

Review

Organic–inorganic hybrid materials: Metallacalixarenes. Synthesis and applications

Joanna Kulesza^{a,b,*}, Bráulio Silva Barros^b, Severino Alves Júnior^a^a Departamento de Química Fundamental, Universidade Federal de Pernambuco (UFPE), Av. Prof. Moraes Rego, 1235 - Cidade Universitária, 50670-901 Recife, PE, Brazil^b Escola de Ciências e Tecnologia, Universidade Federal do Rio Grande do Norte (UFRN), Campus Universitário Lagoa Nova, 59078-970 Natal, RN, Brazil

Contents

1. Introduction.....	2193
2. Metallacalixarenes based on 1,3-benzenedicarboxylates.....	2194
2.1. Metallacalixarenes with Cu nodes.....	2195
2.2. Metallacalixarenes with Zn nodes.....	2199
3. Metallacalixarenes based on heterocycles.....	2200
3.1. Pyrimidine-based metallacalixarenes.....	2200
3.2. Imidazole- and benzimidazole-based metallacalixarenes.....	2202
3.3. Phenanthroline-based metallacalixarenes.....	2202
3.4. Bipyrazine-based metallacalixarenes.....	2203
4. Metallacalixarenes based on nucleobases.....	2205
5. Novel class of metallacalixarenes based on Re carbonyl corners.....	2209
6. Conclusions.....	2211
Acknowledgements.....	2211
References.....	2211

ARTICLE INFO

Article history:

Received 16 September 2012

Accepted 19 March 2013

Available online xxx

Keywords:

Metallacalixarenes

Coordination polymers

1,3-bdc

Cyclic discrete oligomers

Heterocycles

ABSTRACT

This review focuses on the synthesis and applications of organic–inorganic hybrid materials called metallacalixarenes. Two different subclasses of metallacalixarenes are presented: cyclic discrete oligomers based on heterocycles or nucleobases and metallacalixarenes as part of a polymeric network based on 1,3-dicarboxylate ligands. In addition to their potential application in gas adsorption/separations, magnetism and catalysis, metallacalixarenes might complex cations, anions, or neutral molecules due to their calixarene-like cavities.

© 2013 Elsevier B.V. All rights reserved.

Abbreviations: Ac, acetate; ACN, acetonitrile; acac, acetylacetonate; AdH, adenine; Ado, adenosine; 5'-ADP, adenosine-5'-diphosphate; 9-AllAd, 9-allyladenine; AlMe₃, trimethylaluminum; 3'-AMP, adenosine-3'-monophosphate; 5'-AMP, adenosine-5'-monophosphate; 5'-ATP, adenosine-5'-triphosphate; 1,3-H₂bdc, 1,3-benzenedicarboxylic acid; 5-OEt-1,3-bdc, 5-ethoxy-1,3-benzenedicarboxylate; 5-OPr, 5-propoxy-1,3-benzenedicarboxylate; bmp, bipyrimidine; bzp, 2,2'-bipyrazine; bu₂bipy, 4,4'-di-tert-butyl-2,2'-bipyridine; BzimH, benzimidazole; bzqnH, 7,8-benzoquinoline; CD, circular dichroism; Cp, η⁵-pentamethylcyclopentadienyl; ct-DNA, Calf thymus DNA; dhnq, 5,8-dihydroxy-1,4-naphthaquinone; dabco, diazabicyclooctane; dach, 1,2-diaminocyclohexane; 1D, one dimensional; 3D, three dimensional; 2D, two dimensional; DMF, dimethylformamide; 2-dmpmoH, 4,6-dimethyl-2-hydroxypyrimidine; DMSO, dimethylsulfoxide; dpk, 2,2'-dipyridylketone; en, 1,2-diaminoethane; 9-EtAd, 9-Ethyladenine; GeMe₃, trimethylgallium; gly, glycine; GuH₂, guanine; Guo, guanosine; ¹H NMR, proton nuclear magnetic resonance; his, histidine; HxH₂, hypoxanthine; Imach₂, imidazole-4-carboxylic acid; ImH, imidazole; 9-MeAd, 9-methyladenine; 5'-MeAMP, adenosine-5'-monophosphate methyl ester; LD, linear dichroism; mbzim, 2-methylbenzimidazole; 9-MeGuH, 9-methylguanidine; 9-MeHxH, 9-methylhypoxanthine; 9-MePu, 9-methylpurine; 2-MpymoH, 4-methyl-2-hydroxypyrimidine; Me₃tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; MOFs, metal-organic frameworks; pdc, 1-methylpyrrole; phen, 4,7-phenanthroline; pprd, 4-(2-pyridyl)pyrimidine; puH, purine; 6-PutH₂, 6-thiopurine; py, pyridine; pym, pyrimidine; 2-pymoH, 2-hydroxypyrimidine; 4-pymoH, 4-hydroxypyrimidine; SBUs, secondary building units; tacn, triazacyclononane; tfbdc, tetrafluoro-1,3-dicarboxylate; thaq, 1,2,4-trihydroxy-9,10-antraquinone; THF, tetrahydrofuran; THpH, theophylline; thpyH, 2(2'-thienyl)pyridine; thq, tetrahydroxy-1,4-quinone; tmen, tetramethylethylenediamine; trimH₃, trimesic acid; U, uracil dianion; UH, uracil monoanion; UH₂, uracil; UV, ultraviolet.

* Corresponding author at: Escola de Ciências e Tecnologia, Universidade Federal do Rio Grande do Norte (UFRN), Campus Universitário Lagoa Nova, 59078-970 Natal, RN, Brazil. Tel.: +55 84 33422347; fax: +55 84 33422303.

E-mail address: kulesza.joanna@gmail.com (J. Kulesza).

1. Introduction

The self-assembly process provides infinite possibilities for designing new functional materials. The well-known calix[*n*]arenes are bowl-shaped (in other words, cavity-shaped) oligomers obtained spontaneously in the condensation reaction between *p*-alkylphenols and formaldehyde under alkaline conditions [1]. The number of monomers in the calixarene structure (*n*) varies from 4 to 20, although in the case of hetero- or oxacalixarenes, the smallest possible number of phenol groups is 3 [2]. The various possible structures of calixarenes result from the easy rotation of the bridged Ar–CH₂–Ar groups, leading to the different calixarene conformations (Fig. 1).

Since their discovery, calixarenes have become the subject of great interest, and many research efforts have focused on modifying their structure. Upper-rim phosphacalixarenes and their metal complexes [3] and metal complexes of calixarenes based on *N*-heterocyclic carbenes [4–7] are just a few examples of possible calixarene skeletal modifications that have been recently reported.

Calixarenes have been employed in many applications because their structures can be tailored for use as cation, anion or neutral-molecule receptors [8].

Although the calixarene definition is unambiguous, the term “metallacalixarenes” is not used consistently and not restricted to any formal nomenclature; therefore, every definition is subject to scrutiny. In addition, this term is often confused with “metallo-calixarenes”, which is simply ascribed to the metal complexes of classical calixarenes formed by the encapsulation of a metal cation within the calixarene cavity.

The name “metallacalixarenes” was first coined by Lippert, who compared the structures of self-assembled platinum and palladium discrete cyclic oligomers derived from the nucleobases, guanine and theophylline, to the classical calixarene structure, in 1992 [9]. Thus, metallacalixarenes were initially defined as a class of metal-cycles in which *cis* square-planar metal entities, such as *cis*-L₂M²⁺ (where M = Pt²⁺ or Pd²⁺ and L = an amine or other ligand), replace the CH₂ groups of classical calixarenes and the calixarene phenol rings are replaced by ditopic *N*-heterocyclic arene ligands, mimicking calixarene walls.

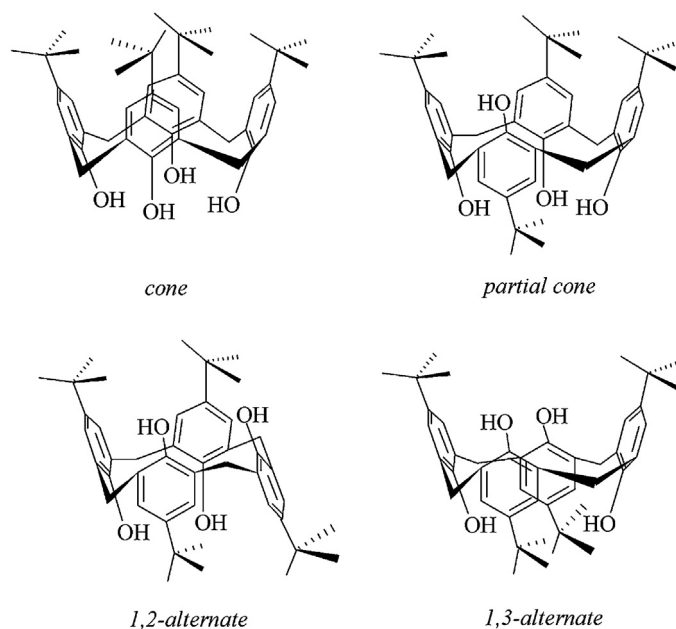


Fig. 1. Four basic calix[4]arene conformations.

