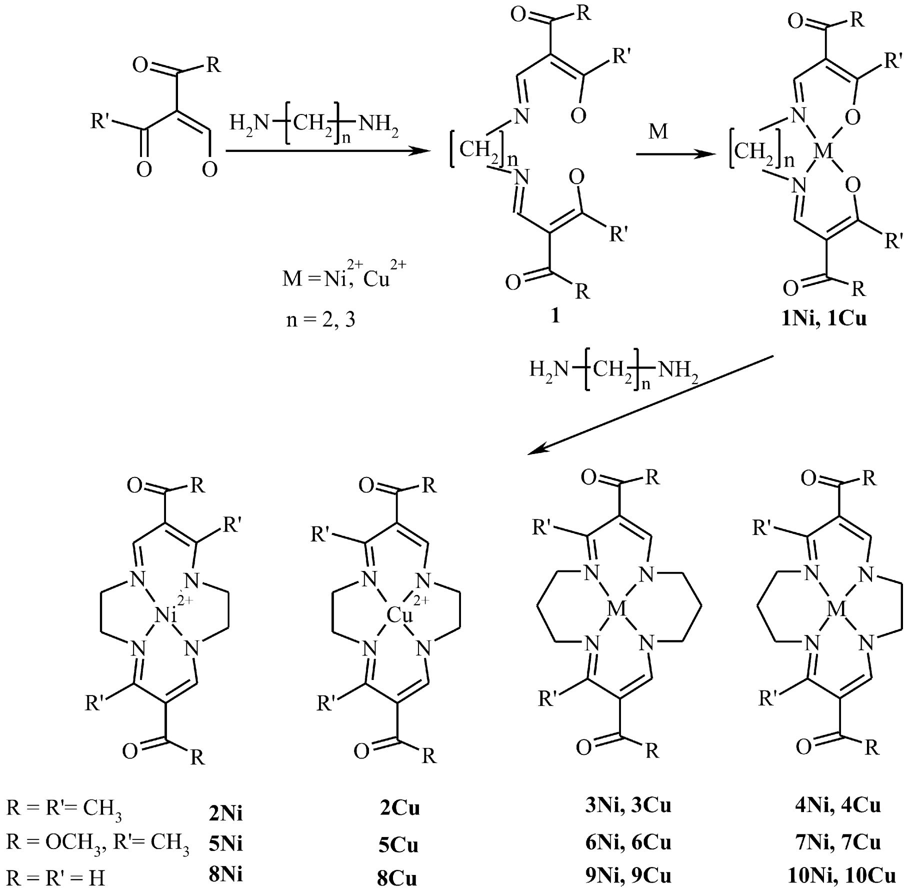


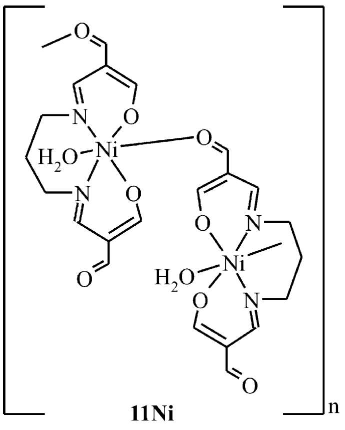
Scheme 1.

large amplitude mechanical motion triggered and controlled under external stimulation have experienced a rapid development during last decades [1,2]. Such molecules are usually described as "molecular machines or devices". Molecular motors and machines can be designed starting from several kinds of molecular and supramolecular systems.

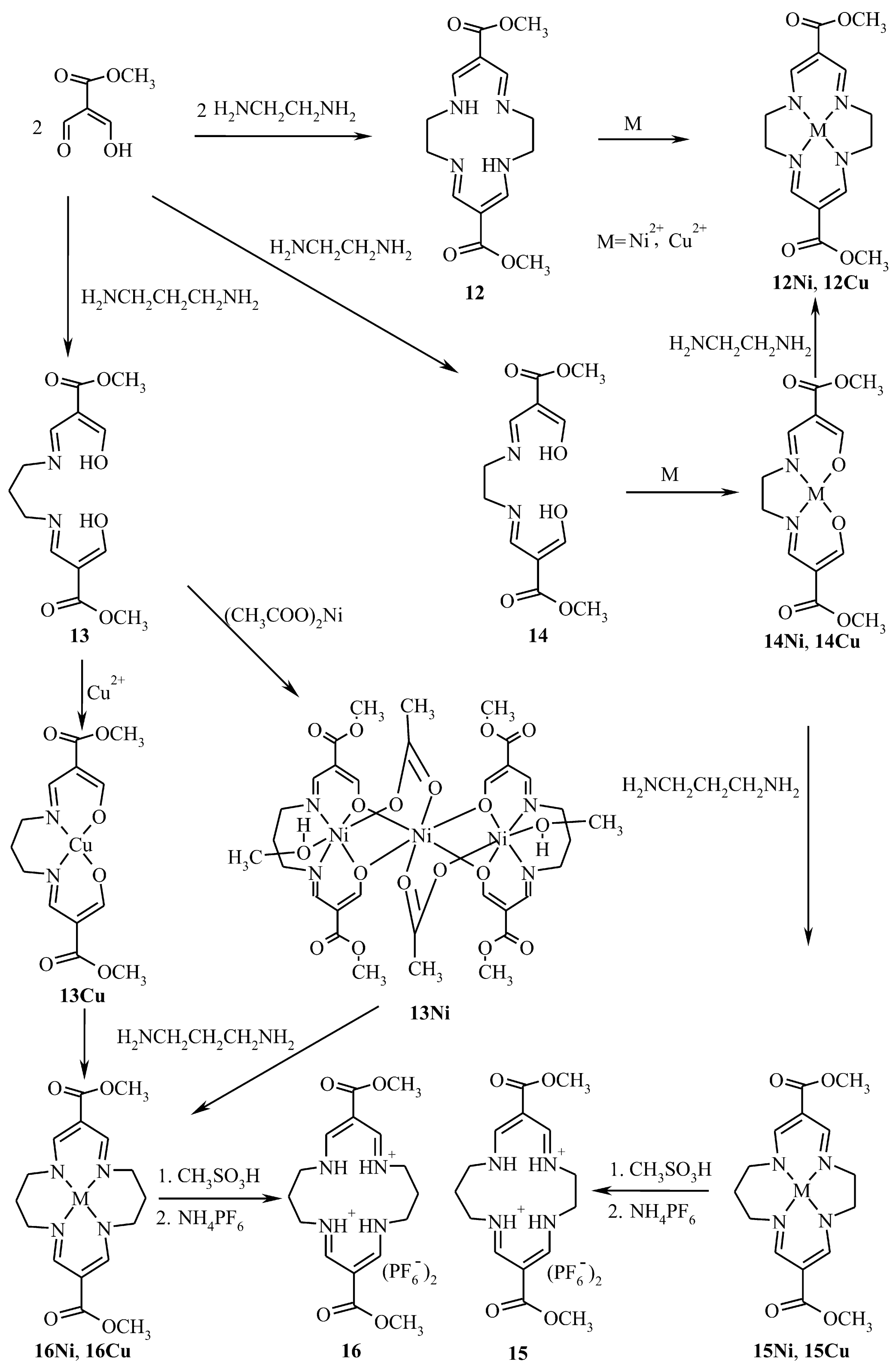
Although at the beginning of supramolecular chemistry, transition metals and their complexes were not regarded as useful or important components of the nanoscale devices, the situation has changed. Nowadays, the transition metals are almost routinely used to build large-scale molecular and supramolecular structures. Such structures often exhibit interesting properties different from those of their components. Transition metals are commonly utilized to construct wires, switches, memories, logic gates, light or electron driven molecular motors and 2D or 3D molecular networks [3–17].

The interlocked compounds, rotaxanes and catenanes are particularly suitable for molecular devices since, so-called, "mechanical bond" keeps components together, and, at the same time, it allows their relatively large amplitude motion. Important features of these systems result from non-covalent interactions between their components containing complementary recognition sites. These interactions are also responsible for the template-directed syntheses of mechanically bonded molecules. In 1983, Dierich-Buchecker and Sauvage [18–20] achieved a high yield synthesis of catenanes making use of preorganization around a copper(I) template. Several rotaxanes and catenanes involve two interlocked organic fragments exhibiting donor–acceptor interactions. A fairly strong interaction of a quaternary alkylated 4,4′-bipyridine unit with π-electron-rich aromatic systems was applied by Stoddart in a very efficient synthesis of interlocked molecules [21]. Hydrogen bonding [22] as well as a variety of non-covalent interactions [23] was also utilized in the processes of self-assembly. As can be seen from different physicochemical studies, the "mechanical bond" can be misleadingly interpreted as being purely based on just a mechanical interlocking of, at least, two macrocycles. In our studies we also want to establish the nature of such interactions in terms of properties of electron density distributions. This may help in rational crystal engineering of complex supramolecular architectures with predefined physicochemical properties.

Controlled relative movement of interacting components [24] can be realized by the incorporation of two or more competing recognition sites into one of the components of mechanically inter-



Scheme 2.



Scheme 3.

locked molecule. These sites can be switched off and on as the effect of an external stimulation. The energy to power molecular machines can be supplied as light, electricity, or chemical energy similarly to that in macroscopic machines. Design of externally stimulated molecular machines is exceptionally attractive because they could work practically without production of waste. Electroactive systems are of particular interests as they can be interfaced via the electrode with the external world. Reversibility of the switching reaction and the chemical stability of such systems are the main requirements especially in practical devices. The use of electroactive transition metal complexes as recognition sites is advantageous, firstly, due to the availability of different oxidation states of the metal centers, and secondly, due to avoiding difficulties associated with the organic radicals generated in the electrode processes [17].

The synthetic strategy initiated by Busch [25,26], and further developed in recent years, have resulted in an impressive variety of new teraimine macrocyclic ligand superstructures [27]. Macrocyclic tetraimines form stable complexes with nickel(II) and copper(II) ions and can be reversibly oxidized to 3+ oxidation state. The double bonds in planar β-diimine 6-membered chelate rings are delocalised. Therefore, these rings can be recognized through π–π donor–acceptor interactions. 14-Membered tetraimines, depending on substituents at the *meso* positions (at the central carbon atoms of the 6-membered chelate rings) and oxidation state of coordinated metal ion, can form cationic or neutral complexes, and be used as either π-electron acceptors or donors, respectively. Tetraimine macrocyclic transition metal complexes are one of our main topics studied for years now. Our long range aim is to use these molecular fragments as building blocks for molecular devices and in this review we would like to summarize our results which we have accomplished within last ca. 10 years of our activities.

2. Synthesis and characterisation of neutral macrocyclic tetraimine complexes of transition metals

The first tetraimine complexes, in the literature often referred to as Jäger macrocycles (**2**–**7**, Scheme 1), were synthesized by template condensation of bis(β-ketoaldimine)nickel(II) or copper(II) (**1**) complexes with ethylene- or 1,3-propylenediamine [28–30].

In early papers, the *cis* configuration with respect to the position of methyl substituents was assigned to all macrocyclic products. However, it was found later that the direct template synthesis of 14-membered nickel(II) complexes (**2Ni** and **5Ni**) results in the *trans* isomers as the main products [31–33]. The *cis* isomers are obtained from nickel salts and free ligands synthesized by demetallation of copper complexes [34,35]. Formation of the *trans* isomer of the 16-membered nickel(II) Jäger complex as a minor, and more soluble, condensation product was confirmed by Cameron [36]. Jäger cyclization procedure – with the application of triformylmethane as the starting material – leads to the formation of unsubstituted complexes **8** and **9** [37,38].

In our syntheses the unsubstituted 15-membered complexes **10** are formed as minor products only. The structures of the main products of the ring closure (**8** or **9**) were determined by the size of the last diamine used in template condensation.

The open chain nickel(II) complex substituted with the formyl groups and containing propylene bridge differs substantially in properties from all other square planar complexes **1**. It was isolated as a sparingly soluble paramagnetic oligomer **11**. It is bridged by one of the exocyclic aldehyde groups coordinated to nickel(II) ion of the next unit. The sixth coordination site around nickel(II) ion was filled with water molecule (Scheme 2) [39].

Another malonic aldehyde derivative—methyl ester of 2-formyl-3-hydroxypropenoic acid reacts with ethylenediamine giving the 14-membered macrocycle **12** (Scheme 3), but analogous reaction with 1,3-propylenediamine results in the formation of insoluble polymers [40]. Therefore, 15- and 16-membered neutral macrocyclic complexes (**15** and **16**) were obtained following the Jäger template procedure (Scheme 3) [33]. The dimeric structure, bridged by the additional nickel(II) cation and two acetate anions, of the intermediate paramagnetic complex **13Ni** was confirmed by X-ray crystallographic studies [40]. Hexafluorophosphate salts of diprotonated free ligands **15** and **16** were isolated by demetallation of their complexes in dilute methanesulfonic acid [33].

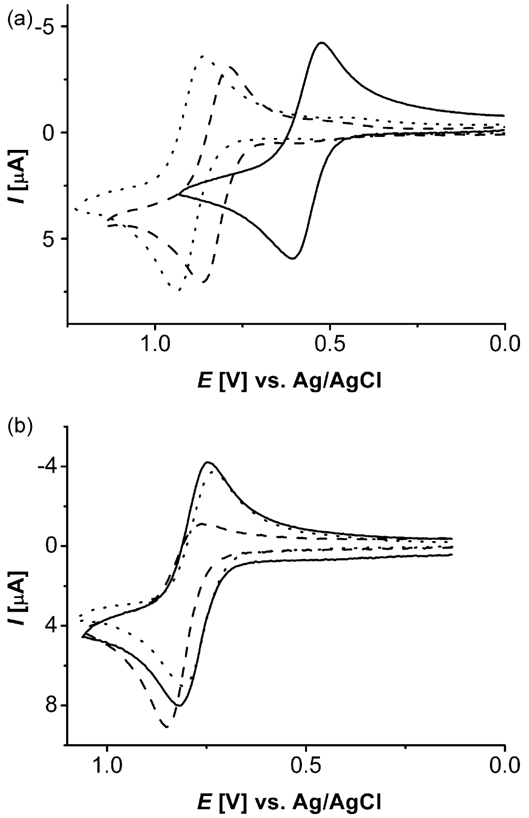


Fig. 1. Voltammetric behavior of esters: (a) (—) **12Cu**, (----) **15Cu**, (···) **16Cu** and (b) (—) **12Ni**, (----) **15Ni**, (···) **16Ni** recorded using GCE electrode in 0.1 M Bu_4NPF_6/CH_3CN solution, scan rate 0.05 V/s.

Redox behavior: **12Ni** and **16Ni** show almost reversible redox behavior with the ratio of the cathodic to anodic voltammetric peak currents close to unity and the peak potential differences, $E_{pa} - E_{pc}$, close to 60 mV (Fig. 1) while **15Ni** remains irreversible [33].

The reversibility of electrochemical behavior suggests that the reduced M^{II} and oxidized M^{III} forms appear in a similar planar configuration, so electron release does not require larger reorganization of the complex. The lower reversibility of the non-planar **15Ni** vs. **16Ni** indicates larger structural changes accompanying the electron transfer in these complexes. Also, the substitution of **9Ni** with two additional methyl groups (Jäger-type complex, **3Ni**) introduces chemical irreversibility [38]. The oxidation of **12Cu** proceeds at less positive potentials than that of **15Ni**, thus indicating its better electron donor properties. Similarly, for the 14-membered ligands, **12Cu** oxidizes easier than **12Ni**, whereas the opposite occurs for **16Cu** and **16Ni**. Hence, the formal potential of the M^{II}–M^{III} complex couple is determined by both the electronic and structural factors and can be tuned by small changes of the ligand structure and metal center. The reversibility of **12Cu** and small value of the formal potential suggests that it can be a promising electron donor for new donor–acceptor dyads. We, therefore, have established a common scale for the macrocyclic donors under study and some important acceptor compounds: *p*-benzoquinone, **Q**; chloranil, **CA**; tetracyanoethylene, **TCNE** and tetracyanoquinodimethane, **TCNQ** (see Fig. 2).