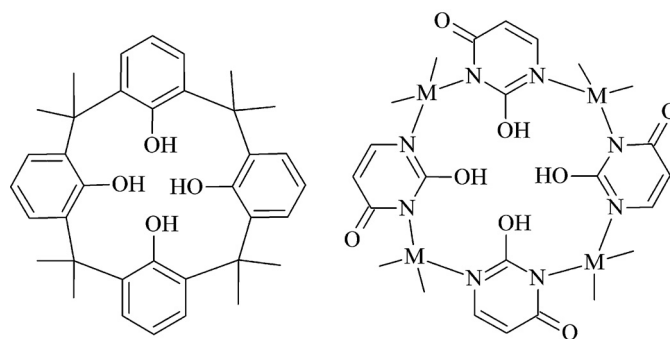


Fig. 2. Schematic representation of the structural analogy between a classical calix[4]arene (on the left) and a metallacalix[4]arene based on the uracil ligand (on the right): M = Pt²⁺ or Pd²⁺.

The schematic representation of the structural analogy between the classical calix[4]arene and a cyclic, self-assembling, uracil-based structure called a metallacalix[4]arene is presented in Fig. 2.

The presence of seemingly rigid *cis* square-planar metal entities in metallacalixarene structures does not exclude the formation of different conformers as observed for classical calixarenes (see Fig. 1).

A cyclic structure consisting of three metal nodes and three organic linkers could be regarded as the simplest trinuclear metallacalixarene, a metal analog of a calix[3]arene. However, the cyclic diadeninium disilver perchlorate monohydrate, [Ag₂(1-AdH₂⁺-N₃,N₉)₂](ClO₄)₄·H₂O, obtained from the reaction of adenine (AdH) with AgClO₄ in HClO₄ is considered by some authors to be the first metallacalixarene [10] (Fig. 3).

Nonetheless, to name this structure a “metallacalixarene” is questionable because it is difficult to find an analogy between the bowl-shaped classical calixarene and this dimer.

Some examples of other structures arguably called “metallacalixarenes” are listed below.

For instance, the product, [Cu₂(AdH-N₃,N₉)₄(H₂O)₂](ClO₄)₄, formed by the reaction of adenine with CuClO₄ at pH = 4 (Fig. 4) [11] and similar structures such as [Cu₂(Ad-N₃,N₉)₄(H₂O)₂].6H₂O [12] and [Cu₂(AdH-N₃,N₉)₄Cl₂].6H₂O [13] were called metallacalixarenes.

In this structure, a dimer was formed from the fusion of two so-called “metallacalixarenes” consisting of copper cations coordinated to two N₃ and two N₉ nitrogen atoms of four different adenine molecules and to the oxygen atom of a water molecule.

The reaction of the monosodium salt of adenosine-5'-monophosphoric acid (AMP) with cadmium nitrate in the presence of nitric acid led to the formation of a binuclear complex, [Cd(AdH₂⁺-N₃,N₉)(NO₃)₂·H₂O]₂(NO₃)₂, which was also called a “metallacalixarene” [14].

It is rather reasonable that the smallest, simplest metallacalixarene that can be formed is a trinuclear complex. It should be kept in mind, however, that not all trinuclear metallacycles can be defined as metallacalix[3]arenes. According to the definition of

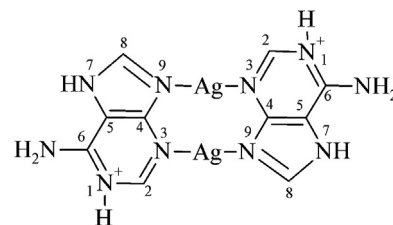


Fig. 3. Chemical structure of the dimeric complex, [Ag₂(1-AdH₂⁺-N₃,N₉)₂](ClO₄)₄·H₂O.

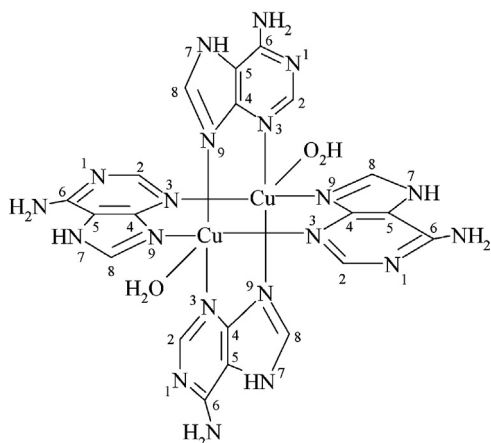


Fig. 4. Schematic representation of the complex, $[\text{Cu}_2(\text{AdH-N}_3,\text{N}_9)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_4$.

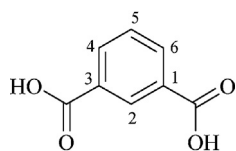


Fig. 5. Chemical structure of 1,3-benzenedicarboxylic acid (1,3- H_2 bdc) showing the atom-numbering scheme.

Alessio et al. [15], when both coordinate vectors of the angular linkers are above or below the M_3 plane (determined by three metal centers), the metallacycle can be termed a metallacalix[3]arene with two possible conformers: *cone* and *partial cone*. When the ligands are coplanar with the M_3 plane or are perpendicular to this plane, the metallacycles are defined as molecular triangles or molecular triangle prisms, respectively.

Moreover, metallacycles should have relatively large aromatic linkers, which define the walls of the metallacalix[3]arenes [15]. Otherwise, they resemble triangle prisms, not metallacalix[3]arenes. However, the concept of “relatively large aromatic linkers” remains unclear.

Metallacalixarenes are not only attributed to structures based on *N*-heterocyclic ligands and palladium or platinum entities. Zaworotko et al. reported various metallacalixarenes based on 1,3-benzenedicarboxylates (1,3-bdc) (Fig. 5) and zinc or copper metal clusters [16].

However, these metallacalixarenes are hybrid materials classified as coordination polymers, or so-called metal–organic frameworks (MOFs), because the metallacalixarene unit is part of the polymeric network.

Using dimetal tetracarboxylate “paddlewheel” clusters as secondary building units (SBUs) is a common motif in the structure of coordination polymers [17] (Fig. 6). The cluster is composed of four carboxylate moieties bridging two metal ions in the equatorial

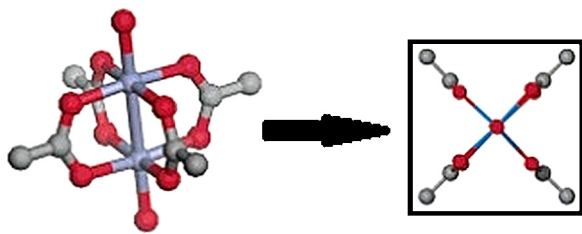


Fig. 6. Dimetal tetracarboxylate paddlewheel, $[\text{M}_2(\text{RCO}_4)_2\text{L}_2]_n$ (M = metal): viewed from the side and the top. Color code: gray-carbon, red-oxygen, blue-metal.

Reprinted with permission from [18], Copyright 2003, American Chemical Society.

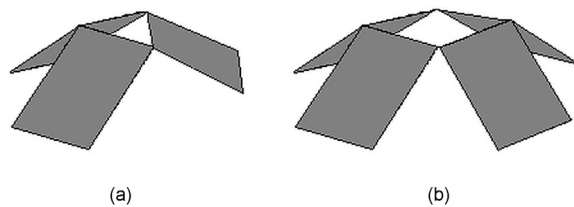


Fig. 7. Assembly of three (a) and four (b) square SBUs leading to bowl-shaped structures resembling calix[3]arenes and calix[4]arenes, respectively.

positions and two apical ligands that each coordinate to one of the metal cations.

The self-assembly of three or four “paddlewheel” SBUs consisting of a metal cluster and nonlinear 1,3-benzenedicarboxylates generates 2D tetragonal undulating-sheet structures with bowls resembling calix[3]arenes or calix[4]arenes, respectively [18] (Fig. 7).

Metallacalixarenes might find use in a number of applications. The presence of metal ions in their structures is responsible for their magnetic, optical and catalytic properties. Metallacalixarenes based on *N*-heterocyclic linkers are positively charged discrete oligomers, which might serve as excellent receptors for anions and mononucleotides. Finally, metallacalixarenes based on 1,3-dicarboxylates that are part of a polymeric network can reversibly adsorb gases and vapors, thanks to large void spaces and high surface areas. These examples of applications for metallacalixarenes demonstrate their potentially greater usefulness in comparison to that of classical organic calixarenes.

Several papers on metallacycles based on *N*-heterocycles and nucleobases, including those called metallacalixarenes, have been reported [19–25].

A very recent tutorial review describes some examples of metallatriangles and metallasquares based on substituted pyrimidine and 2,2'-bipyrazine ligands, and special attention is paid to strategies for reducing the number of possible isomers formed simultaneously during the synthesis [25].

Our review contains many interesting examples of metallacalixarenes that were omitted in the previous papers. Moreover, this review includes metallacalixarenes reported in the last five years, including a new family of metallacalixarenes based on Re carbonyl corners, which have not been previously reviewed.