2.1. Experimental charge density analysis of a model Ni macrocycle

In our quest for the nature of “mechanical bond” we have studied details of experimental electron density distribution, including atomic charges and *d*-orbital populations [41], in supramolecu-

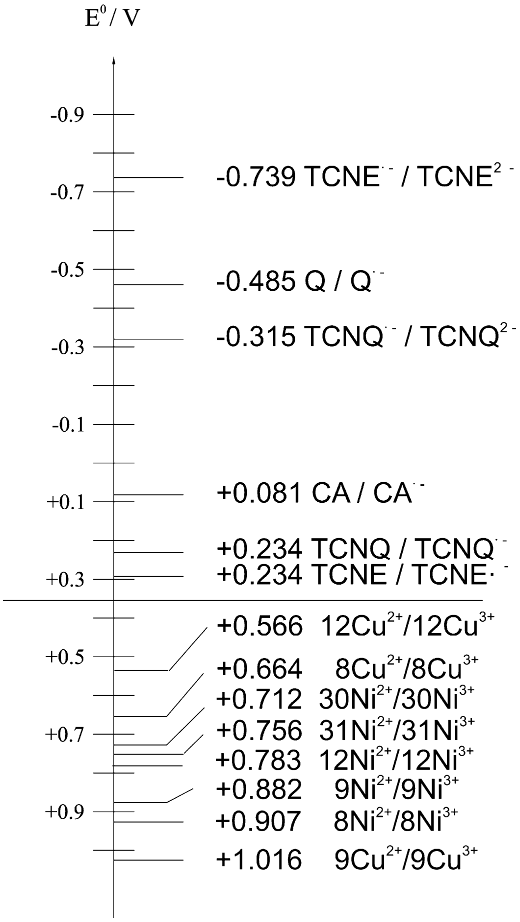


Fig. 2. Positioning of donors and acceptors under investigation on the common electric redox potential scale [*E* in volts, vs. AgCl/Ag]. The potentials were measured under the same conditions: 0.1 M Bu_4NPF_6 in CH_3CN, scan rate 0.05 V/s.

lar crystals of a model Ni macrocycle using the Hansen–Coppens approach [42]. Precise and accurate high resolution X-ray data were obtained for **16Ni**. This molecule can be treated as a building block for molecular devices. We have used the topological analysis – Bader's AIM (Atoms-in-Molecules) theory [43] – of the electron density for characterisation of interatomic and molecular interactions.

The **16Ni** molecule crystallizes in the $P2_1/c$ space group at the inversion center (see Fig. 3). Therefore, only half of the molecule is independent. The Ni atom is in a square planar environment coordinated by four nitrogen atoms. The integrated charge of particular atoms is the following: Ni1 = 0.699 e, O1 = −0.952 e, O2 = −0.989 e, N1 = −0.901 e, N2 = −0.895 e. The **16Ni** molecule as a whole is neutral. Although the Ni atom in **16Ni** is positive, its charge is significantly smaller than formal +2 e units. Both oxygen and nitrogen atoms are strongly negatively charged.

The values of rho at bond critical points, $\rho(\mathbf{r}_{BCP})$, for the Ni–N bonds are in the range from ca. 0.70 up to 0.75 e Å^{-3} with positive Laplacian values in the range from ca. 10.7 e Å^{-5} up to 11.7 e Å^{-5}, for the C–O bonds from 1.68 (O2–C8) through 2.06 (O2–C7) up to 2.92 e Å^{-3} (for the O1–C7 bond). There are 2 values of $\rho(\mathbf{r}_{BCP})$ for the N–C bonds: ca. 1.7 e Å^{-3} for N1–C1 and N2–C5 and ca. 2.5 e Å^{-3} for N1–C2 and N2–C4, respectively. For most of the CC bonds $\rho(\mathbf{r}_{BCP})$ is equal to ca. 2 e Å^{-3}, however for the C5C6 bond, $\rho(\mathbf{r}_{BCP})$ is smaller and amounts to ca. 1.7 e Å^{-3}. The values of Laplacian for all these bonds are negative indicating share type (covalent) bonds. The valence shell charge concentration (VSCC) of the Ni and nitrogen atoms are not in direct contact (see Fig. 3b). This indicates non-covalent bonding. For the Laplacian of the electron density evaluated in the plane of the macrocyclic ring, a typical map for square planar complex was obtained with four charge concentrations – $3d_{xy}$ orbitals – pointing towards the regions between the M–N bonds and charge depletions directed towards the (3,−1) critical points (CPs) of the negative Laplacian for the nitrogen atoms.

The *d*-electron density can be described in terms of multipole density functions; therefore, it is possible to obtain *d*-orbital populations from the values of multipoles. In the case of our compound and assuming that the **16Ni** molecule is almost a square planar complex, the following values of electron populations were obtained: $d(z^2) = 1.77(1)$, $d(xz) = 1.882(7)$, $d(yz) = 1.882(7)$, $d(x^2-y^2) = 0.71(1)$, $d(xy) = 1.93(1)$, which gives in total *d*-pop = 8.17 electrons with the lowest population of the dx^2-y^2 orbital.

The experimental electrostatic potential (ESP) surface for the **16Ni** molecule is presented in Fig. 3c. A positive isosurface surrounds the whole molecule. The experimental electrostatic potential exhibits very high positive values in the region of the propylene linker. The lowest, negative values of ESP are around the oxygen atoms (especially the carbonyl group) and Ni atom, despite the positive charge at the metal center. This can also be observed by calculation of the ESP property along the line perpendicular to the macrocyclic ring. The ESP changes sign at about 1.30 Å from the metal center and takes the lowest negative values (about −0.1 e Å^{-1}) at about 1.88 Å from that center.

Our experimental results are supported by quantum mechanical computational studies of the compound performed at the HF and DFT levels of theory. The above mentioned properties will be used in subsequent papers as reference values to detect and describe the M···M′ interactions in bismacrocycles which is being completed now, and – hopefully – attraction between the catenanes subunits. This is our small step towards a quantitative characterisation of interactions in molecular scale devices.

3. Superstructured macrocyclic aldehyde or ketone functionalized tetraimines

An important feature of the Jäger complexes is the reactivity of carbonyl oxygen atoms at the *meso* positions. These groups can be *O*-methylated transforming neutral macrocyclic complexes into reactive enol-ether di-cations **17Ni** (Scheme 4) [44,45]. The appended methoxy substituents are readily replaced by amino residues leading to the formation of the cyclidene complexes **18Ni**. The saddle shape of [16]cylidenes facilitates closure of the ring with diamines varying in length from 1,3-propanediamine to 1,12-dodecanediamine, and a variety of alkyldiamines containing aromatic rings or other heteroatoms [46–50]. Similar procedure for ring closure can be applied in the case of [15]cyclidenes. On the other hand, [14]cyclidenes are planar and very long bridges are necessary in order to close the second ring [51]. Alternatively, the second ring may be constructed in two steps, by the reaction of the *O*-methylated Jäger complexes **17Ni** with an alkylamine followed by bridging with an α,ω-dibromide or ditosylate. Coordinated nickel(II) ion can be easily removed from the cyclidene moiety and substituted with another transition metal ion. Several iron(II) and cobalt(II) lacunar cyclidene complexes, with different ring sizes as well as different R^1, R^2 and R^3 substituents, were studied in detail by Busch and coworkers as synthetic dioxygen carriers. In result, some very efficient synthetic dioxygen carriers were developed [27].

The cyclidene bridging reactions at high dilution are accompanied by an intermolecular cyclization process leading to bismacrocyclic dimers **20Ni** as minor products [50]. These dinuclear complexes were selectively synthesized according to two step procedure shown in Scheme 4 [52].

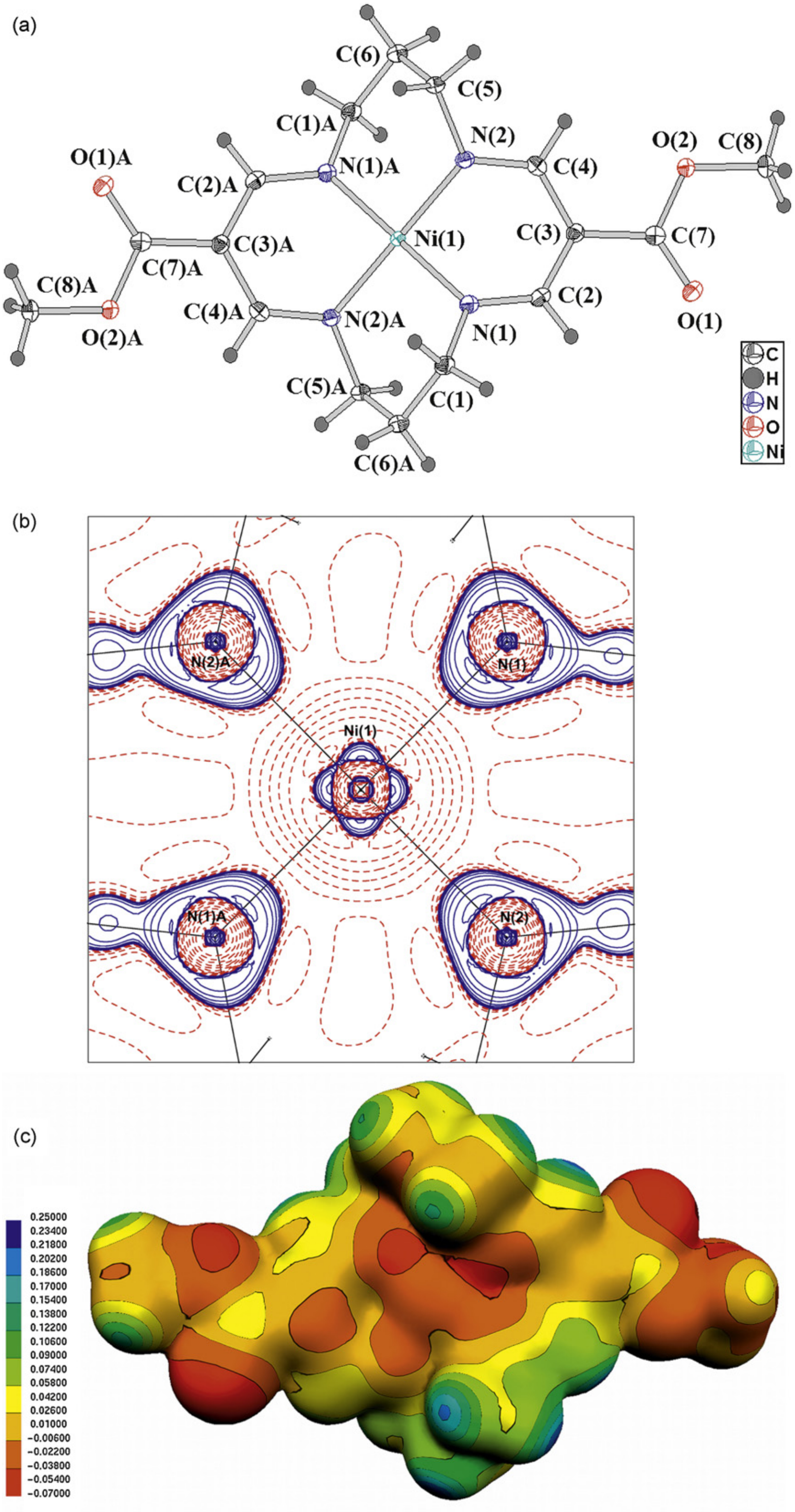
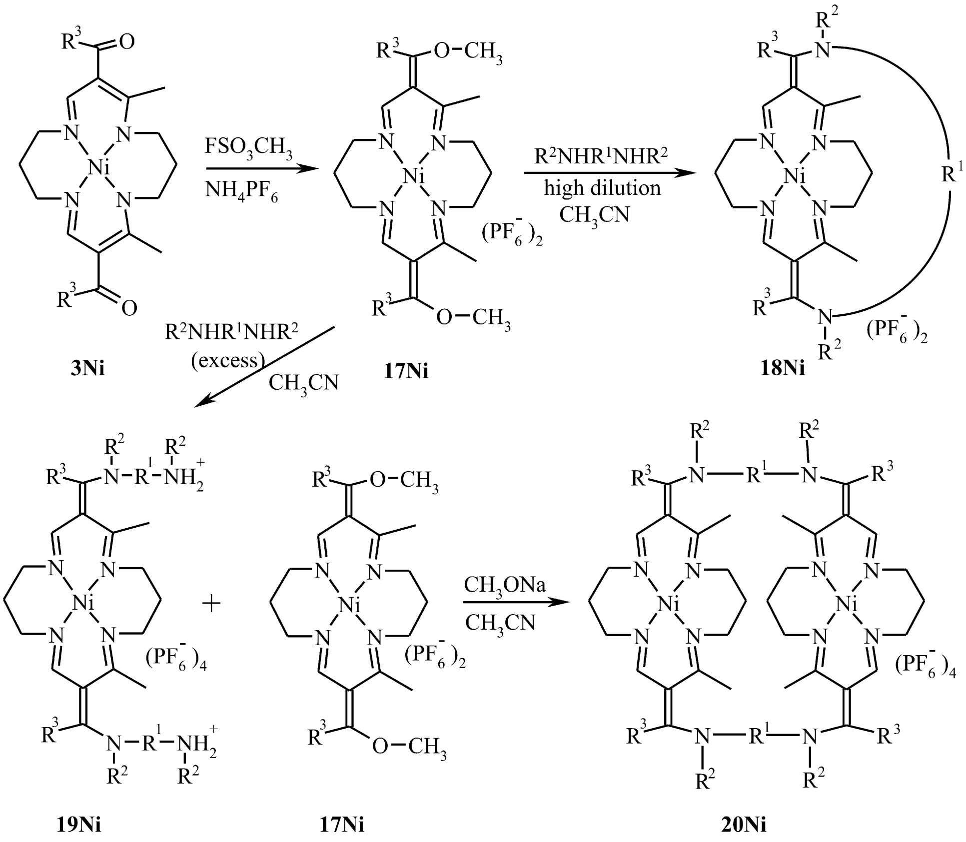


Fig. 3. (a) Thermal ellipsoids with atom numbering scheme in **16Ni**. The symmetry relation (inversion center) is shown using atom labels with "A" letter, (b) negative Laplacian maps in the plane defined by metal ion center and four nitrogen atoms in **16Ni**. The blue solid lines and red dashed lines indicate positive and negative values of the L(r), respectively. The contour spacing is in steps of $0.05 \times 2^{n-1}$ (positive values) and $-0.05 \times 2^{n-1}$ (negative values) in [e Å^{-5}] for $n = 1$–50, and (c) envelope of electron density with the electrostatic potential mapped on. The value of isosurface of $\rho(\mathbf{r})$ is equal to 0.01 e Å^{-3}. Figures were reproduced from Ref. [41] with permission of the copyright holders.



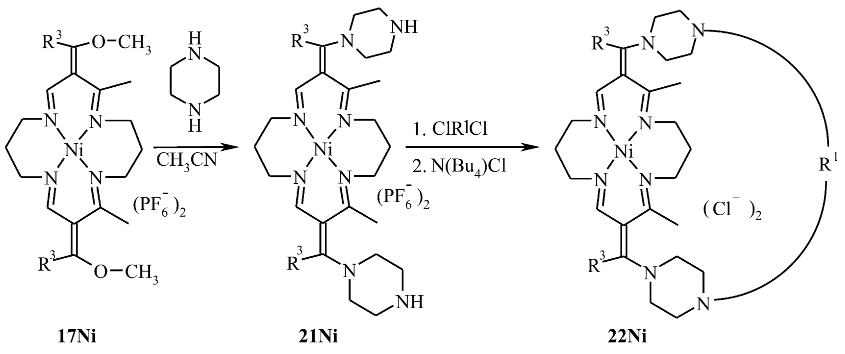
Scheme 4.

A different kind of macrobicyclic complexes is the vaulted cyclidene designed to bind simultaneously dioxygen and an organic substrate. The size of cavity was increased by incorporation of piperazine rings into the cyclidene bridge [53–57]. Piperazine rings serve as the rigid risers forming hydrophobic walls of the cyclidene cavity. Also rigid and hydrophobic durene or anthracene groups were used for the construction of the roof (**22Ni**, Scheme 5). Even larger cavities were constructed using dipiperazine risers (i.e. supervaulted cyclidenes—**23**, Scheme 6). ^{13}C NMR titration experiments showed that the vaulted cyclidenes form inclusion complexes by hydrophobic interactions with such guests as alcohols and phenols [57,58]. Association in aqueous solution between guest molecules and the vaulted cyclidene hosts were studied applying the effect of the paramagnetic copper(II) [58] or cobalt(II) ion [59] using the spin-lattice relaxation rates (T_1) of the guest protons. In the latter case, both deoxygenated and oxygenated cobalt(II) host complexes were investigated.

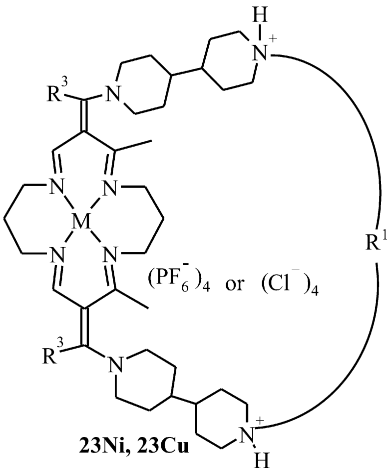
The ^{1}H NMR relaxation time measurements of a series of alcohols, show that the OH group remains associated with the solvent while the alkyl group protrudes into the cavity. The values of binding constants were estimated to be about 10 M^{-1}. Phenol guests are completely engulfed in the supervaulted complexes (**23Cu**) while they are only partially enclosed by the vaulted ones (**22Cu**) [59].

[14]Cyclidenes are planar and very long bridges are necessary to close the second ring [51]. Therefore, bridging reactions of the *O*-methylated complexes **24** with diamines lead to bismacrocyclic dimers **25** as major products [60]. Two step procedure, similar to the one applied by Busch for synthesis of the cyclic dimmers, using different metal complexes (**24Cu** and **24Ni**) in each step, affords heteronuclear complexes **25NiCu** [61,62].

Some groups containing heteroatoms as, for example, disulfido group, were incorporated into aliphatic bridging chains [63]. 1,10-Diaza[18]crown-6 was also successfully used as a bridging component [64]. Higher cyclic oligomers were also formed as minor products and identified by ESI mass spectrometry [60,63]. However,



Scheme 5.

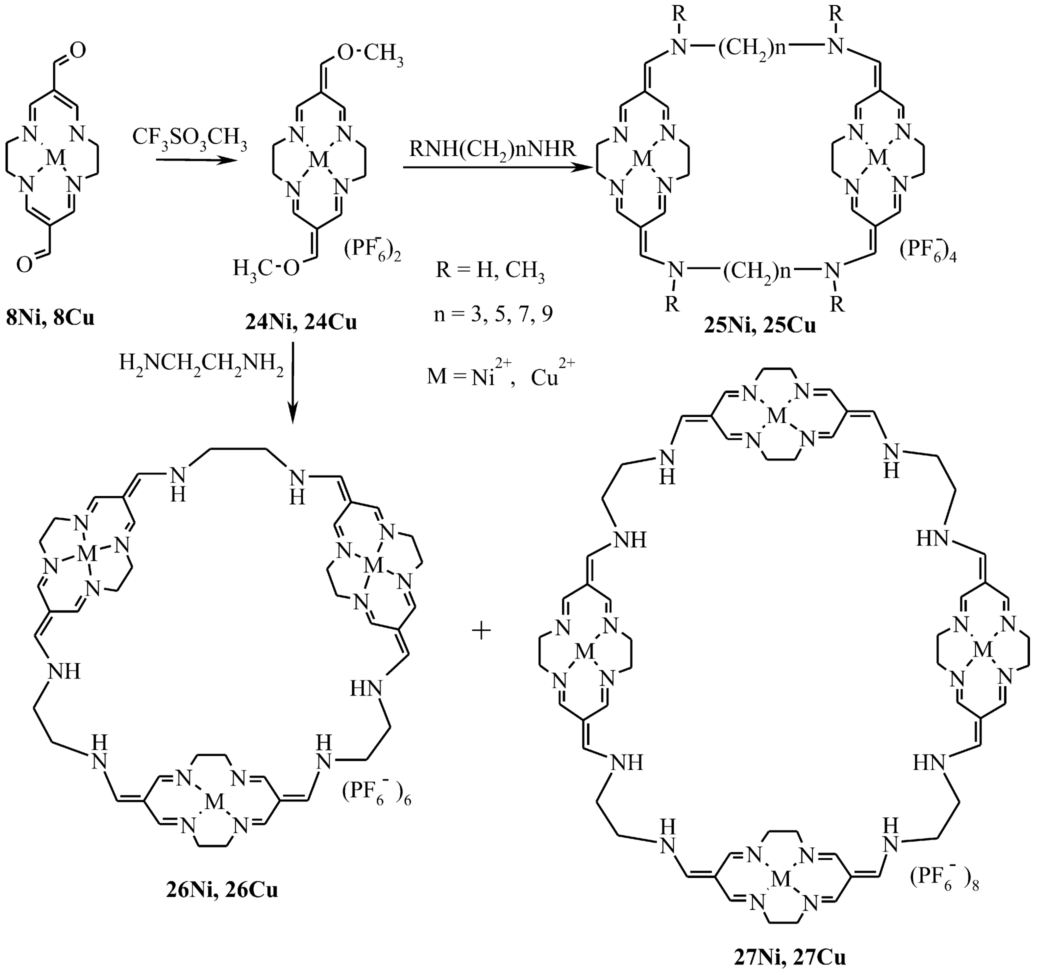


Scheme 6.

when 1,2-diaminoethane was used as a linker, the cyclic trimers **26** and tetramers **27** were isolated as major products (Scheme 7) [65]. Most of analytical and spectroscopic data for cyclic oligomers are identical or very similar, therefore, ESI mass spectrometry is the best method for the identification of isolated compounds. Differently than in case of simple organic molecules, mass spectra of oligocyclidene cations usually contain a large number of peaks. The charge of the original cation is lowered due to dissociation of some protons or association with anions, and several such particles are recorded. However, the isotopic patterns of these peaks depend on the number of coordinated nickel or copper cations owing to the presence of natural isotope mixtures. Typical isotopic patterns of copper(II) cyclidene complexes containing 1, 2, 3 and 4 macrocyclic units are shown in Fig. 4.

Structural properties: In general, structures of bismacrocycles described above have many common structural features. Most of the dinuclear cyclidene derivatives crystallize at special positions (around the symmetry centers) in the monoclinic crystal system. In consequence, only halves of the molecules are independent. Despite different metal ions, the bismacrocyles form quite similar rectangular molecules (for examples see Figs. 5–7). Each bismacrocycle consists of two macrocyclic fragments, which close the macrocyclic cavity and are linked by aliphatic chains (three, six or seven carbon long).

There are two groups of structures with slightly different $\mathrm{M^{II}}\cdots\mathrm{M^{II}}$ distances from ca. 4.1 Å to 4.5 Å for bismacrocycles with six and three carbon long aliphatic linkers, respectively, and from 6.8 Å to 7.8 Å for bismacrocycles with seven carbon long aliphatic linkers. The second distance characterising the size of cavity in bismacrocycles, i.e. the separation of the aliphatic linkers, is in the range from 14.5 Å up to ca. 15.5 Å for the methylated compounds. We also want to stress that in almost all bismacrocycles the separation of the external nitrogen atoms is longer than the separation of the metal centers. This means that an attraction is present in bismacrocycles between the face-to-face arranged macrocyclic fragments.



Scheme 7.

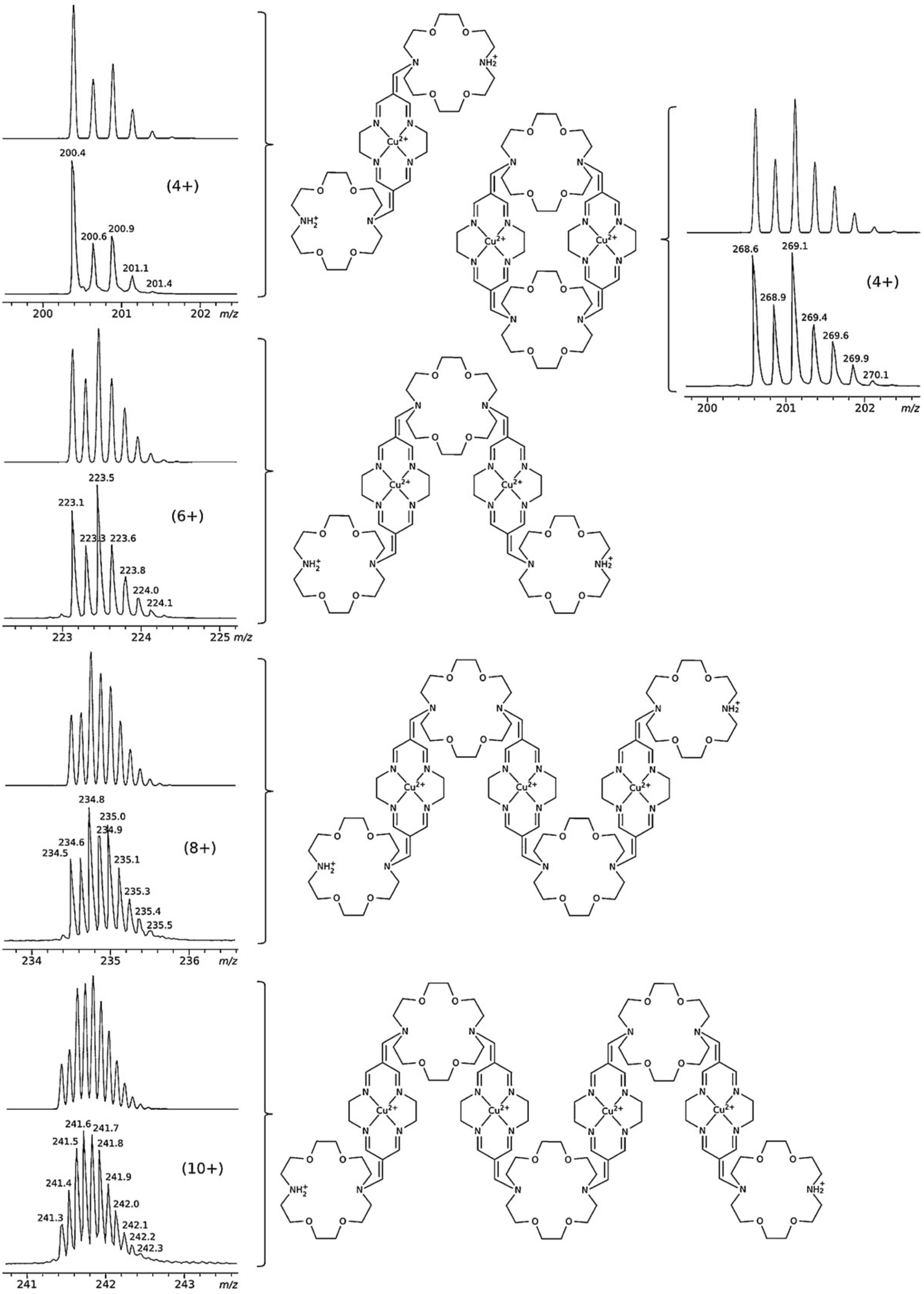


Fig. 4. Calculated (above) and observed (below) isotopic patterns of cyclidene oligomers bridged with 1,10-diaza[18]crown-6 [66].

The presence of small guest molecules (these are usually disordered water molecules) in the cavities formed by bismacrocycles in the solid state, is one of the most important differences compared to the previously studied bismacrocycles. Usually these guest molecules are located a bit off the center of the cavities.

Positively charged bismacrocyclic cations are surrounded by negatively charged counterions and water molecules. A representative example of this common situation is shown in the next figure.

From the point of view of the 3D arrangement of molecules, these structures consist of impressive rectangular boxes (Fig. 7)

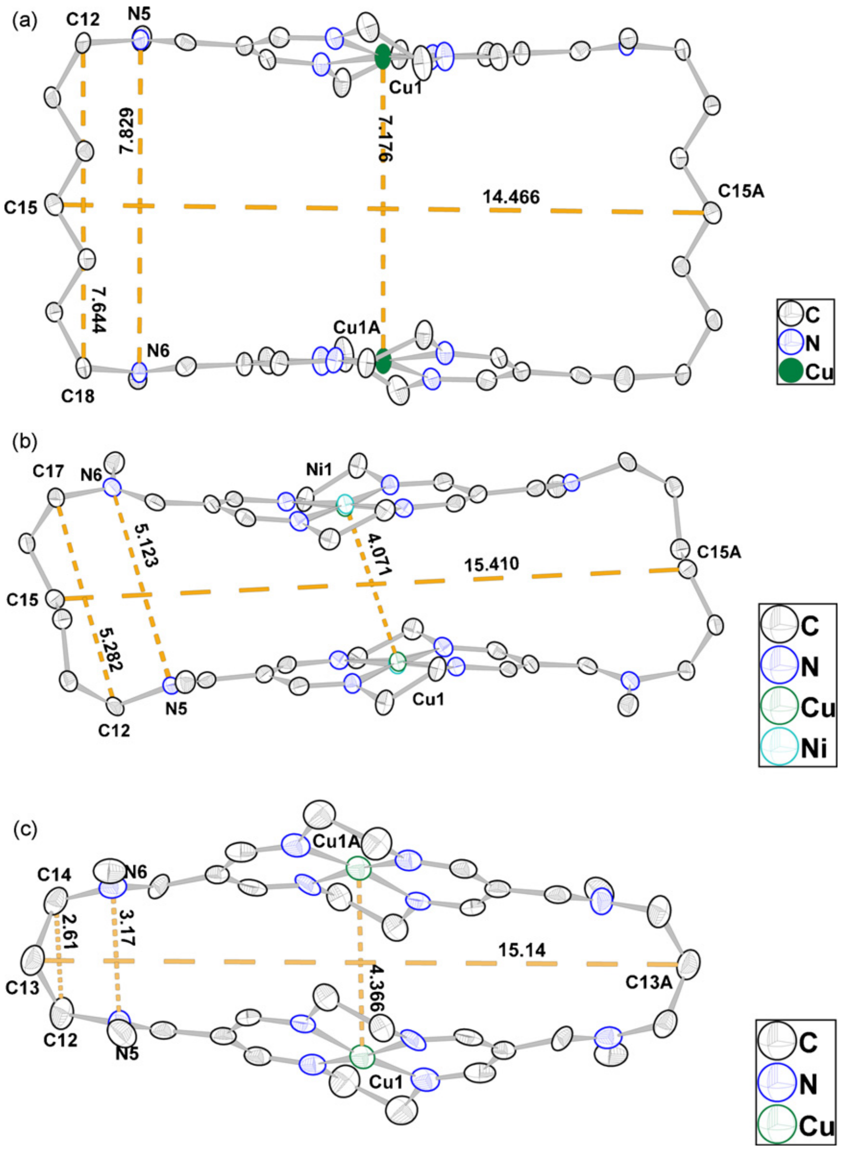


Fig. 5. Definition of the most important interatomic distances in bismacrocycles: (a) **25Cu** ($n = 7$, R=CH$_3$) × 4PF$_6^-$, (b) **25CuNi** ($n = 6$, R=CH$_3$) × 4PF$_6$, and (c) **25Cu** ($n = 3$, R=CH$_3$) × 4NO$_3^-$.

with the long axis of a bismacrocyclic moiety, more or less, parallel to the line defining the longer cavity size (also parallel to the macrocyclic planes). In the other group of structures this angle significantly deviates from 180°.

For the *N*-methylated species (**25**), the exocyclic iminomethylidene groups are slightly out of the macrocycle plane and some larger deviations from planarity are observed. This increasing steric strain is associated with the flow of electron density towards the central metal cations. For the bismacrocyclic dinuclear complexes containing two nickel or two copper ions, the intramolecular interactions between the metallic centers are strengthened through methylation of the macrocyclic components relative to the nonmethylated species. This feature is also observed in the electrochemical experiments.

The introduction of small changes in the molecular structure of the compounds by such means as methylation or elongation of spacers, leads to a significant modulation of the electrochemical and supramolecular properties.

Structure of homonuclear tris macrocycles: A significant extension of the concept of two interacting, more or less, face-to-face macrocycles are tris derivatives **26Ni** and **26Cu** (Scheme 7 and Fig. 8). Their triangle constitution has been confirmed by single crystal X-ray investigations [65].