Although coordination polymers have recently been a hot topic, those based on 1,3-benzenedicarboxylates that form cavity-shaped metallacalixarenes have not been reviewed up to this point. Due to the undulating-sheet structure of metallacalixarenes, solvent and/or guest molecules might become trapped within the narrow part of the hourglass-shaped channels, preventing their mobility. Therefore, they might be more promising candidates for selective gas/vapor storage than coordination polymers based on the 1,4-bdc linear ligand, which do not have hourglass-shaped channels.

2. Metallacalixarenes based on 1,3-benzenedicarboxylates

Carboxylate ligands have been commonly used to synthesize a diverse suite of coordination polymers. In this section, we address 1,3-benzenedicarboxylate ligands that form cavity-shaped metallacalixarenes in a self-assembly process with metal clusters.

The structure of the coordination polymers depends on many factors, such as the coordination geometry of the metal ion, the choice of the organic linker, the nature of the counterion and so on. For instance, a bulky substituent at the 5-position of 1,3- H_2 bdc can generate low-dimensional 1D zigzag coordination polymers instead of 2D metallacalixarenes [26]. In addition, different methods for synthesizing coordination polymers, such as the slow diffusion of solutions containing organic linkers and metal salts,

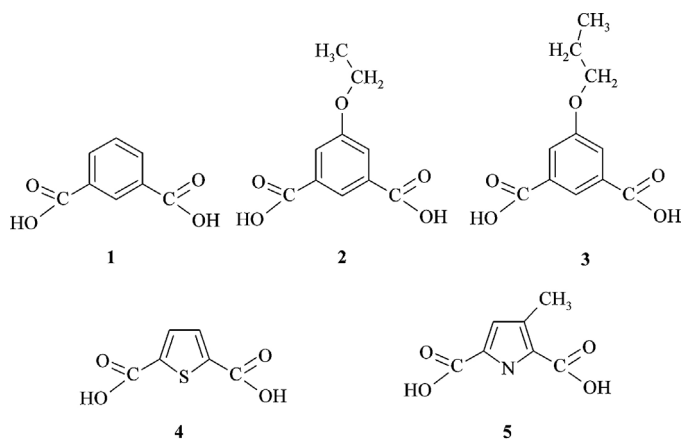


Fig. 8. Organic linkers used by the Zaworotko group to prepare metallacalixarenes: (1) 1,3-benzenedicarboxylic acid (1,3-H₂bdc), (2) 5-ethoxy-1,3-benzenedicarboxylic acid (5-OEt-1,3-H₂bdc), (3) 5-propoxy-1,3-benzenedicarboxylic acid (5-OPr-1,3-H₂bdc), (4) thiophene-2,5-dicarboxylic acid (tdc), (5) 1-methylpyrrole-2,4-dicarboxylic acid (pdc).

hydro- or solvothermal synthesis assisted by microwave irradiation or conventional heating in an oven, greatly affects the structure of the resulting coordination polymer.

Zaworotko et al. noted that more than one type of network might be formed from the same building blocks and 1,3-bdc linker [27]. This phenomenon is called supramolecular isomerism. Five different structures, such as nanoballs, metallacalixarenes, Kagomé lattices, USF-1 and CdSO₄ nets, might be obtained from the same building blocks (paddlewheel metal clusters) and linker depending on the crystallization conditions, including the type of solvent, presence and type of templates and identity of the axial ligands. However, this review deals only with metallacalixarenes with the other structures being outside the scope of this work.

2.1. Metallacalixarenes with Cu nodes

Zaworotko et al. have advanced the field of metallacalixarenes based on the 1,3-dicarboxylates presented in Fig. 8 [18]. In 1,3-H₂bdc (1) and two of its derivatives with substituents in the 5-position, 5-OEt-1,3-H₂bdc (2) and 5-OPr-1,3-H₂bdc (3), the carboxylate groups form an angle of 120°, whereas thiophene-2,5-dicarboxylic acid (tdc) (4) and 1-methylpyrrole-2,4-dicarboxylic acid (pdc) (5) have angles of 157 and 145°, respectively, between the carboxylates.

Using a self-assembly process, polymers with bowl-like structures similar to calixarenes were formed from four paddlewheel-type SBUs. The products were obtained from the slow diffusion

of an ethanolic or methanolic solution containing a dicarboxylic acid into an aqueous or methanolic solution of Cu(NO₃)₂·2.5H₂O in a 1:1 molar ratio. Pyridine, 2,6-lutidine or 4-picoline was added as a base in a threefold excess with respect to the ligand. Nitrobenzene, benzene, *o*-dichlorobenzene and naphthalene were used as template molecules. This method provided good quality crystals in low to moderate yields (7.5–50%); nevertheless, the crystallization process required up to 6 months when the resulting solution was left standing at room temperature.

By analogy to the calixarenes, metallacalixarenes can exist as different atropisomers (conformers) (Fig. 9), which depend on the solvent and template molecules used. In each case, the organic base was coordinatively bonded to the copper metal in the apical position, and the template molecules occupied the void spaces in the framework.

When the unsubstituted 1,3-bdc ligand (1) was used with benzene as the template and pyridine as the organic base, two atropisomers were formed, *cone* and *1,3-alternate*.

In the *cone* conformer, the generated sheets were eclipsed in such a way that the cones stacked one into another, whereas in the *1,3-alternate* atropisomer, hourglass-shaped channels were formed. Each cone had an outer diameter of 0.94 nm and a depth of 0.84 nm. The disordered guest molecules occupied the empty bowls, which had a solvent-accessible volume of 0.513 nm³, as well as the channels formed between the adjacent bowls. The narrow part of the channels blocked the free movement of the benzene guest molecules.

The same structure has been found previously by the authors using dimethylformamide (DMF) as the reaction solvent instead of water [16].

The addition of nitrobenzene promoted the formation of *partial-cone* SBUs with three dicarboxylate ligands oriented up and one oriented down [18]. Each cone contained a disordered nitrobenzene molecule and had an outer diameter slightly bigger than that of the previous structure (0.98 nm) and a depth almost two times smaller (0.42 nm). Apparently, the nitrobenzene molecules were involved in π - π stacking interactions with the walls of the cavity, causing the flattening of the bowls and consequently leading to a lack of solvent-accessible area.

The bowls were stacked in an ABCABC fashion with ethanol molecules situated between the layers, which were separated by ca. 0.94 nm (Fig. 10).

When *o*-dichlorobenzene was used, the *1,2-alternate* atropisomer was formed with the template molecule within the cavity involved in CH \cdots π interactions with three of the bdc ligands.

The formed sheets were arranged in an ABCDABCD fashion with an interlayer separation of ca. 0.98 nm. As in the previous structure containing nitrobenzene, no solvent was found within the cavity.

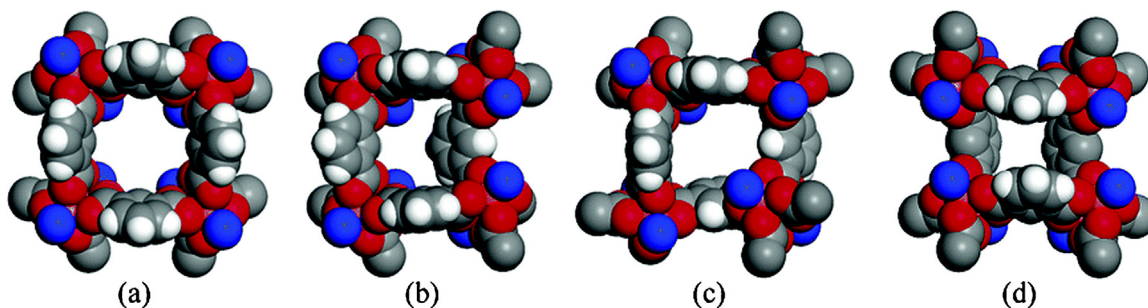


Fig. 9. SBUs in the structures of coordination polymers synthesized by Zaworotko et al.: (a) *cone*, (b) *partial cone*, (c) *1,2-alternate*, (d) *1,3-alternate*. Color code: gray-carbon, white-hydrogen, red-oxygen, pink-copper. Coordinated pyridine ligands and their derivatives are represented as a single nitrogen atom in blue, and the remaining atoms are removed for clarity.

Reprinted with permission from [18], Copyright 2003, American Chemical Society.

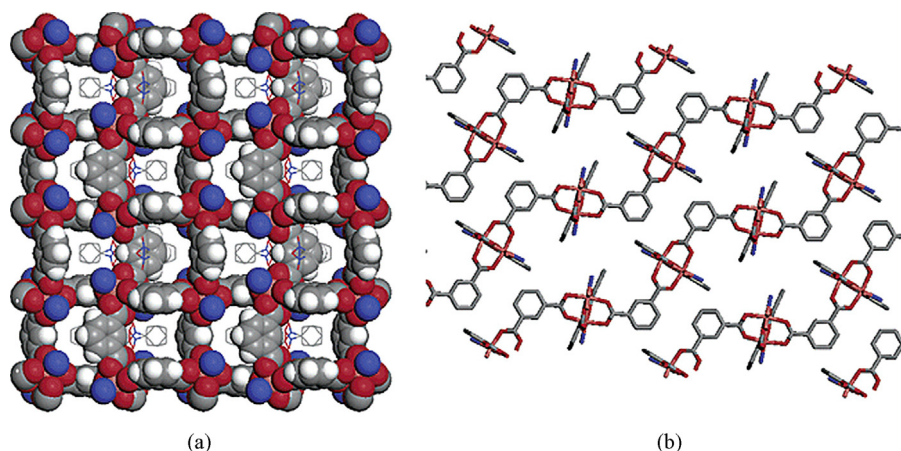


Fig. 10. Structure of $\{[Cu_2(1,3\text{-}bdc)_2(py)_2]_4 \cdot 4\text{Nitrobenzene } 2\text{EtOH}\}_n$: (a) top view showing the *partial-cone* SBUs and disordered nitrobenzene guest molecules, (b) side view illustrating the undulating-sheet layers. The ethanol molecules situated between the layers are omitted. Color code: gray-carbon, white-hydrogen, red-oxygen, pink-copper. Coordinated pyridine ligands are represented as a single nitrogen atom in blue, and the remaining atoms are removed for clarity. Reprinted with permission from [18], Copyright 2003, American Chemical Society.