The trismacrocyclic molecules carry a formal +6 charge and thus are surrounded by a shell of counterions. They form a triangle void in the inside of the moieties and can host even a few small organic guest molecules such as solvent or counterion moieties. The typical distances between the metal ions in these molecules are the following: 7.68 Å, 7.65 Å and 9.28 Å for the Cu···Cu distances in **26Cu** and 8.60 Å, 8.85 Å and 8.68 Å for the Ni···Ni distances in **26Ni**. The size of the voids is big enough to form complexes with molecules having appropriate shape such as triptycene.

Both trismacrocyclic compounds form 3D lattices utilising numerous weak intermolecular interactions. The triangle molecules are packed in such a way as to optimize interactions between the macrocyclic fragments from neighboring molecules (Fig. 9). Packing of bis-, and particularly trismacrocycles is a good example of "geometrical chemistry"—chemistry dealing with compounds resembling simple geometrical figures.

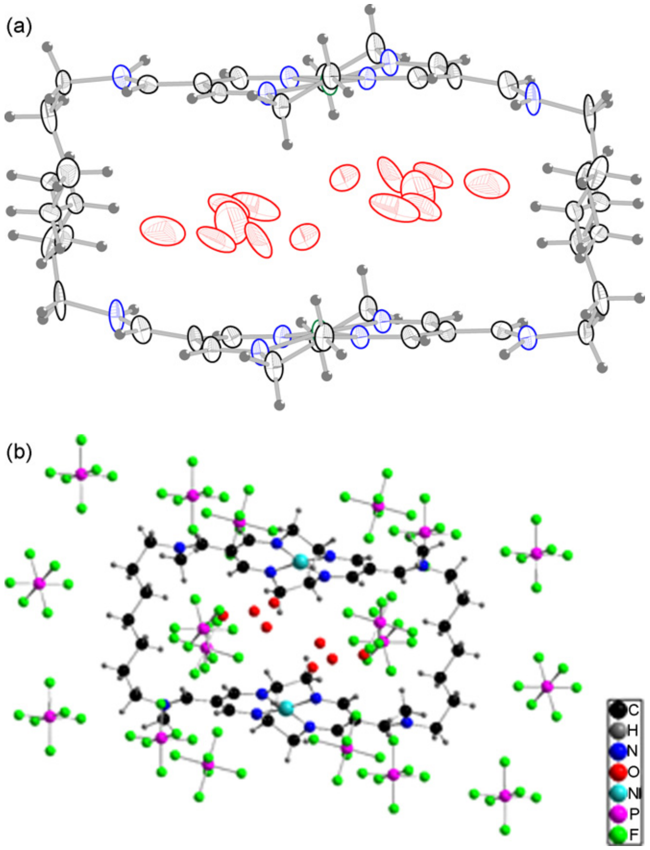


Fig. 6. Distribution of the guest moieties in the bismacrocyclic cavities and the closest counterions in **25Cu** (a) and **25Ni** (b) ($n = 7$, R═CH_3) × $4PF_6^-$, respectively.

4. Superstructured neutral macrocyclic functionalized tetraimines

All macrocyclic complexes shown in Schemes 1 and 3 are substituted at the *meso* positions with reactive acetyl, formyl or carbomethoxy groups. These groups can be transformed into other ones to achieve more complex ligand superstructures. The acetyl substituted nickel(II) complexes (e.g. **3Ni**, Scheme 8) react with *p*-toluenesulfonic acid to give deacylated parent complex **28Ni**, which later can be reacted with various electrophiles [67–69].

Reacylation of **28Ni** with long chain dicarboxylic acid chlorides at high dilution leads to the formation of the macrobicyclic products **30Ni** shown in Scheme 9 [70]. The acylation of **28Ni**, as well as its 15-membered analogue, with adipoyl chloride at high concentration results in the formation of face-to-face bismacrocyclic dinuclear complexes (**31Ni** or 15-membered analogue) [71]. Macrocyclic fragments linked with two aliphatic chains in

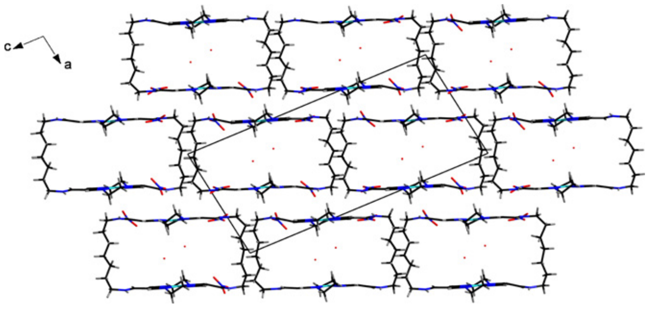


Fig. 7. Example of typical packing—3D crystal structure of **25Ni** ($n = 7$, R═H) × $4NO_3^-$.

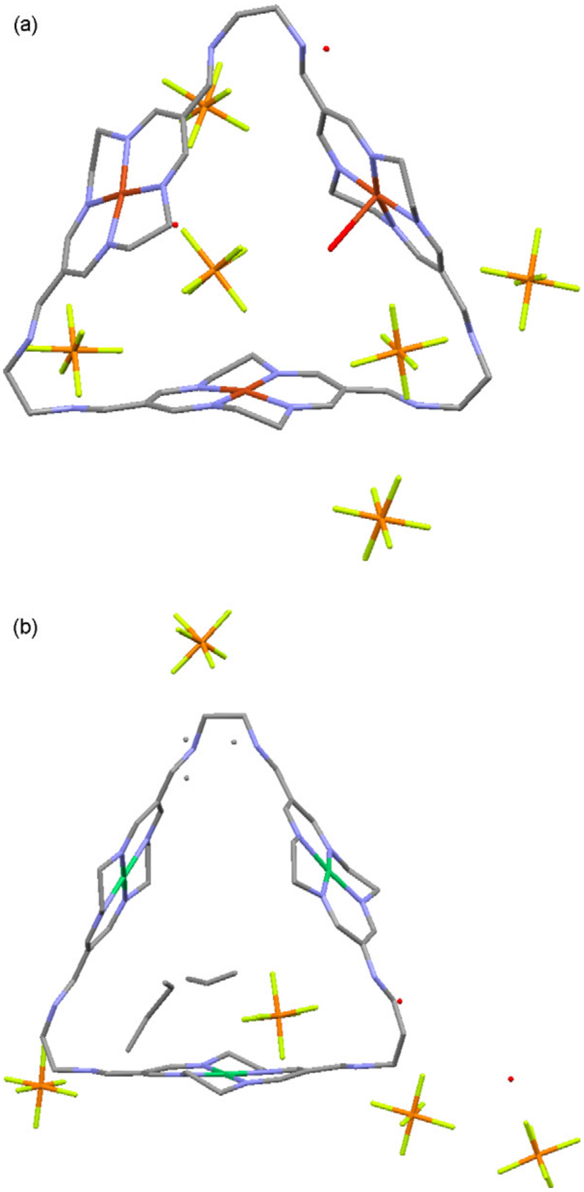


Fig. 8. Single crystal X-ray molecular structure of (a) **26Cu** and (b) **26Ni** trismacrocycles.

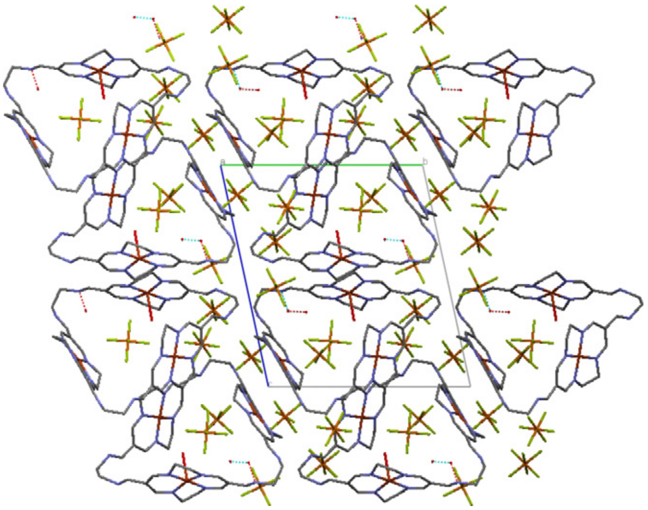
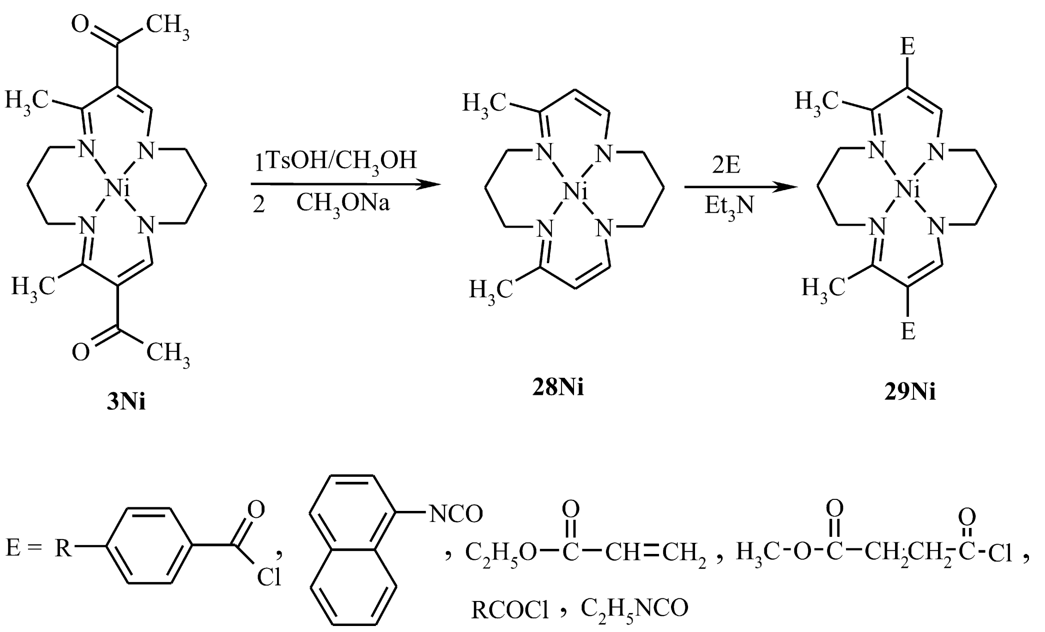


Fig. 9. An example of 3D structure of a model **26Cu** trismacrocycle.



Scheme 8.

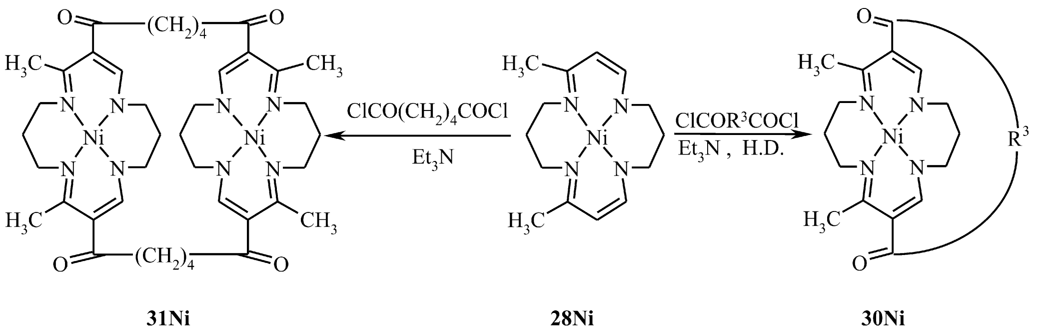
complex **31Ni** form large cavity which can host smaller organic molecules.

The cavity has an ellipsoidal shape due to non-planarity of the macrocyclic rings and in the solid state contains one toluene molecule surrounded by two bismacrocyclic units [71]. The distance between nickel(II) cations is equal to ca. 9.3 Å and ca. 10.1 Å between the most distant carbon atoms of the aliphatic linkers. The cavities can host some smaller organic moieties such as $CHCl_3$ or toluene. Significant interactions with organic donors (**TCNQ** and *p*-quinone) in solution were confirmed by electrochemical studies. For a given length of chain, the cavity size adjusts to the shape of the guest molecule. The guest molecules have a tendency to enter the bismacrocyclic rings thus gluing them together via weak intermolecular interactions. The host–guest interactions in the solution lead to the decrease of the energy gap between the HOMO of the donor nickel(II) complex and the LUMO of the acceptor (i.e. **TCNQ** or quinone). Upon mixing, the anodic peak corresponding to the oxidation of the nickel(II) centers is shifted to more positive potentials exhibiting stronger interactions between the acceptor and the neutral nickel complex than between the acceptor and the oxidized nickel(III) complex. At the same time, the quinone reduction is shifted to less negative potentials. These host–guest interactions decreasing the energy gap between the HOMO of the donor species and the LUMO of acceptors lead to the observed non-additive CT properties of the systems.

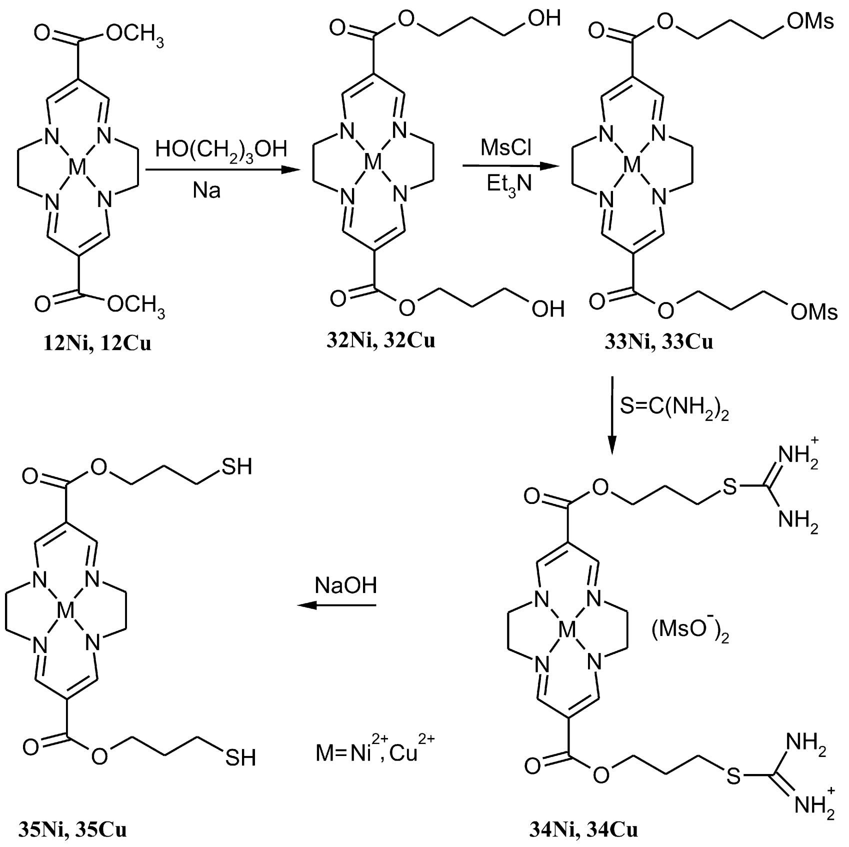
The bismacrocyclic complex containing quite planar 15-membered rings forms a rectangular cavity (Ni···Ni distance equal 5.2 Å) too small to accommodate any organic guests.

Our attempts of the hydrolysis of the diesters **12Ni** and **12Cu** to carboxylic acids, or transformation into amides, in reaction with α,ω-diamines were not successful. However, the transesterification reaction, catalyzed by sodium alkoxide in the presence of large excess of an alcohol, used as a solvent, proceeds at the elevated temperature. Ethylene, 1,3-propylene and 1,5-pentamethylene glycols were used to move the reaction centers away from the negatively charged ligand. Reaction of dihydroxy derivatives (e.g. **32Ni**, **32Cu**, Scheme 10) with the mesyl chloride gave reactive dimesylates which then were transformed into dithiols **35Ni** and **35Cu** [72] in a standard procedure.

The dithiol compounds were used for the modification of electrode surfaces [72,73]. When the electrode modified with two-component monolayer **35Cu** + **C6SH** (n-hexanethiol) is in the solution containing an acceptor **F_4TCNQ** (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane), the Cu^{2+} electrode processes are shifted towards more positive potentials (Fig. 10). This suggests donor–acceptor interactions between **F_4TCNQ** and the macrocyclic complex immobilized on the surface of the electrode. The donor properties of macrocyclic compound self-assembled on the gold surface are weakened by the electron-deficient **F_4TCNQ** dissolved in the solution. If the acceptor molecule is chosen to be a charged bismacrocyclic Cu^{II} or Ni^{II} complex, **25Cu** or **25Ni** ($n = 7$, R=H)



Scheme 9.



Scheme 10.

additional signals at more positive potentials are observed pointing to the formation of a unique host–guest complex between the mononuclear **35Cu** donor and the bismacrocyclic acceptor of suitable size (Fig. 11). The macrocyclic complex of Cu^{II} immobilized on the Au surface constitutes the axis of the pseudorotaxane. Upon application of positive potentials the pseudorotaxane thread undergoes oxidation and dethreading takes place since the positively charged Cu^{III} center repulses the bismacrocyclic complex (**25**) to the solution.

The dimesyl derivatives **33Ni** and **33Cu** were bridged with dimercapto-substituted aromatic ethers (Scheme 11 and Fig. 12)

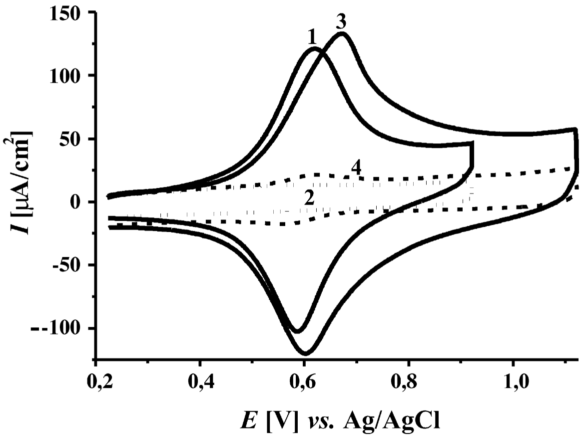


Fig. 10. Comparison of cyclic voltammograms recorded for gold electrode modified with single component monolayer—**C6SH** and mixed—**35Cu** + **C6SH** monolayer in the supporting electrolyte (0.1 M Bu_4NPF_6/CH_3CN), in the absence and in the presence of 1×10^{-5} M **F_4TCNQ**; (1) **35Cu** + **C6SH** and (2) **C6SH** in the absence of **F_4TCNQ**, (3) **35Cu** + **C6SH** and (4) **C6SH** in 1×10^{-5} M **F_4TCNQ**. Scan rate: 0.5 V/s.

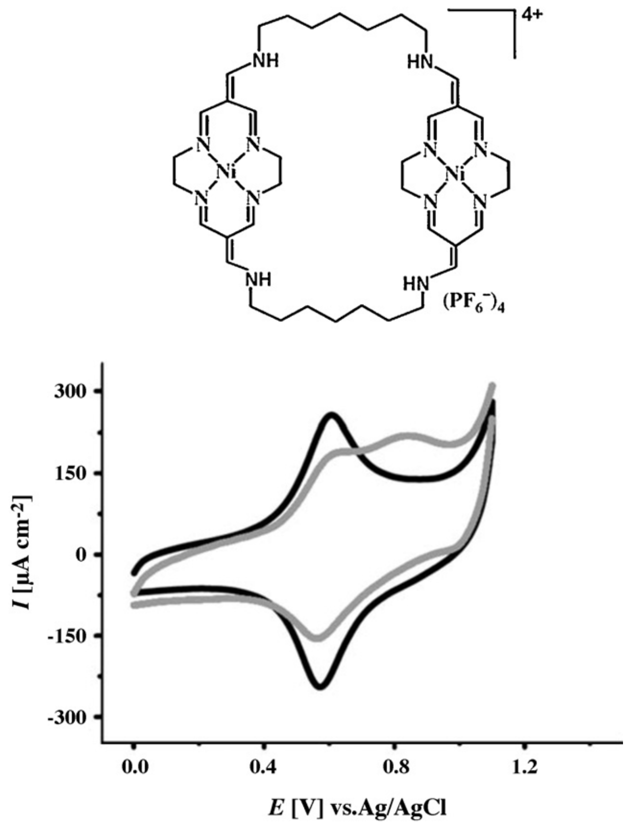
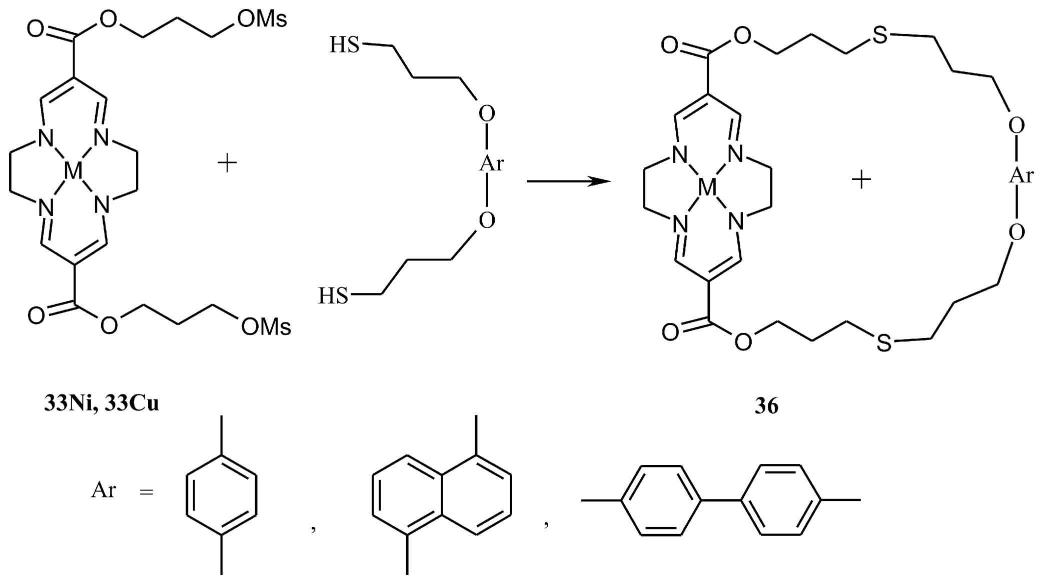


Fig. 11. Comparison of cyclic voltammograms recorded for modified gold electrode: **35Cu** + **C6SH** (black line) and **35Cu** + **C6SH** monolayer in the presence of 1×10^{-5} M **25Ni** (gray line). 0.1 M Bu_4NPF_6/CH_3CN, scan rate: 0.5 V/s.



33Ni, 33Cu

36

Scheme 11.

to obtain the neutral "lacunar" receptors for electron deficient aromatic guest molecules [74]. The X-ray structural studies revealed, that independently of the chain length and an aromatic linking group, the bridge adopts an "equatorial" conformation around the macrocycle due to interactions of the aromatic donor with protons of ethylenediamine bridge in the macrocycle. In all lacunar molecules with aromatic fragments, the angle between respective macrocyclic least-squares plane and the aromatic fragment indicates that these two molecular fragments are nearly perpendicular to each other. For example, in the **36NiPh** structure the conformation of the molecules seems to be induced by cooperative C–H···π interactions of hydrogen atoms from the ethylene bridges to the phenyl or naphthyl rings (Fig. 12) of the aromatic fragment. Apparently, such interactions can work as a template in the cyclization reactions and they exclude the possibility of forming linear products. The first step is the deprotonation of the SH group, and followed by S_N2 (or addition) reaction with the macrocyclic compound takes place. The reaction intermediate undergoes conformation changes from the linear form to the bent one where some extra stabilization by the C–H···π interactions occurs. The next step is deprotonation of the remaining SH group which allows the intramolecular S_N2 reaction to proceed.

Transesterification of **12Ni** and **12Cu** with 4-penten-1-ol gave macrocyclic complexes (**37Ni** and **37Cu**) functionalized with carbon–carbon double bonds at the ends of alkyl chains. The metathesis reaction in the presence of Grubbs I catalyst, followed by catalytic hydrogenation, results in the formation of neutral face-to-face bismacrocyclic dinuclear complexes **38Ni** and **38Cu** (Scheme 12) [75]. The formation of cyclic trimers as minor products was confirmed by Field Desorption (FD) mass spectrometry.

5. Synthesis and characteristics of mixed bismacrocycles with neutral and charged macrocyclic components

After standard transformations outlined in Scheme 13, the neutral dihydroxy derivatives **39** gave protonated diamines **42**, which afterwards were used as bridging units for cyclidene ring closure.

All four possible combinations of dinuclear complexes coordinating nickel(II) and/or copper(II) in neutral and cationic macrocycles (**43**) were synthesized and characterised by X-ray crystallography [76]. All these molecules form very similar crystal and molecular structures crystallizing in the monoclinic $P2_1/n$ space group. Even visual inspection of the molecules **43** (see Fig. 13) shows that their central cyclic fragments are attracting each other. In these molecules they are shifted parallel in such a way as to maximize interactions between the metal centers and the π-electrons of the other fragment. These interactions can be characterised by, for example, metal ion···metal ion (M···M′) distance or the shortest distances between the metal ions and the closest atoms from the other cyclic molecular fragment. The M···M′ distances are the following: 4.658 Å, 4.652 Å, 4.577 Å, 4.648 Å for **43NiNi**, **43NiCu**, **43CuNi** and **43CuCu**, respectively.

However, the shortest M···C (from the other cyclidene fragment) distances are by far shorter and equal to: 3.604 Å, 3.706 Å for **43NiNi**, 3.556 Å, 3.596 Å for **43NiCu**, 3.655 Å, 3.514 Å for **43CuNi** and 3.497 Å, 3.593 Å for **43CuCu**.

Redox properties: The electrochemical behavior of the dinuclear neutral-charged complexes was studied by cyclic and differential pulse voltammetry. Simple exchange of the copper to nickel center completely changes the potentials of the peaks and hence no overlapping is seen. This indicates non-additive properties in such novel donor–acceptor systems (Fig. 4 and Table 1) (Fig. 14).

Table 1

Comparison of the redox properties of monomacrocyclic complexes and homo- and heteronuclear bismacrocyclic complexes. Volts vs. AgCl/Ag.

Compound	$E^{0'}_{\text{M neutral}}$ [V]	$E^{0'}_{\text{M charged}}$ [V]	$E_{\text{pa ligand}}$ [V]	ΔE [V] ($E^{0'}_{\text{M charged}} - E^{0'}_{\text{M neutral}}$)
43NiNi (**Ni$_{\mathbf{n}}$Ni$_{\mathbf{ch}}$**)$_-$	0.767	–	1.587	0.685
43CuCu (**Cu$_{\mathbf{n}}$Cu$_{\mathbf{ch}}$**)	0.555	1.081	1.762	0.526
43CuNi (**Cu$_{\mathbf{n}}$Ni$_{\mathbf{ch}}$**)	0.542	1.396	1.708	0.854
43NiCu (**Ni$_{\mathbf{n}}$Cu$_{\mathbf{ch}}$**)	0.777	1.078	1.567	0.264

n, neutral; **ch**, charged.

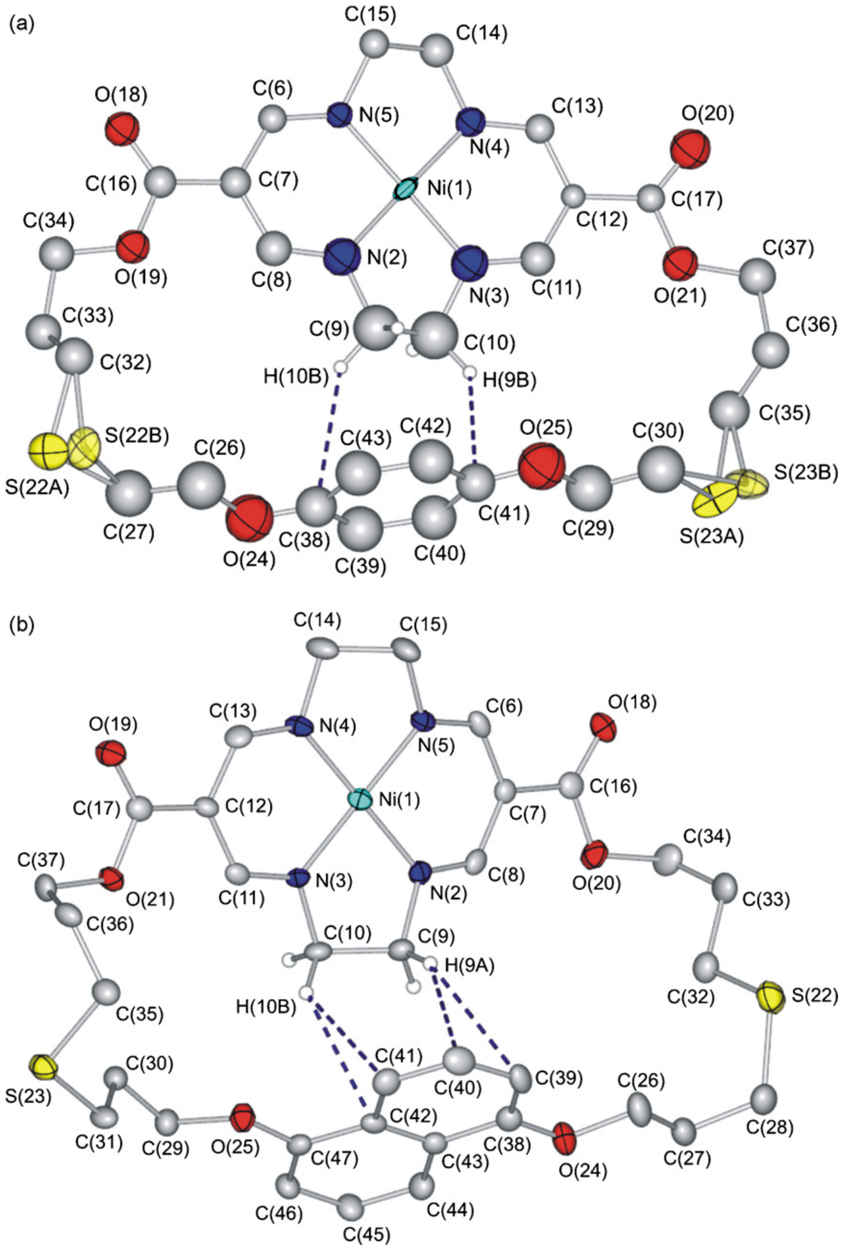


Fig. 12. Examples of "lacunar" receptors for electron deficient aromatic guest molecules (a) **36NiPh** and (b) **36NiNaph**. Labelling of atoms and estimation of atomic thermal motions as Anisotropic Displacement Parameters (ADPs). Hydrogen atoms omitted for clarity except those involved in C–H···π interactions. Disordered sulfur in **36NiPh** structure.