Two isostructural frameworks based on 5-substituted bdc with the formulas, $\{[Cu_2(5\text{-OEt-bdc})_2(py)_2]_4 \cdot 8H_2O\}_n$ and $\{[Cu_2(5\text{-OPr-bdc})_2(py)_2]_4 \cdot \text{Guest}\}_n$, were obtained in the absence and presence of template molecules, such as nitrobenzene, benzene, *o*-dichlorobenzene and naphthalene. Moreover, the framework with the 5-OEt-1,3-bdc linker was isolated from a variety of solvents, including methanol (MeOH), ethanol (EtOH) and dimethyl sulfoxide (DMSO), and in the presence of different bases, such as pyridine or 2,6-lutidine. In each case, the isolated product contained two atropisomers, *cone* and *1,3-alternate*, which was also the case for the structure based on the unsubstituted bdc. However, the structures based on 5-substituted bdc had only one type of cavity. The alkyl chains of the bdc derivatives prevented the formation of the channels observed in the structure containing unsubstituted bdc, drastically reducing the solvent-accessible area. Presumably, the alkyl chains might play the role of the template in the formation of these structures exclusively because the presence or absence of template molecules did not affect the formation of the atropisomers. Each cone had the same outer diameter (*ca.* 0.94 nm), but due to the presence of the alkyl chains, they were much deeper (1.30 nm) than the cones in the framework with unsubstituted bdc.

Two coordination polymers, $\{[Cu_2(pdc)_2(py)_2]_4 \cdot 4\text{MeOH}\}_n$ and $\{[Cu_2(pdc)_2(4\text{-pic})_2]_4 \cdot 4H_2O\}_n$, were obtained *via* the slow diffusion

of a methanolic solution containing pdc (5) and pyridine or 4-picoline into a methanolic solution of copper nitrate in the absence and presence of nitrobenzene, respectively. In both cases, undulating sheets of *1,2-alternate* SBU atropisomers were formed with disordered methanol or water guest molecules between the layers (Fig. 11a).

In a thiophene-2,5-dicarboxylate (tdc)-based structure, each *1,2-atropisomer* contained one naphthalene and two methanol molecules inside the cavity (Fig. 11b).

An interesting new trend in the field of coordination polymers is the preparation of dynamic MOFs able to open or close their pores in the presence of specific guest molecules. To provide MOFs with dynamic properties, flexible elements must be incorporated into the molecular building blocks as an architectural element. One approach is the use of weak linkers in the MOF structure [28,29]. Another efficient way to prepare dynamic MOFs has been reported by Zaworotko et al., who synthesized a series of 2D MOFs constructed from the Cu-based paddlewheel cluster and fluorinated 1,3-bdc, namely, 2,4,5,6-tetrafluoro-1,3-benzenedicarboxylate (TFBDC) [30]. The introduction of fluorine atoms into the bdc ligand provides a higher degree of torsional flexibility to the carboxyl groups, resulting in flexible and dynamic MOF materials.

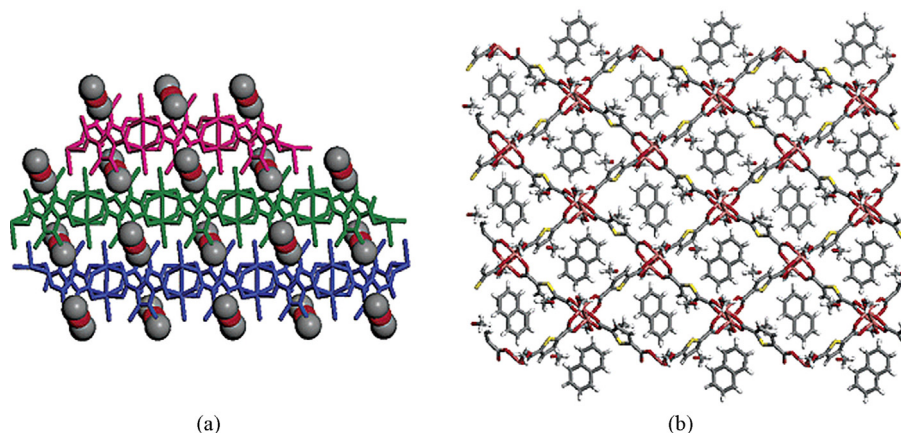


Fig. 11. *1,2-alternate* SBUs in pdc- and tdc-based 2D structures: (a) side view of $\{[Cu_2(pdc)_2(py)_2]_4\}_n$ showing the ABCABC packing with disordered MeOH molecules between the layers (layers are shown in different colors for clarity), (b) 2D sheets of $\{[Cu_2(tdc)_2(MeOH)_2]_4 \cdot 4\text{Naphthalene } 8\text{MeOH}\}_n$ showing the square grid-cavity structure with one naphthalene and two methanol guest molecules in each cavity. Color code: gray-carbon, white-hydrogen, red-oxygen, yellow-sulfur, pink-copper. Reprinted with permission from [18], Copyright 2003, American Chemical Society.

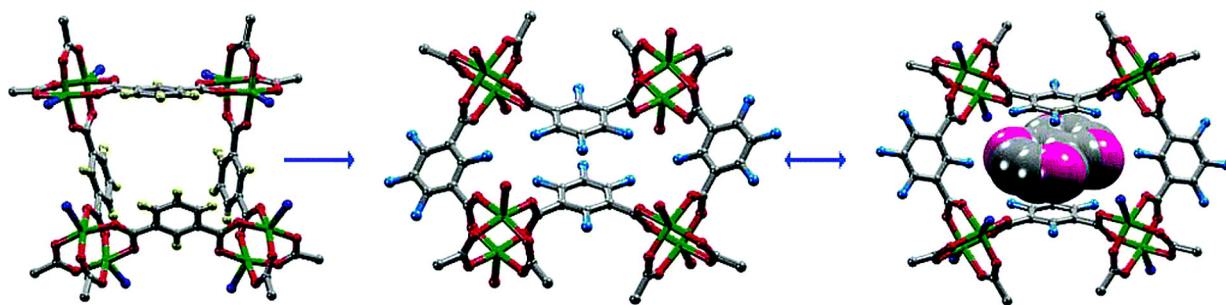


Fig. 12. The diverse pore structures (closed and partially open cavities) formed using fluorine-substituted bdc compared to the rigid open cavities obtained with unsubstituted bdc (on the left). Color code: gray-carbon, yellow-hydrogen, light blue-fluorine, red-oxygen, dark blue-nitrogen, green-copper. Reprinted with permission from [30], Copyright 2007, American Chemical Society.

The polymers were prepared by layering an ethanolic solution containing TFBDC and different bases (quinoline, 2,6-lutidine or 2-picoline) onto an ethanolic solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. Various template molecules (*o*-xylene, dichlorobenzene, chlorobenzene, benzene and hexafluorobenzene) were tested. Crystals were obtained within 24 h in very low to moderate yields (6–38.5%).

Depending on the choice of the template molecule, the cavities formed were either closed or partially open to guest molecules. This feature is very advantageous compared to the rigid cavities formed by unsubstituted 1,3-bdc where this dynamic behavior has not been observed.

When xylene was used as a template molecule, a closely packed MOF was formed without open cavities for guest molecules. When templates such as *o*-dichlorobenzene or chlorobenzene were employed, structures with partially open intra- or interlayer cavities were obtained. Therefore, there is no doubt that the size of the template molecule influenced the whether the pores were open or closed (Fig. 12).

MOFs with guest-dependent cavities might have potential in the development of highly selective sensors that can simultaneously recognize different guest species.

Dong-Xu et al. have reported the synthesis of a 2D coordination polymer based on Cu cluster and 1,3- H_2bdc by the slow diffusion of an aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution into a DMF/EtOH (1/1) solution of 1,3- H_2bdc in the presence of benzimidazole [31]. Crystals of the coordination polymer, $[\text{Cu}_2(\text{bdc})_2(\text{DMF})](\text{DMF}) \cdot \text{H}_2\text{O} \cdot (\text{EtOH})_{0.5}$, were formed with a yield of 59% within several days of standing at room temperature. The structure was similar to that reported by Zaworotko [18] and had the same bowl dimensions: an outer diameter of 0.94 nm and a depth of 0.84 nm. Each square pyramidal copper ion was coordinated to four carboxylate oxygen atoms

and one solvent molecule (ethanol, water or DMF), which could be easily removed to give exposed metal sites, at the apical position (Fig. 13).