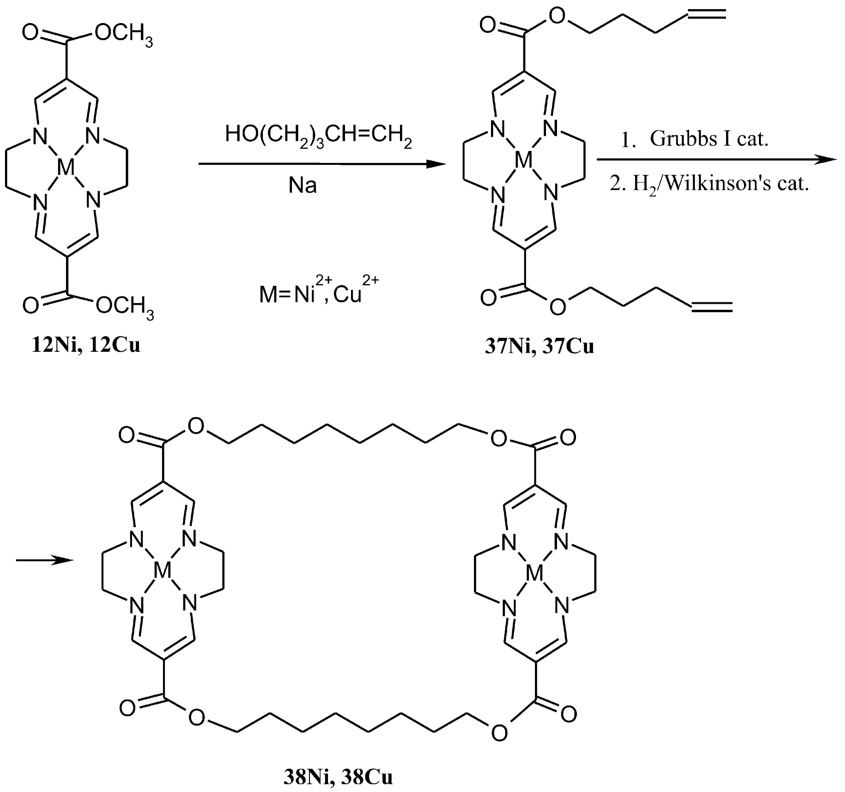
6. Cyclidene complexes as receptors

Receptor properties of metallomacrocyclic hosts have recently been extensively reviewed by Korendovych et al. [77], therefore in this work we would like to concentrate on cyclidene derivatives acting as receptors. A metal containing molecular ditopic receptor **44** (Scheme 14) was prepared from 15-membered nickel(II) cyclidene complex functionalized with two cyclen recognition sites. ^{1}H NMR titration demonstrates that the molecule binds dicarboxylic acids with equilibrium constants ranging from 10 to $10^4\,M^{-1}$ [78]. Studies of host–guest interactions between similar [15]cyclidene nickel(II) complexes functionalized with two crown ethers (**45** and **46**) and α,ω-diammonium cations by ^{1}H NMR titration in CD_3CN showed that 1:1 complexes are formed with $K_{assoc} \sim 10^3$ to $10^5\,M^{-1}$. The benzo-15-crown-5 derivative (**46**) showed substantial selectivity in binding of trimethylene- and tetramethylenediammonium cations [79].

A higher affinity of the benzo-18-crown-6 pendant arms of the host **45** to the diammonium substrates resulted in stronger, but less selective, binding properties.

In order to select structural elements which could be used as recognition sites, the host–guest interactions of biscyclidenes with electron-rich aromatic compounds (**47**–**52**, Scheme 15) were studied by spectroscopic methods. The neutral complexes **12Ni** and **12Cu** were also investigated as potential π-donors.

Despite the fact that ESI-MS might not reflect accurately the solution binding affinities, it provides important information on host–guest complexes and the nature of their interactions. The ESI mass spectra of an equimolar mixture of the neutral complexes **12Cu** or **12Ni** and bismacrocyclic receptors **25Ni** or **25Cu** (n = 7, R═H) confirmed the formation of the host–guest complexes [30]. New peaks corresponding to the formation of the 1:1 adducts **25Ni** + **12Ni**, **25Ni** + **12Cu**, **25Cu** + **12Ni** and **25Cu** + **12Cu**, respectively, were observed in the spectra. In order to compare the



Scheme 12.

affinities of bismacrocyclic receptors towards neutral guests, the ESI mass spectra of equimolar mixtures of **12Cu** and **25Ni** complexes linked with 5-, 7- and 9-methylene chains were measured. The spectra show, that the cavity size in **25Ni**, which contains $(CH_2)_5$ chains, is too small to accommodate guest molecules. On the other hand, the cavity size in the receptor, which contains $(CH_2)_9$ bridges, is too large to enable simultaneous and equally strong interactions of the guest molecules with both sides of the host cation. Therefore, the intensity of the common peak is very low in comparison with the peak of **12Cu** associated with the host containing $(CH_2)_7$ bridges [33].

The ^1H NMR spectra of mixtures of aromatic guests (Scheme 15) and dinickel bismacrocyclic complexes (**25Ni**) linked with three, five or six carbon atom long chains gave a simple sum of the spectra of the mixture components. On the other hand, the spectra of mixture containing **25Ni** bridged with 7-methylene chains, showed substantial changes of the proton resonance frequencies relative to the spectra of pure components. The ^1H NMR signals of aromatic guests were also substantially broadened in the presence of the paramagnetic **25Cu** host complexes containing $(CH_2)_7$ linkers. Since such broadening was not observed in the case of dicopper receptors with smaller cavities, this result confirms the formation of the host–guest complexes [62].

The 1:1 stoichiometry of the host–guest complexes was established by the Job's method of continuous variations [80]. The association constants, collected in Table 2, were determined by ^1H NMR titration from the dependencies of the proton resonance frequencies of the guest molecules on the ratio of the host/guest concentrations [62,65,66].

Association constants collected in Table 1 are, at least, one order of magnitude higher than those estimated for the host–guest inclusion complexes of vaulted cyclidenes with alcohols or phenols formed due to hydrophobic interactions [55,56]. Larger values of the association constants are observed for hosts bridged with secondary amines which are better acceptors than *N*-methylated ones. This confirms π–π character of interactions responsible for the host–guests complex formation. Despite its poor donor properties, the molecule of 9,10-dimethyltriptycene (**52**) perfectly fits to the triangular shape of receptor **26Ni** cavity forming a relatively stable complex (Table 2).

In the case of cationic bismacrocycles **25**, the *N*-methylation weakens the electron-acceptor properties of the complexes which leads to a less effective binding of the π-electron-donating guests.

It also increases the stability of the lower oxidation states. In the case of the copper *N*-methylated complexes (**25Cu**), both Cu^{II}/Cu^{I} and Cu^{II}/Cu^{III} reversible one electron transfers are seen in the voltammograms [62]. These changes in electrochemical properties are interpreted as the consequences of steric repulsion between the methyl substituents and the macrocyclic ring.

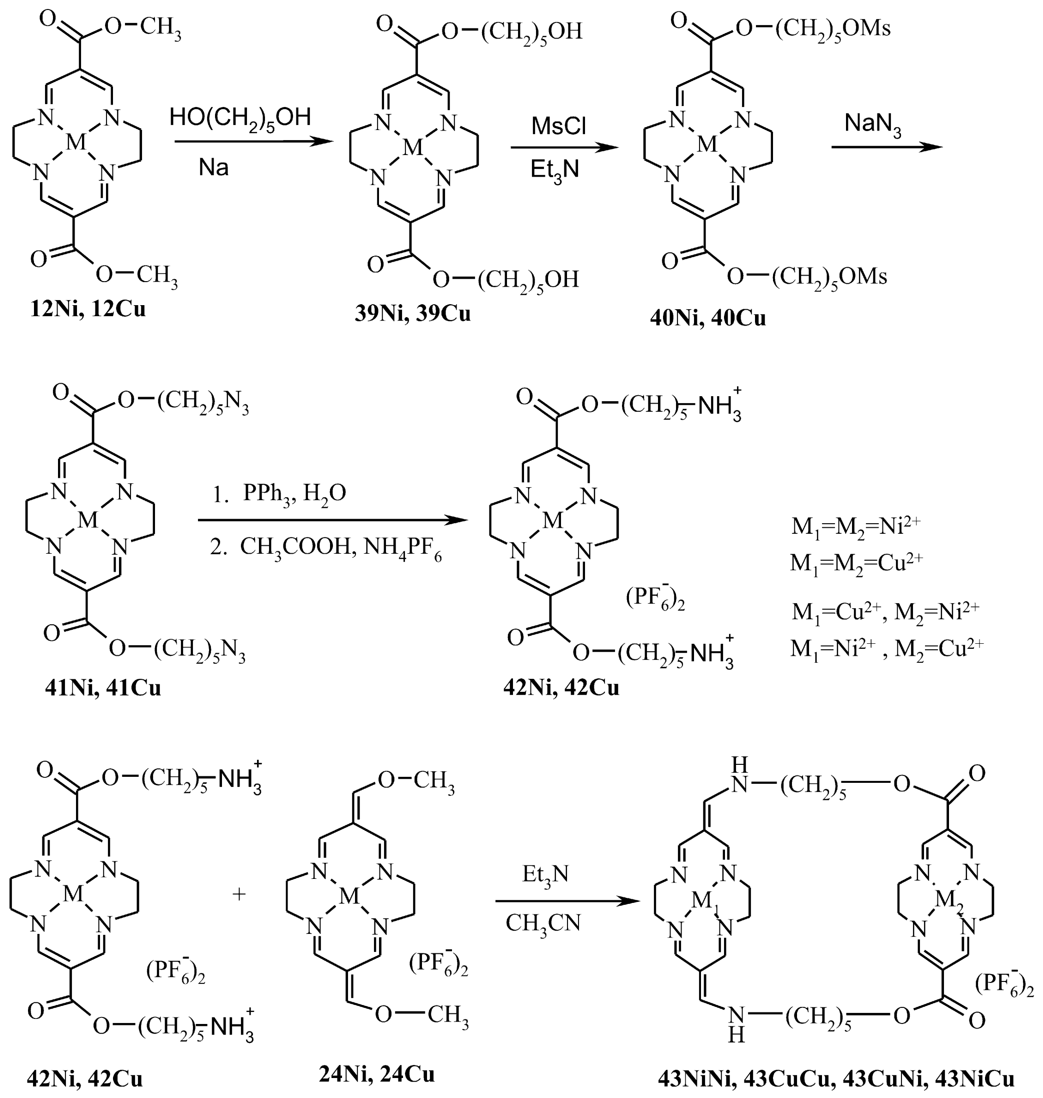
7. Assembling of catenane structures

The dibenzo-24-crown-8 molecule contains in its structure two electron-rich benzene rings and the cavity large enough to

Table 2
Association constants of host–guest complexes formed by cyclidene receptors.

Host[a]	Solvent	Guest	K_{assoc} [M^{-1}]	Ref.
25Ni$(CH_2)_7$	CD_3CN	**47**	361 ± 29	[65]
25Ni$(CH_2)_7$	CD_3CN	**48**	221 ± 26	[62]
25Ni$(CH_2)_7$	CD_3CN	**49**	198 ± 28	[62]
25Ni$(CH_2)_7$	CD_3CN	**50**	91 ± 18	[62]
25Ni$(CH_2)_7$	CD_3CN/D_2O (1:1)	**50**	150 ± 20	[65]
25Ni$(CH_2)_7$	CD_3CN	**51**	295 ± 40	[62]
25Ni$[CH_3,(CH_2)_7]$	CD_3CN	**49**	123 ± 19	[62]
25Ni$[CH_3,(CH_2)_7]$	CD_3CN	**50**	62 ± 7	[62]
25Ni$(CH_2)_9$	CD_3CN	**49**	103 ± 16	[66]
25Cu$(CH_2)_7$	CD_3CN	**48**	340 ± 53	[66]
26Ni$(CH_2)_2$	CD_3CN	**52**	164 ± 18	[65]

[a] Linker aliphatic chain and N-substituent in parentheses.



Scheme 13.

accommodate the cyclidene moiety. Indeed, the cyclization reaction of the [14]cyclidene complex **24Ni** with 1,7-heptanediamine in the presence of an excess of dibenzo-24-crown-8, afforded the bis[14]cyclidene **25Ni** and the [2]catenane **53Ni** (Scheme 16). Similar reaction with **24Cu** gave bis[14]cyclidene **25Cu** and [2]catenane **53Cu** [60]. Interlocked structures of [2]catenanes were unambiguously identified by ESI mass spectrometry, spectroscopic and analytical methods.

The synthetic strategy applied to obtain face-to-face heterodinuclear bismacrocyclic complexes (Scheme 17) was different than that described for the homodinuclear systems. In the first step, the copper(II) coordinated macrocycle **24Cu** was functionalized with two pendant diamino linkers to give **54Cu** which was then cyclized by using the second macrocyclic unit that contained a coordinated nickel(II) ion (**24Ni**). In the presence of an excess of dibenzo[24]crown-8, the heterodinuclear bismacrocycle **25NiCu** and [2]catenane **53NiCu** were formed [81].

53NiCu crystallizes in the triclinic *P*−1 space group with one molecule in the independent part of the unit cell. The bismacrocyclic ring is positively charged because of the presence of Ni^{II} and Cu^{II} cations. This is why both interlocked rings are surrounded by four PF_6^- anions. The crown ether and the grand bisazamacrocyclic ring in **53NiCu** form a sandwich-like structure (Fig. 15) in such a way that one of the crown ether aromatic rings is located between the two metal-coordinated macrocyclic rings. The second aromatic ring is located almost parallel to the previous one outside the two linked macrocycles. Thus, the one aromatic ring of the crown ether is interlocked between the two macrocycles, and one of the macrocyclic rings is positioned between the two aromatic rings of the crown ether.

The macrocyclic fragments with aminomethylidyne ends are linked with each other by aliphatic chains consisting of 7 carbon atoms each. Therefore, the linked azamacrocyclic fragment of **53NiCu** forms a rectangular cavity with dimensions of 6.91 Å (Cu···Ni) × 15.47 Å (C28···C35). The M···M′ distance is comparable with similar distances in the homonuclear catenanes (see Fig. 16): (7.07 Å for **53Cu**, 6.75 Å for **53Ni** and 6.91 Å for **53NiCu**). The azamacrocyclic rings are evidently interacting via the guest aromatic ring because the distance between the metal ions is shorter than the distances between the exocyclic carbon atoms (7.15 Å for N···N and 7.23 Å for C···C interatomic exocyclic distances).

8. Electrochemically triggered intramolecular motion in catenanes

The most remarkable feature of the catenanes is that internal rearrangement of the compound can be electrochemically triggered. If both of the coordinated ions were identical (as in **53Ni**

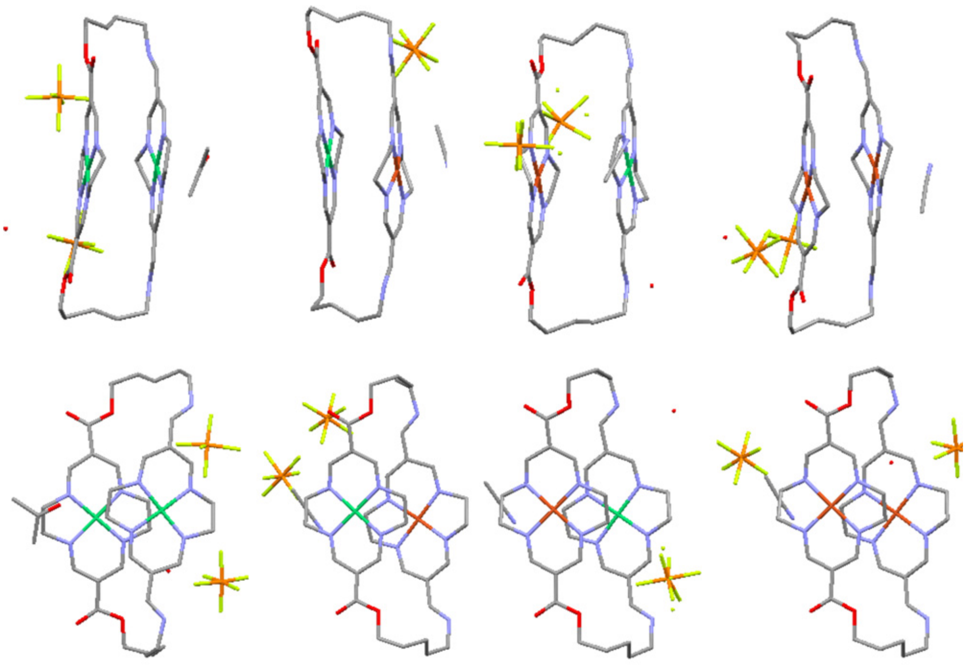

(A) 43NiNi (B) 43NiCu (C) 43CuNi (D) 43CuCu

Fig. 13. Two projections of the mixed dinuclear cyclidene complexes coordinating nickel(II) and/or copper(II) in neutral cationic macrocycles: (A) **43NiNi**, (B) **43NiCu**, (C) **43CuNi**, and (D) **43CuCu**. Hydrogen atoms omitted for clarity [unpublished results].