The authors used benzimidazole as a base instead of pyridine, which was employed by the previous authors [18], to avoid base coordination to the metal cluster and to provide unsaturated open metal sites. These structures have potential for use in catalysis and gas adsorption. Although the authors did not use a template benzene molecule as the previous authors did [18], they obtained a similar framework. Therefore, it is not unreasonable to presume that the template molecule does not always determine the structure; the solvent and organic base play a crucial role as well. In this structure, the adjacent layers are held together by van der Waals interactions. The surface area of this coordination polymer was $629 \text{ m}^2 \text{ g}^{-1}$ (Langmuir) and $374 \text{ m}^2 \text{ g}^{-1}$ (BET) at 77 K and reached a plateau at a pressure of 1 atm. This material exhibited moderate adsorption of methanol/benzene vapors.

Gao et al. have reported the synthesis of a 2D network based on the paddlewheel-type SBUs with the formula, $[\text{Cu}(1,3\text{-bdc})(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})$, by the mixed-solvents method [32].

By heating equimolar amounts of 1,3- H_2bdc and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with imidazole as the base in a $\text{H}_2\text{O} : n\text{-propyl alcohol}$ (3:2) solvent mixture at 160°C for 5 days, a blue crystalline product was obtained. Apparently, the mixed-solvents synthesis played a crucial role in the crystallization of the desired product. The synthesis was also attempted using pure water or other alcohol solvents, such as ethyl alcohol, ethylene glycol, *iso*-propyl alcohol and *n*- and *iso*-butyl alcohol; however, no high quality crystals were obtained. Thus, the samples were not characterized.

The asymmetric unit in this polymer consisted of one 1,3-bdc ligand, one copper metal ion with a pseudo-octahedral

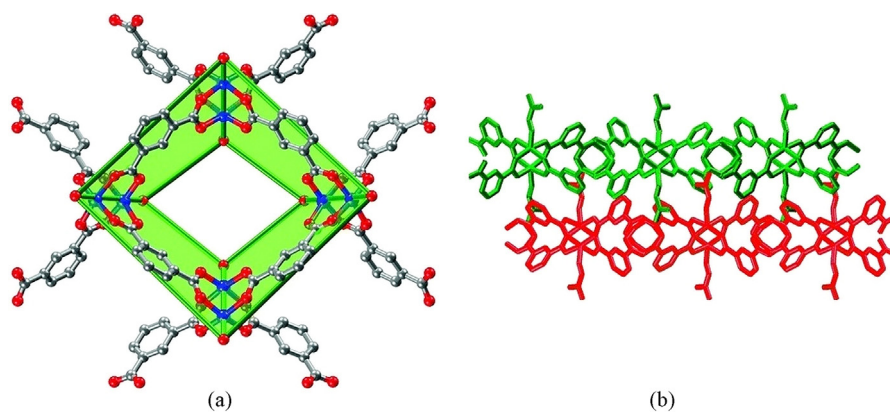


Fig. 13. Structure of $[\text{Cu}_2(\text{bdc})_2(\text{DMF})](\text{DMF}) \cdot \text{H}_2\text{O} \cdot (\text{EtOH})_{0.5}$. The bowl-shaped $[\text{Cu}_2(\text{bdc})_2]_4$ structural unit with open metal sites at the apical position of the metal cluster (a). Color code: gray-carbon, red-oxygen, blue-copper. The view of two adjacent layers showing the van der Waals interactions (b). Reprinted with permission from [31], Copyright 2007, American Chemical Society.

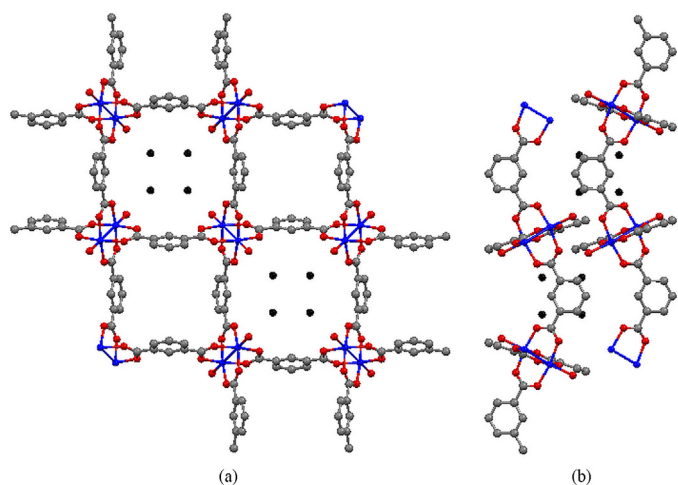


Fig. 14. Packing diagram of the coordination polymer, $[\text{Cu}(1,3\text{-bdc})(\text{H}_2\text{O})]\cdot(\text{H}_2\text{O})$: cavity view (a), view of two adjacent undulating-sheet layers (b). The water guest molecules are represented as small black dots.

coordination sphere, one coordinated water molecule and one free water molecule. However, unsaturated active metal sites might be obtained upon solvent removal. The packing of the coordination polymer is presented in Fig. 14.

The square grids formed zigzag layers, which were held together along the *c*-axis by hydrogen bonds between a water molecule in one layer and the carboxylate oxygen atoms in an adjacent layer. As a consequence, the interlayer separation in this structure (0.68 nm) is much smaller than in similar frameworks reported by other authors [18]. Presumably, the voids between the layers are too small to accommodate any solvent molecules larger than water molecules.

Lee and co-workers have reported the synthesis of a very similar 2D network with one less water molecule, $[\text{Cu}(1,3\text{-bdc})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$, using a hydro(solvo)thermal reaction [33]. Equimolar amounts of $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ and 1,3- H_2bdc were dissolved in a benzene/water (3/5 mL) solvent mixture and heated at 180 °C for 3 days to produce the green crystalline product with a yield of 78.1%.

Solvothermal reactions of $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ with 1,3- H_2bdc in the presence or absence of an organic base (pyridine or Bu_4NOH) under various conditions (DMF/EtOH at 25 °C for 1 day, DMF/EtOH at 70–100 °C for 1–3 days or DMF/EtOH/(pyridine or Bu_4NOH) at 70 °C for 3 days) failed to produce X-ray-quality crystals. Therefore, the samples obtained under these conditions were not characterized. Evidently, the presence of benzene somehow promoted the formation of single crystals.

Although this polymer had the same framework as the one obtained by Gao et al. [32], the product colors differed, and the size of the cavity was larger in the second case (9.6 Å), most likely due to the presence of two water guest molecules.

Zhong et al. have reported a systematic study of the solvent influence on the formation of different frameworks derived from copper ion and 1,3- bdc [34]. Hydrothermal and hydro(solvo)thermal reactions provided structures with the following formulas: $[\text{Cu}_2(1,3\text{-bdc})_2(\text{ACN})(\text{H}_2\text{O})](\text{H}_2\text{O})_{2.25}$, $[\text{Cu}(1,3\text{-bdc})(\text{H}_2\text{O})](\text{H}_2\text{O})_2$, $\text{Cu}(1,3\text{-bdc})(\text{C}_2\text{H}_5\text{OH})$, $\text{Cu}_2(1,3\text{-bdc})_2(\text{DEF})(\text{H}_2\text{O})$ and $[\text{Cu}_4(1,3\text{-bdc})_4(\text{DMF})_2(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})](\text{DMF})_2$. Regardless of the solvent used, all structures exhibited similar 2D bowl-shaped structures, specifically, metallacalixarenes with paddlewheel copper clusters as the building blocks. Although similar frameworks have been reported previously, these investigations are still required because

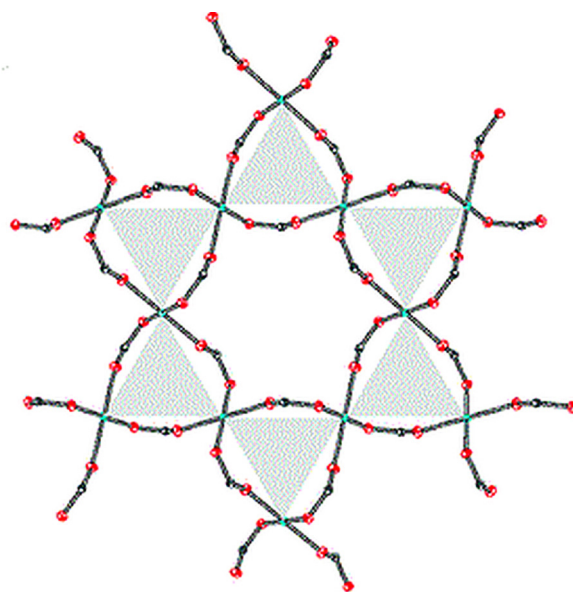


Fig. 15. The organic–inorganic hybrid Kagomé lattice consisting of six $[\text{Cu}_3(\text{OCO})_3]$ triangles. Color code: gray-carbon, red-oxygen, light blue-copper. Reprinted with permission from [35], Copyright 2008, American Chemical Society.

the role of the solvent in the self-assembly of coordination polymers is still not evident, often leading to unpredictable structures.