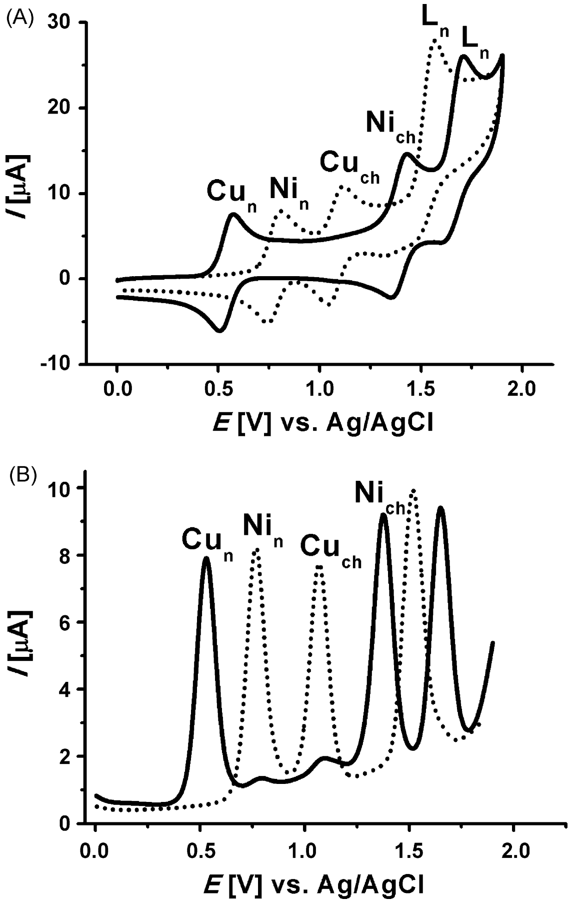
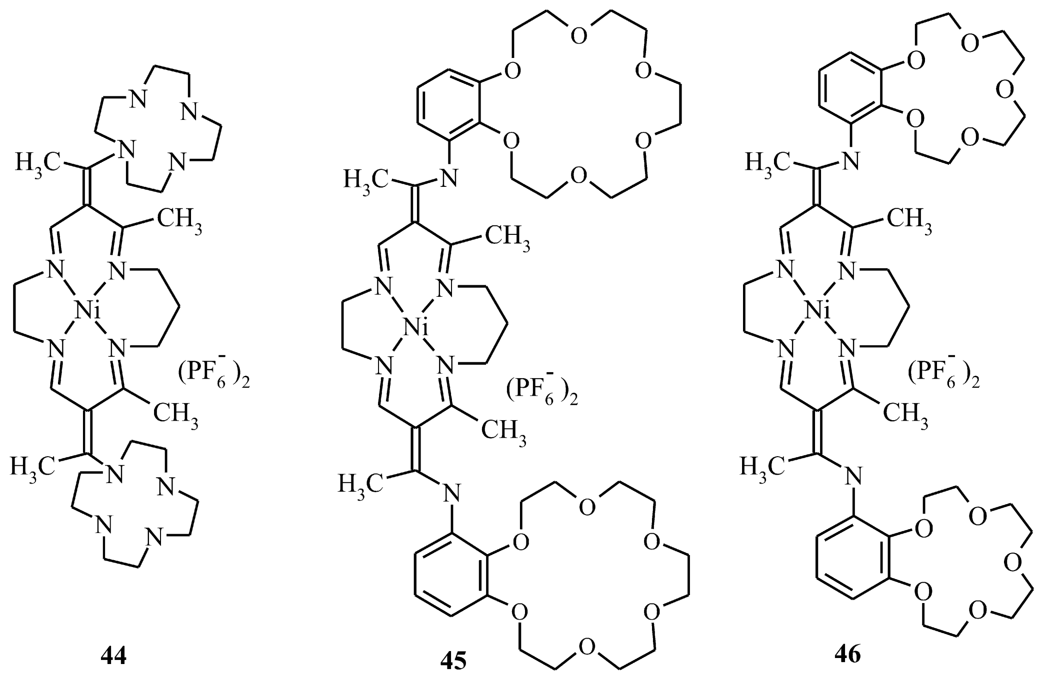


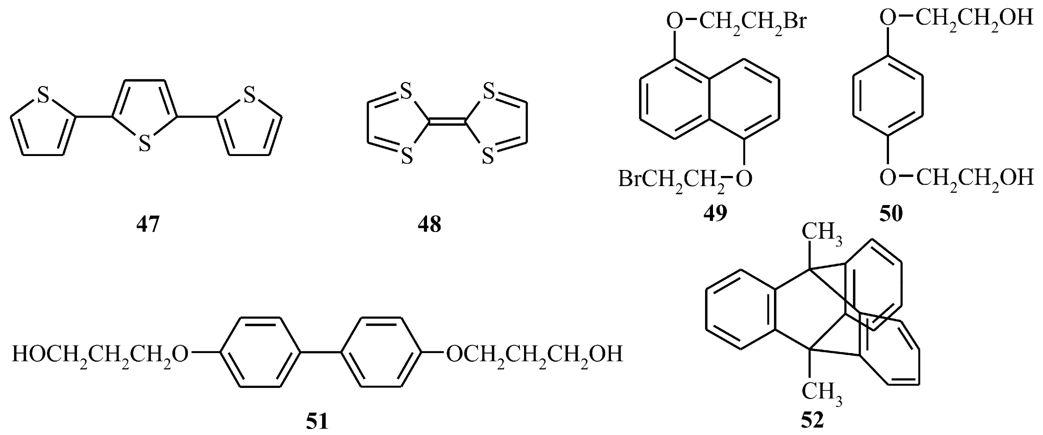
Fig. 14. Comparison of CV (a) and DP (b) voltammetry for 5×10^{-4} M **Cu_nNi_{ch}** (**43CuNi**) and **Ni_nCu_{ch}** (**43NiCu**) in 0.1 M Bu_4NPF_6/CH_3CN solution: (a) $v = 0.05$ V/s and (b) $\Delta E = 25$ mV.

or **53Cu**), the translocation of the crown ether moiety from one site to the other produced the same catenane arrangement. However, intertwining of the dibenzo-24-crown-8 with a heterodinuclear bismacrocyclic complex **53NiCu** lead to two possible arrangements, where the π-electron-rich benzene rings were located in the vicinity of either the copper or nickel-complexing macrocycle, depending on the oxidation state of the coordinated ions.

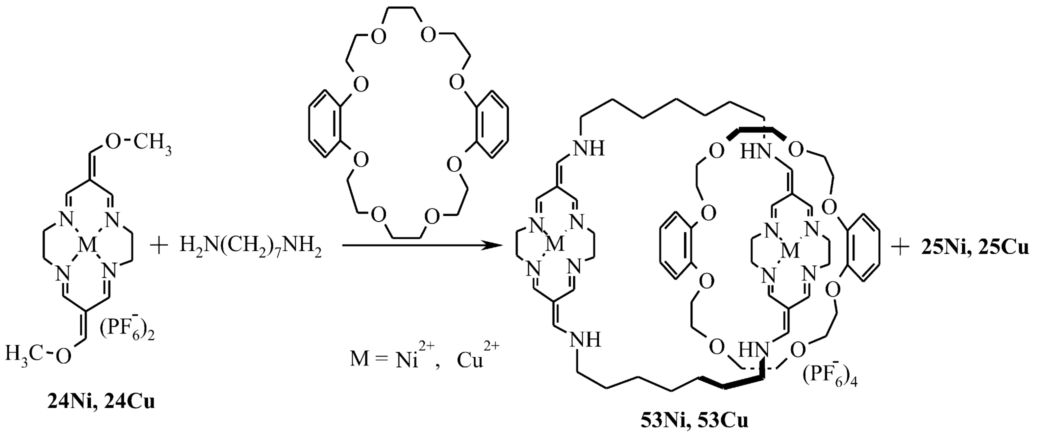
Perhaps the most revealing electrochemical technique is Osteryoung's square wave voltammetry which shows (Fig. 17) splitting of Ni oxidation signals in the case of the NiCu–catenane system. The peak at +1.65 V corresponds to the oxidation of the crown moiety in the catenane. The extent of splitting of the Ni oxidation peaks at ca. 1.35 V, is not a function of concentration of the catenane, but is the function of time and temperature. Such behavior may be understood assuming formation of two different populations of the Ni^{II} centers. Each of them has a different local microenvironment around Ni^{II} although this happens within the same molecule. The donor properties of the first group of Ni^{II} centers are affected by the vicinity of the electron-rich crown ether while the other group is not. At lower frequencies, upon oxidation of Cu^{II} to Cu^{III}, the crown ether unit has enough time to relocate from its initial position close to the Ni^{II} center towards the more positively charged Cu^{III} center. As a result of this relocation, the Ni^{II} to Ni^{III} oxidation process appears at more positive potential since it is free from the influence of the π-electron-rich crown ether. However, when the timescale is decreased or temperature is lowered, the movement of the crown ether unit is too slow and in a fraction of the molecules the Ni^{II} cations remain weakly interacting with the crown ether, giving rise to the splitting of peaks. Hence, the decrease of temperature (Fig. 17b) leads to a better development of the negative peak corresponding to the oxidation of nickel centers still surrounded by the crown ether. Therefore, the "frozen" interconversion within the molecule can be clearly shown at lower temperatures where the movement of the crown ether unit is slowed down. The most remarkable feature of this new catenane is that each electrochemical step triggers a rearrangement of the compound. The intramolecular movement upon the application of



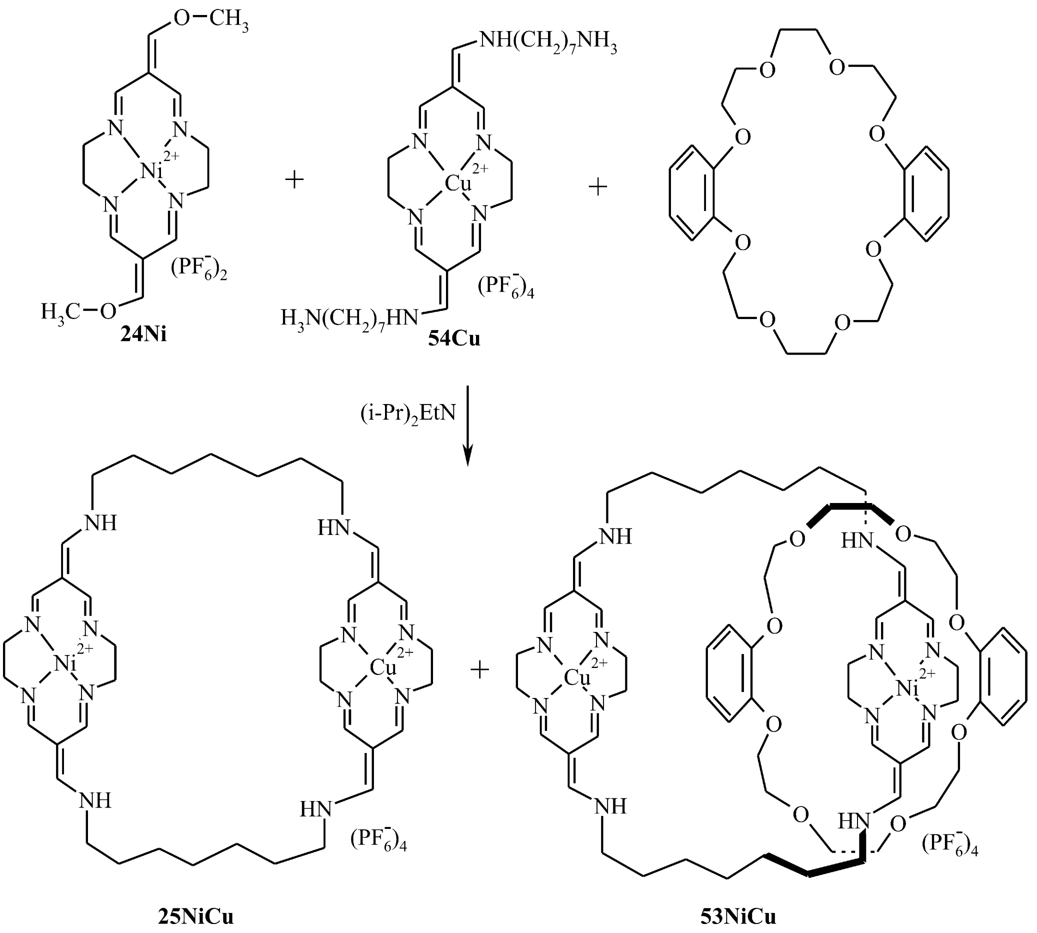
Scheme 14.



Scheme 15.



Scheme 16.



Scheme 17.

appropriate potential is clearly seen in the normal pulse voltammetry experiment with different initial potentials (Fig. 18) [81,82]. The potential between the pulse application, E_i, is set at a chosen value for 2 s and then 50 ms pulses of increasing amplitude are applied to the electrode. When E_i is set to 0.7 V (Fig. 18A), no redox reaction can proceed in these 2 s, and only during the pulse application can some movement of the crown towards Cu^{III} be triggered. A part of the Ni^{II} centers is then freed from the crown influence. The forma-

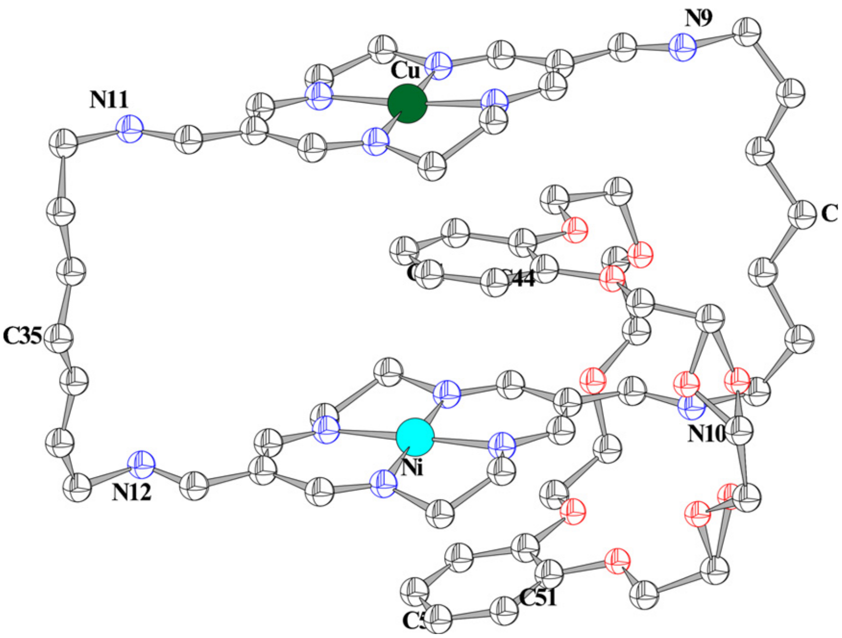


Fig. 15. Heteronuclear catenane structure **53NiCu**.

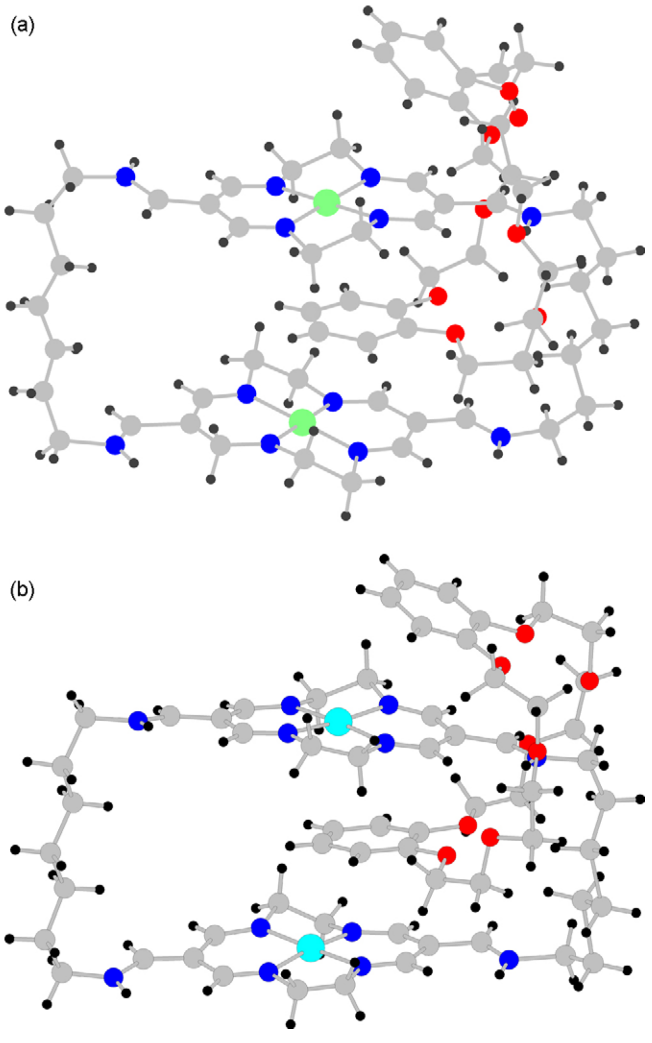


Fig. 16. Homonuclear catenane structures (a) **53Ni** and (b) **53Cu**.

tion of these two different populations of the Ni centers results in the splitting of waves which is even better distinguishable when the curves are differentiated (Fig. 18, broken line). At 1.15 V, Cu^{III} is generated in the vicinity of the electrode during the 2 s at E_i and induces a swing of the crown unit towards the oxidized copper center (Fig. 18B). The more positive Ni^{II} oxidation peak for the Ni center freed from the influence of the crown ether clearly dominates in the voltammogram. When E_i potential is set to 1.5 V, both Ni^{III} and Cu^{III} complexes are generated. Under these conditions the crown ether is located close to the nickel center again and the Ni^{II}/Ni^{III} peak reappears at more negative potential (Fig. 18C). Under appropriately chosen conditions one can, hence, detect the presence of two Ni^{II}/Ni^{III} oxidation waves. These electrochemically switched relocations reflect a shuttle-like behavior triggered by application of an appropriate potential.