The reported frameworks differed in the identity of the solvent molecule(s) coordinated to the open metal site or located in the open channels. The different chemical affinities of the frameworks for the solvents were reflected in the porosity of these materials and, consequently, in the gas adsorption properties. Larger layer-to-layer separation distances correlated with higher surface areas. $[\text{Cu}_4(1,3\text{-bdc})_4(\text{DMF})_2(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})](\text{DMF})_2$ had the largest interlayer distance (0.77 nm), the highest surface area (approximately 70 mL (STP) g^{-1} at 77 K) and the highest H_2 uptake (0.8 wt%) of the coordination polymers reported by Zhong.

Because of its small interlayer spacing (ca. 0.68 nm), $[\text{Cu}(1,3\text{-bdc})(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ had a low affinity for nitrogen adsorption, resulting in a small surface area (approximately 20 mL (STP) g^{-1} at 77 K). On the other hand, the smaller hydrogen molecule is much easier to adsorb than nitrogen; thus, despite the rather low hydrogen uptake of 0.2 wt%, this framework can be used as a potential material for N_2/H_2 separations.

When $\text{Cu}(\text{OH})_2$ and 1,3- H_2bdc were mixed in a molar ratio of 3:4 in the presence of imidazole (1:2 molar ratio of imidazole to 1,3- H_2bdc) and $\text{Cu}(\text{OH})\text{F}$ (1:4 molar ratio of $\text{Cu}(\text{OH})\text{F}$ to 1,3- H_2bdc) in water at 150 °C for 5 days, the main product obtained was an organic–inorganic hybrid Kagomé lattice consisting of six $[\text{Cu}_3(\text{OCO})_3]$ triangles (Fig. 15) [35]. However, these synthetic conditions led to the formation of a mixture of compounds, including the powder starting materials (1,3- H_2bdc , $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})\text{F}$) and a green impurity, $\text{C}_{32}\text{H}_{24}\text{Cu}_6\text{O}_{26}$ (copper-containing by-product of ligand oxidation), from which the desired crystalline product was isolated.

Each carboxylate group in this structure bridges two copper ions to form a lattice composed of $[\text{Cu}_3(\text{OCO})_3]$ triangles, which resemble calix[3]arene units, in the *ab* plane. However, Kagomé structures are outside the scope of this review. Nevertheless, the appropriate selection of the synthetic conditions plays a crucial role in the formation of the desired product; a $\text{Cu}(\text{H}_2\text{O})(1,3\text{-bdc})\cdot\text{H}_2\text{O}$ polymer having the bowl-shaped metallacalix[4]arene structure described earlier [32] could be formed as well. It might be assumed that the reaction in pure water without any auxiliary solvent, such

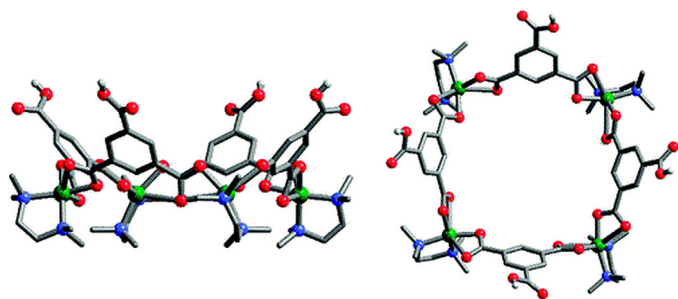


Fig. 16. Side and top views of the metallacalixarene, $[\text{Cu}_4(\text{tmen})_4(\text{Htrim})_4] \cdot n\text{H}_2\text{O}$. Color code: gray-carbon, white-hydrogen, red-oxygen, green-copper, blue-nitrogen. Reprinted with permission from [36], Copyright 2009, American Chemical Society.

as benzene or alcohol, as reported previously [32,33] might lead to the Kagomé lattice instead of metallacalixarenes.

In 2009, a new family of metallacalixarenes synthesized from 5-substituted 1,3-benzenedicarboxylates and $[\text{Cu}(\text{tmen})]^{2+}$ cations was reported [36]. The reaction between the copper complex, $[\text{Cu}(\text{acac})(\text{tmen})]\text{ClO}_4$, where acac = acetylacetonate and tmen = tetramethylethylenediamine, and trimesic acid (H_3trim) in the presence of triethylamine in a molar ratio of 3:2:6 in 10:5:1:1 MeOH/ACN/ H_2O /DMF led to the formation of a metallacalixarene with the formula, $[\text{Cu}_4(\text{tmen})_4(\text{Htrim})_4] \cdot n\text{H}_2\text{O}$ ($n=2, 8$ and 12). When 5-hydroxy-1,3-benzenedicarboxylate was employed in the synthesis, a similar metallacalixarene structure was obtained.

The structure consisted of tetranuclear complexes with the copper ions connected by two carboxylates (Fig. 16).

Each copper ion is hexacoordinated by the two tmen nitrogen atoms and four oxygens from two chelating carboxylate groups. One carboxylic acid group remained protonated.

The tetranuclear rings formed parallel ABABAB stacking layers, generating channels with water guest molecules. The water molecules were located inside the metallacalixarene, forming an octameric water cluster, which could be removed by heating without structural changes to the framework. This result suggests that a single-crystal-to-single-crystal transformation occurred. Moreover, this process was reversible; the structure was retained when exposed to moisture.

The magnetic properties were investigated; however, no exchange interaction between the copper ions was detected.

2.2. Metallacalixarenes with Zn nodes

Zn-metallacalixarenes are not nearly as common as Cu-metallacalixarenes mostly because the zinc cation prefers tetrahedral coordination instead of square planar or square pyramidal coordination like copper. This preference often leads to the formation of 3D structures instead of calixarene-like 2D frameworks.

A Zn-based metallacalixarene was first reported by Zaworotko et al., who synthesized the bowl-shaped coordination polymer, $[\text{Zn}_2(1,3\text{-bdc})_2(\text{py})_2]_4$, from the dizinc tetracarboxylate cluster and the angular 1,3-bdc [16]. The reaction was performed by refluxing a methanolic solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1,3- H_2bdc (molar ratio 1:1) in the presence of pyridine and benzene for 30 min. After slow cooling to room temperature, the colorless crystalline product was obtained. As in the case of the Cu-based analog, the bowls were occupied by disordered benzene or pyridine guest molecules. The layers were packed in a way that produced hourglass-shaped channels.

Two years later, Zaworotko et al. reported a series of Zn-metallacalixarenes with the general formula, $\{[\text{Zn}_2(1,3\text{-bdc})_2(\text{L})_2]_4\}_n$, where L = coordinated base [37], that are the structural analogs of those published for the copper cluster [18].

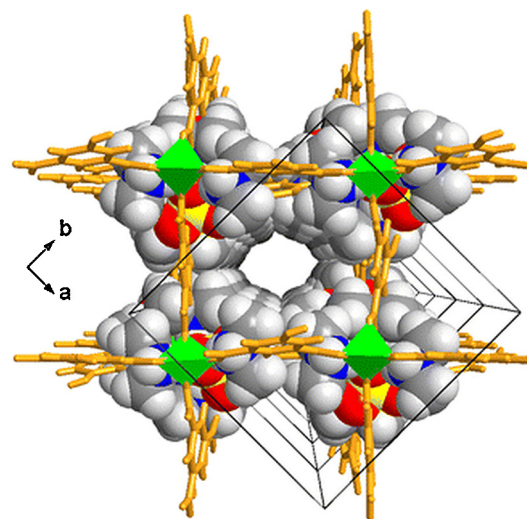


Fig. 17. A partially expanded net of the $\{[\text{NH}_2(\text{CH}_3)_2]_4[\text{Zn}(5\text{-OH-1,3-bdc})_2](\text{SO}_4)\}_n$ structure showing the counterions with the space-filling model. Color code: gray-carbon, white-hydrogen, red-oxygen, green-zinc, blue-nitrogen, yellow-sulfur. Reprinted with permission from [38], Copyright 2010, Springer.

The Zn-based metallacalixarenes were obtained similarly to their copper analogs by slow diffusion via the layering of an ethanolic or methanolic 1,3- H_2bdc solution onto an ethanolic or methanolic solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio. The reactions were performed in the presence of a base (in a threefold excess with respect to 1,3-bdc) and 2 mL of a template molecule. Pyridine, 2-picoline, 4-picoline, 3,5-lutidine, 4-methoxypyridine and isoquinoline were used as the base, and in each case, they were coordinatively bonded to the metal cluster.

In each structure, the zinc cation had a square pyramidal geometry. This coordination geometry is rather rare for the zinc cation but necessary to obtain structures such as metallacalixarenes. Square SBUs consisting of four dizinc metal clusters and four 1,3-bdc linkers formed 2D undulating-sheet structures similar to that reported for the series of Cu-metallacalixarenes. In the case of the Cu coordination polymers, the choice of an appropriate template molecule resulted in the formation of different conformers. The addition of benzene resulted in two different conformers, *cone* and *1,3-alternate*, whereas nitrobenzene and *o*-dichlorobenzene were responsible for the formation of *partial cone* and *1,2-alternate* conformers, respectively [18]. However, it seems that this trend does not apply to Zn-based metallacalixarenes because the same reaction performed in the presence of benzene but with different bases (pyridine or 4-methoxypyridine) led to different coordination polymers consisting of the *cone* and *1,3-alternate* conformers in the first case and the *1,2-alternate* conformer in the second case. Therefore, the choice of the base is also a very important factor that affects the polymer structure. Nevertheless, no systematic studies of the influence of the base on the formation of the conformers have been performed.