9. General geometric features of Cu^{II} and Ni^{II} complexes of tetraimine macrocyclic structures

The tetraimine rings studied form square planar complexes with Ni^{II} and Cu^{II} ions and have intermediate bonds lengths (between typical single or double ones) in the 6-membered fragments of the main macrocyclic ring. This reflects the delocalisation of electrons. The 14-membered rings are planar whereas the larger, 15- and 16-membered rings, deviate from planarity. The planes of the macrocyclic rings are directed parallel to each other in the case of bismacrocycles and catenanes. In the protonated free ligands, the conformation of the molecules is completely different than in the complexed forms [33]. All compounds create very interesting arrangements of molecules in their crystal lattices with different kinds of interactions such as: hydrogen bonds, π···π and C–H···A, where A stands for an acceptor atom.

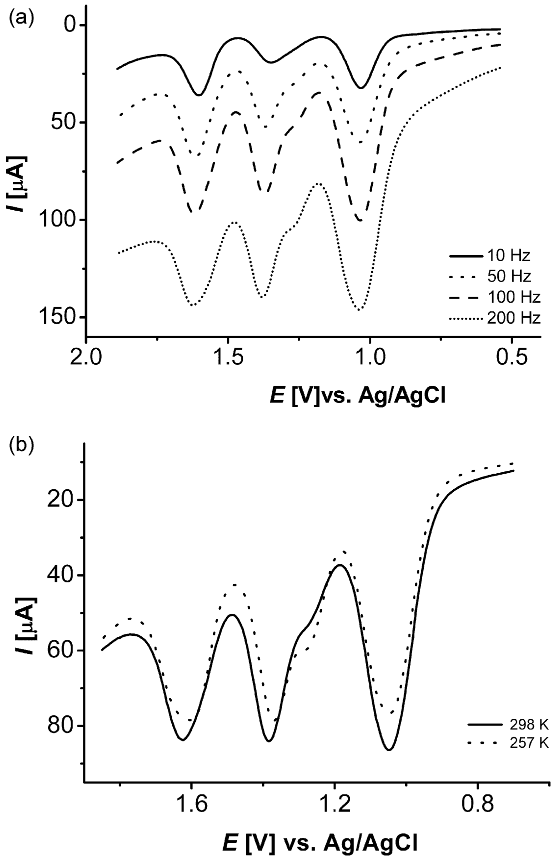


Fig. 17. (a) OSW voltammograms 1 mM **53NiCu** in 0.1 M Bu_4NPF_6/CH_3CN solution recorded on GCE, ν = 10 Hz, ν = 50 Hz, ν = 100 Hz, and ν = 200 Hz and (b) OSW voltammograms 1 mM **53NiCu** in 0.1 M TBAHFP/AN recorded on GCE, ν = 100 Hz, at temperatures 298 and 257 K.

Most of the compounds studied crystallize in lower symmetry centrosymmetric space groups such as: $P\bar{1}$ or $P2_1/c$ with only a few exceptions. The molecules having the C_i symmetry are located at the special positions (at inversion centers) in the crystal lattice. The special positions are occupied even when some small deformations from the ideal C_i symmetry are introduced to the molecule, such as: different metal ions (hetero-bismacrocycles) or different (ethylene and propylene) bridges in the same molecule. Most asymmetric molecules occupy the general positions in the crystal lattice (three catenanes and the neutral lacunar complexes).

Numerous macrocycles contain a solvent in their structures (water, acetonitrile or toluene), stabilizing the whole structures and maximizing weak interactions with the molecules. The solvent molecules can be located inside or outside of the cavities created by the bismacrocycles. The 7C linker bis- and 2C linker trismacrocycles have cavities large enough to hold inside small guest molecules (these are usually disordered water or solvent moieties). Usually, these guest molecules are located a bit off the center of the cavities. Such a location of the water molecules enables interactions between the lone electron pairs of the oxygen atoms and the central metal ions. A similar situation exists in catenanes where communication between metal centers is enhanced by the benzene rings of the crown ether units. In general, there are two groups of structures with slightly different intermetallic separation: ca. 4.1–4.5 Å

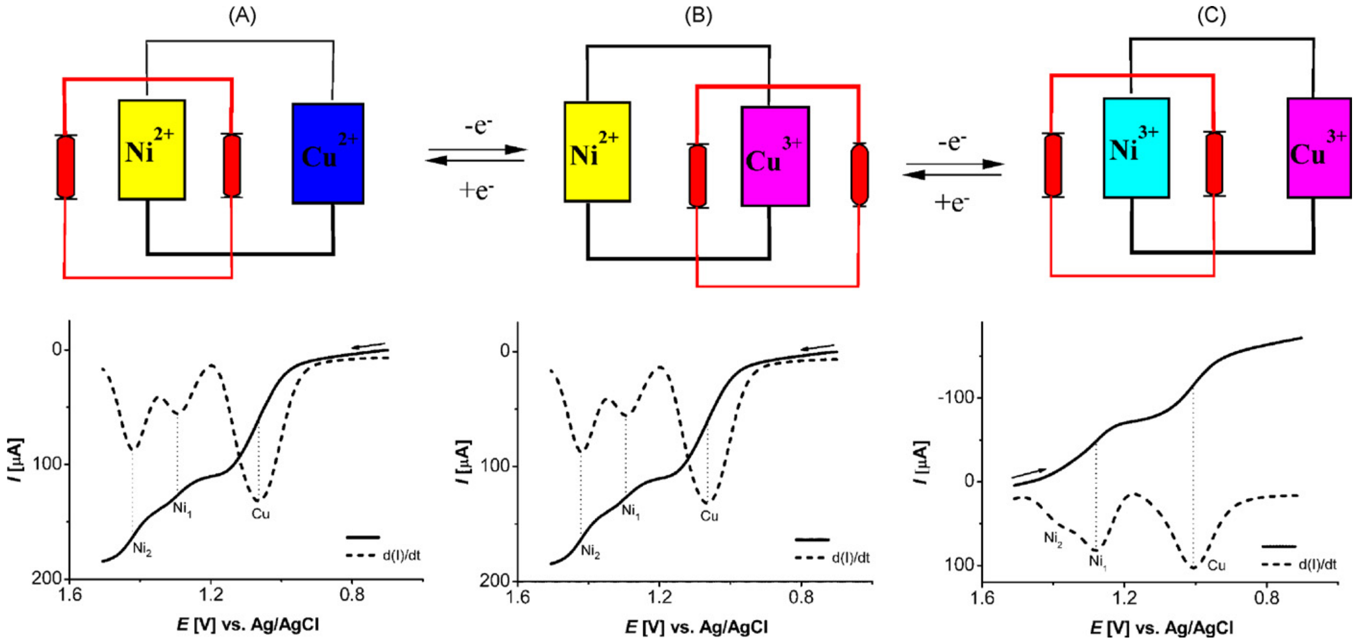


Fig. 18. NP voltammograms and their derivatives for 1 mM **53NiCu** in 0.1 M Bu_4NPF_6/CH_3CN solution recorded on GCE, $t_{pulse} = 50$ ms, $t_{waiting} = 2$ s. Initial potential, E_i: (A) 0.70 V (B) 1.15 V and (C) 1.45 V; (- - -) same curves but after differentiation.

for compounds with 3 and 6 carbon atoms in the aliphatic linker and from 6.8 Å to 7.2 Å for bismacrocycles and catenanes with seven carbon long aliphatic linkers.

Monomacrocyclic and bismacrocyclic complexes create parallel and shifted face-to-face stacks of neighboring molecules in the crystal lattice. The arrangement of stacks can be modified by the counterions and solvent molecules. The counterions in those structures occupy the void positions formed between the neighboring molecules. Typical lengths of the M···N bonds for the presented compounds are around 1.85 Å and 1.91 Å for Ni^{II}, Cu^{II} complexes, respectively. This allows recognition of a specific metal center in a molecule. However, the M···N bond lengths can exhibit significant deviation when a significant disorder of the metal ion positions occurs.

It appears that in the case of bismacrocycles and catenanes, the electron density of the exocyclic nitrogen atoms is conjugated with the delocalised electron density of the macrocyclic ring. In consequence, the N–C and C–C bonds – linking nitrogen atoms with the macrocyclic ring – have intermediary character between single and double bonds. A closer inspection of the numerical values reveals that formally double bonds have bond lengths closer to single bond values, whereas formally single bonds are quite short and similar in lengths to the double C=N bonds.

The intermetallic distances in bismacrocyclic complexes become shorter in the following direction: Ni···Ni, Cu···Ni, Cu···Cu and this can be explained by different strength of the interactions between the metallic centers. Despite the same formal charge at the Ni^{II} and Cu^{II} atoms, one more electron on the copper center decreases the repulsive interactions between positively charged metal ions. The situation is reversed in the catenane structures, where aromatic rings act as π-electron donor systems and, more likely, interact with the more positively charged complex. Surprisingly, compounds with 6 carbon atoms in the aliphatic linkers create structures with the shortest M···M distances despite the six carbon long aliphatic linkers. In this case the aliphatic linkers adopt different conformations than plain *anti*-conformation thus allowing very short intermetallic distances. The M···M distance is even shorter than for the similar bismacrocyclic system with the five carbon long aliphatic spacer (4.253 Å) [83]. For all of the bimetallic structures, except of the 3C bismacrocycles, the N···N and C···C exocyclic distances are longer than the appropriate M···M distance. The second distance characterising the cavity size, i.e. the separation of the aliphatic linkers, is in the range from 14.6 Å up to ca. 15.5 Å for the bismacrocyclic species.

In the case of neutral macrocycles, the majority of interactions between molecules are of the C–H···A type, where the acceptor A is one of the oxygen atoms from the alkoxycarbonyl groups or S atoms in the structures of the lacunar complexes. The possibility of creation of typical hydrogen bonds is excluded in the case of the metallic monomacrocyclic complexes because of the alkoxycarbonyl fragment. However, N–H···N and N–H···O hydrogen bonds are formed by molecules of neutral and protonated free ligands, respectively. Also typical examples of C–H···π interactions between the aromatic rings and carbon atoms of the aliphatic linkers are present in the structures of the lacunar complexes. The average distances calculated between the hydrogen atom and the ring centroid in both cases are about 2.95 Å.

Almost all the compounds presented create stacks of neighboring molecules which resemble a typical face-to-face packing motif of the π-stacking interactions. The arrangement of stacks depends on the solvent molecules and counterions, but also weak interactions can modify the orientation of the stacks. The distances between molecules in stacks of the studied compounds are in the range from 3.3 Å to about 4.0 Å (interplanar separation), where the distance between the metal ions of the neighboring macrocyclic rings varies from 4.2 to 8.4 Å. It seems that this arrangement of the molecules is not caused by the π···π interactions alone, since the π-rich 6-membered rings are practically non-overlapping for almost all of the structures. In the case of the monomacrocycles the characteristic X-displacement is caused by the electrostatic interactions between the positively charged metal center and negatively charged oxygen atom from the alkoxycarbonyl group (distance 3.4–3.8 Å). The shift between the molecules in stacks in the bismacrocyclic species is due to the presence of relatively short C–H···M, and C–H···π interactions (2.5–3.0 Å).

The compounds studied exhibit many possibilities of isomerism not only in solution but also in the solid state. Each 14-membered tetraazamacrocyclic ring contains two ethylene bridges which can be located *trans* or *cis* relative to each other in the same or in the second macrocyclic ring (bismacrocycles and catenanes). The first option is realized for the complexes with 3C and 6C linkers, because of a short distance between the macrocyclic rings causing more steric hindrance in the *trans* arrangement of the ethylene bridges than in the *cis* one. Contrary, for the complexes with 7C linkers, the *trans* arrangements are preferable. The molecules in the catenane structures are located in general positions in the crystal lattice, therefore there is no limitation for possible conformations.

The second type of isomerism occurs in the possible arrangement of functional groups connected to the main macrocyclic ring. In the case of the monomacrocyclic compounds usually these are alkoxycarbonyl groups. The functional groups can adopt either *cis* or *trans* arrangements, respectively to each other. For the centrosymmetric structures of the monomacrocyclic compounds, only the *trans* isomer is possible. The CH–NR–CH_2 groups in the bismacrocyclic complexes can finally adopt both the *trans* or *cis* conformations. This *cis*/*trans* isomerism (*trans* in respect to the same ring and *cis* in respect to second macrocyclic fragment) is observed in the case of the bismacrocyclic compounds with 7C linkers. The bismacrocycles with shorter carbon linkers have opposite *cis*/*trans* arrangement in respect to the same and second macrocyclic ring. The symmetry restriction is lifted in the catenane structures, therefore, all possible arrangements are observed.

10. Prospects

Controlling directional movement: One of the present challenges in chemistry is the problem of controlling relative motion of molecular fragments in complex supramolecules. In our opinion our model tetraimine complexes of transition metals are ideally suited to solve this problem. The pulse voltammetry experiments performed for the heterodinuclear [2]catenane show clearly that the interlocked crown ether relocates between two different metal centers. The intramolecular movement of the crown moiety takes place in response to the potential applied to the electrode. In this system either copper or nickel (or both centers) can be electrochemically oxidized to the higher (+3) oxidation state. The higher oxidation state of a given center induces stronger interactions with the π-electron-rich aromatic system of the crown unit. Such molecules with controlled communication between metal centers or intramolecular movement could be applied as molecular switches. The demonstrated ability to undergo a switchable and easily tunable mechanical movements of the heteronuclear [2]catenane under electrochemical stimulation is an important step towards molecular machinery. This concept of electrochemical stimulation can be extended to some more complex systems. For example, three, or more, tetraimine units containing different transition metals can be used to assemble trismacrocyclic, or more complex molecules, which should create with proper derivatives of crown ethers complex catenanes. Such catenanes should exhibit relative relocation of the crown ether relative to multicyclic units under electrochemical pulses. Using proper sequences of pulses it should be possible to control directional movements. On the way to this aim we have already synthesized trismacrocyclic derivatives which are now appropriately modified to serve as components of complex catenanes.

The other type of directional movement can be realized by construction of polynuclear tetraimine chains to make them act as threads for pseudorotaxanes or rotaxanes anchored on the electrode surfaces. This allows to achieve systems with controllable movements perpendicularly to the electrode surfaces. This is at present our on-going research.

Nature of the "mechanical bond": Another long range aim of our research is focused on the nature of the "mechanical bond". Apparently, using a number of physicochemical methods one can easily show detectable electronic effects associated with interactions of molecular fragments of supramolecular objects such as catenanes and rotaxanes. This is extremely interesting and important to identify and quantify such effects in order to use them in rational design of artificial molecular machines with expected properties. One of the most important tools to achieve this aim could be studies of experimental electron density of supramolecular compounds. This also is our on-going research.

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