A metallacalixarene, $\{[\text{NH}_2(\text{CH}_3)_2]_4[\text{Zn}(5\text{-OH-1,3-bdc})_2](\text{SO}_4)\}_n$, based on the mononuclear $\text{Zn}(\text{O}_2\text{C})_4$ unit and the 5-OH-1,3- H_2bdc linker has been reported by Chun [38]. After stirring $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 5-OH-1,3- H_2bdc in a 1:2 molar ratio in a DMF/ethylene glycol mixture (4:1) in the presence of the base, 1,4-diazabicyclo[2.2.2]octane (dabco), at room temperature, the white precipitate was filtered off, and the residual solution was heated to 110°C for 21 h and then cooled to room temperature, giving the desired crystalline product within days. A 2D square-grid network was formed (Fig. 17).

In this structure, Zn^{2+} is coordinated by four carboxylate groups of the 5-OH-1,3-bdc ligands and four $\text{NH}_2(\text{CH}_3)_2^+$ counter-cations

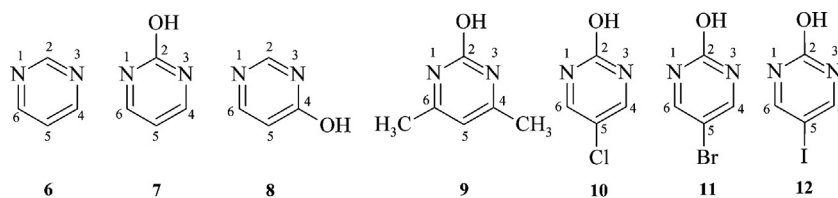


Fig. 18. Chemical structures of pyrimidines used to synthesize metallacalixarenes showing the atom-numbering scheme: (6) pyrimidine (pym), (7) 2-hydroxypyrimidine (2-Hpymo), (8) 4-hydroxypyrimidine (4-Hpymo), (9) 4,6-dimethyl-2-hydroxypyrimidine (2-Hdmpymo), (10) 5-chloro-2-hydroxypyrimidine, (11) 5-bromo-2-hydroxypyrimidine, (12) 5-iodo-2-hydroxypyrimidine.

that were produced by the thermal decomposition of DMF during the synthesis. The cations were hydrogen bonded to the carboxylates in a tetrahedral arrangement. The negative charges on the framework (SO_4^{2-} ions) were situated in the interlayer space and were strongly hydrogen bonded to four counter-cations. The nitrogen and hydrogen sorption properties could not be measured due to the destruction of the framework after the evacuation of the solvent molecules. Therefore, the presence of the solvent molecules and counterions is sometimes essential to maintain the framework structure.

3. Metallacalixarenes based on heterocycles

Numerous metallacalixarenes based on heterocycles can be found in the literature [20–22,25]. They are easily obtained in the reaction of a *cis*-protected metal fragment, such as Pd^{2+} or Pt^{2+} complexes, with an appropriate *N*-heterocyclic ligand having two ligating nitrogen atoms forming an angle of 120° as in the structures of pyridine, pyrimidine, 4,7-phenanthroline and 2,2'-bipyrazine derivatives or 150° as in the imidazole ring. Due to the cationic nature of these compounds, they might show an affinity for anions and, in particular, for mononucleotides.

3.1. Pyrimidine-based metallacalixarenes

Pyrimidine and its derivatives (Fig. 18) have attracted much attention as organic linkers for the synthesis of metallacalixarenes [20–22,39–45]. A class of so-called “platinum pyrimidine blues” is a very promising group of materials for antitumor agents.

Structural analogs of calix[4]arene were obtained in the reaction between $[\text{enM}(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (*en* = ethylenediamine, *M* = Pd^{2+} , Pt^{2+}) and 2-Hpymo (7) in water. Specifically, cyclic complexes of the type, $[\text{enM}(2\text{-pymo-}N1,N3)]_4(\text{NO}_3)_4$ (*M* = Pd^{2+} , Pt^{2+}), were formed and adopted the 1,3-*alternate* conformation [46]. Despite their high positive charge, they were unable to host anions due to the small size of their cavities.

Attempts to coordinate various metal cations, including soft (Pd^{2+} , Pt^{2+}), borderline (Cu^{2+} , Zn^{2+}) and hard (La^{3+} , Be^{2+} , Na^+) cations, to the oxo surface of the metallacalix[4]arene lower rim were unsuccessful [46]. Instead, X-ray crystal structural analysis showed that in the case of $\{[\text{enPt}(2\text{-pymo-}N1,N3)]_4(\text{ClO}_4)_4\}_2 \cdot [\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot 9\text{H}_2\text{O}$, hydrogen-bonding interactions between the water coordinated to the copper center and the oxo surface of two tetranuclear cations occurred, however, without direct interactions between the heterometal and the oxo surface (Fig. 19).

A series of pyrimidine-based metallacalix[4]arenes of the general formula, $[\{\text{Pt}(\text{en})(5\text{-X-pymo})\}_4]^{4+}$ (*en* = ethylenediamine; X = H, Cl, Br or I), were synthesized to investigate their binding abilities of calf-thymus DNA (ct-DNA) [47]. The novel tetranuclear complexes based on pyrimidine derivatives (10–12) were obtained in the reaction of a $[\text{Pt}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ aqueous solution with 5-halo-2-hydroxypyrimidine (5-XpymoH). The resulting complexes were similar in structure to those described

previously, $[\text{enPt}(2\text{-pymo-}N1,N3)]_4(\text{NO}_3)_4$ [46]. The DNA binding studies were performed using titration experiments with methods such as UV–vis spectroscopy, circular dichroism (CD) and flow linear dichroism (LD). For each metallacalix[4]arene based on (7) and (10–12), the observed non-covalent interactions with ct-DNA were expected because the inertness of the Pt–N bonds excludes the formation of a covalent bond to ct-DNA. Moreover, at low metallacalixarene concentrations, the coiling of ct-DNA could be observed.

In view of the enantioselective processes that are important in biological systems, some enantiomerically pure metallacalix[*n*]arenes with the formula, *cis*- $[\text{L}^2\text{PdL}]_n^{n+}$ ($\text{L}^2 = (R,R)$ -1,2-diaminocyclohexane (*R,R*-dach), (*S,S*)-1,2-diaminocyclohexane (*S,S*-dach); *n* = 4, 6; LH = hydroxypyrimidine derivatives (7–9)), were obtained in aqueous media [48].

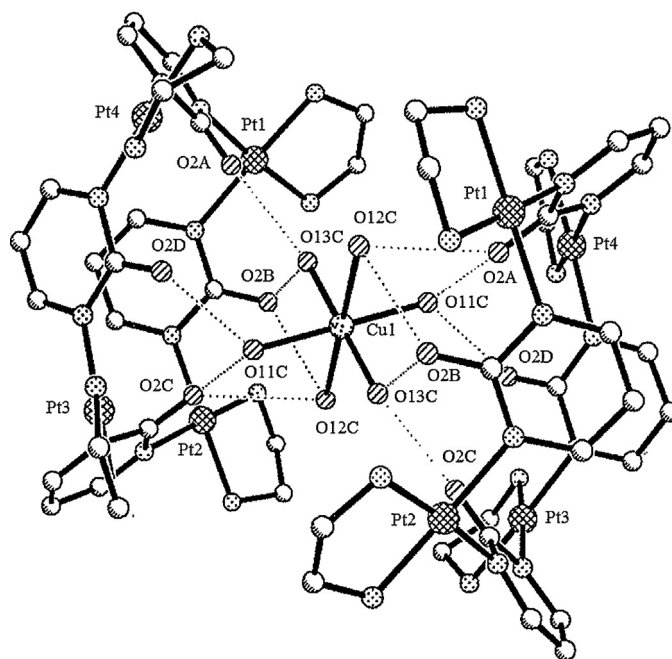


Fig. 19. X-ray crystal structure of $\{[\text{enPt}(2\text{-pymo-}N1,N3)]_4(\text{ClO}_4)_4\}_2 \cdot [\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot 9\text{H}_2\text{O}$ showing a $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cation sandwiched between the oxo surfaces of two metallacalix[4]arenes.

Reprinted with permission from [46], Copyright 2000, American Chemical Society).

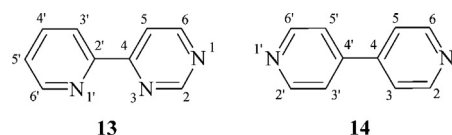


Fig. 20. Chemical structures of 4-(2-pyridyl)pyrimidine (pprd) (13) and 4,4'-bipyrimidine (bpm) (14) used to synthesize metallacalixarenes showing the atom-numbering scheme.

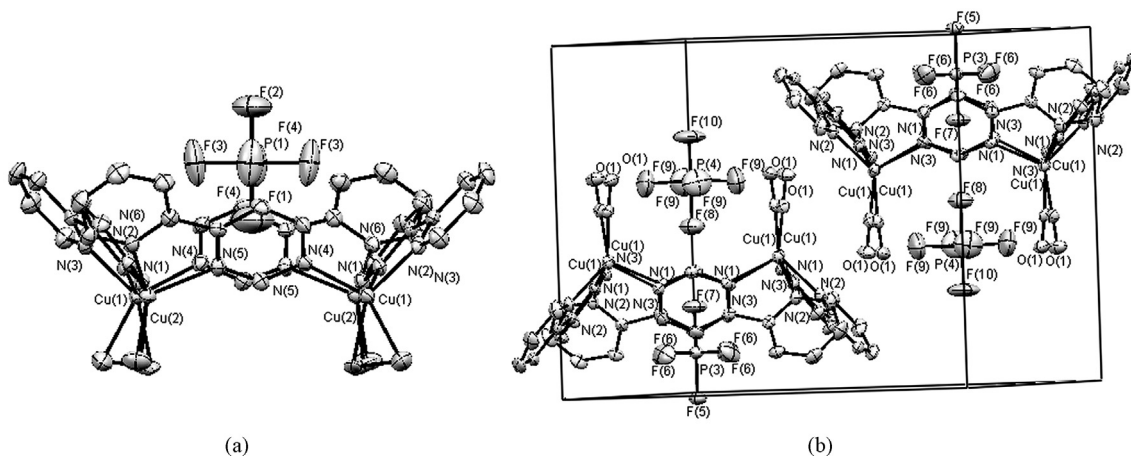


Fig. 21. X-ray crystal structure of $[\text{Cu}_4(\text{pprd})_4(\text{C}_2\text{H}_4)_4](\text{PF}_6)_4$ (a) and the elemental cell showing the packing of two metallacalix[4]arenes, $[\text{Cu}_4(\text{pprd})_4(\text{CO})_4](\text{PF}_6)_4$, in a “head-to-tail” orientation (b). The encapsulated PF_6^- anions are shown.

In all cases, the compounds adopted the *1,3-alternate* conformation. The isolated metallacalix[6]arene was converted into metallacalix[4]arene when heated.

These calixarene-like compounds were able to bind hard metal cations such as Na^+ or La^{3+} on the oxo surface. For example, in a $[(\text{dach})\text{Pd}(2\text{-pymo})]_4^{4+}$ complex containing Na^+ , two hydrated Na^+ cations were found in the asymmetric unit; nevertheless, only one cation was directly bonded to the pyrimidine oxygen atom. The interactions with a La^{3+} cation were observed only in the case of 2-Hpymo-based compounds. The sterically hindered rotation around the Pd–N bonds between the bulky methyl groups and dach prevented interactions with additional metal cations in other cases.

Additionally, investigations on the receptor properties of the metallacalixarenes based on 4-Hpymo (**8**) showed them to be capable of the enantioselective recognition of adenosine monophosphate (AMP) from adenosine, guanosine, thymidine and cytidine monophosphate in aqueous media, illustrating the possibility of using metallacalixarenes as selective DNA-binding drugs.

An interesting approach to form metallacalixarenes was reported by Maekawa et al. using 4-(2-pyridyl)pyrimidine (pprd) (**13**) or 4,4'-bipyrimidine (bpm) (**14**) as the organic linker (Fig. 20) [49,50]. In the reaction of $[\text{Cu}(\text{ACN})_4]\text{PF}_6$ with 4-(2-pyridyl)pyrimidine (pprd) in MeOH under C_2H_4 or CO, cyclic tetramers of the formula, $[\text{Cu}_4(\text{pprd})_4(\text{C}_2\text{H}_4)_4](\text{PF}_6)_4$ or $[\text{Cu}_4(\text{pprd})_4(\text{CO})_4](\text{PF}_6)_4$, respectively, were formed [49].

Fig. 21 presents the X-ray crystal structures of the synthesized cyclic polymers, demonstrating their unequivocal resemblance to classical calixarenes. Moreover, two units in the elemental cell were oriented upside down relative to each other, a typical orientation for calixarenes that is called the “head-to-tail” orientation. In both cases, one PF_6^- anion was found inside the cavity.

The choice of solvent played an important role in the structure of the final product. When acetone was used instead of methanol, no cyclization was observed. Moreover, the reaction showed that cyclic products were most likely anion-templated. When $[\text{Cu}(\text{C}_2\text{H}_4)_n]\text{ClO}_4$ was reacted with pprd in acetone under C_2H_4 , a trimeric metallacalixarene of the formula, $\{[\text{Cu}_3(\text{pprd})_3(\text{C}_2\text{H}_4)_3][\text{ClO}_4]_3\}_3$, was formed (Fig. 22). The smaller ClO_4^- anion induced the formation of a trimer, whereas the larger PF_6^- anion led to the formation of a tetramer. These compounds are promising anion-selective receptors.

Later, the authors applied a similar synthetic approach to form metallacalixarenes based on 4,4'-bipyrimidine (bpm) [50]. The reaction of $[\text{Cu}(\text{ACN})_4]\text{BF}_4$ with bpm in MeOH under C_2H_4 afforded a metallacalix[3]arene with three Cu atoms bridged by three bpm ligands and with three C_2H_4 groups. One BF_4^- anion was located in the triangular Cu_3 cavities.

Similar to the previous example, the reaction in acetone gave polymeric 1D chains and 1D ladder structures instead of metallacalixarenes.

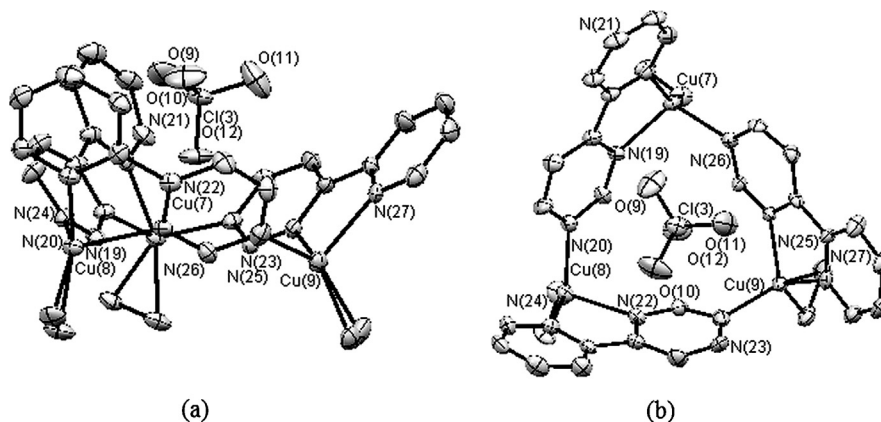


Fig. 22. X-ray crystal structure of a trimer, $\{[\text{Cu}_3(\text{pprd})_3(\text{C}_2\text{H}_4)_3][\text{ClO}_4]_3\}_3$: side view (a), top view (b). The encapsulated ClO_4^- anion is shown.

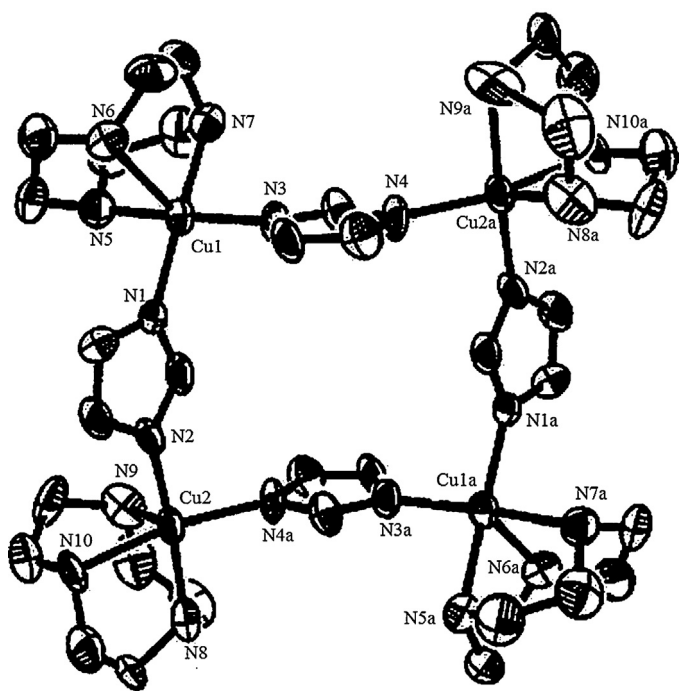


Fig. 23. X-ray crystal structure of $[(\text{tacn})_4\text{Cu}_4(\text{Im-N1,N3})_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$. Reprinted with permission from [52], Copyright 1993, American Chemical Society.

3.2. Imidazole- and benzimidazole-based metallacalixarenes

Metallacalixarenes based on imidazole (ImH) and benzimidazole (bzimH) rings have been widely reported.

$[\text{Cu}(\text{ImH})_2(\text{OAc})_2]$, obtained *in situ* from the reaction of imidazole (ImH) and $\text{Cu}(\text{OAc})_2$ with Me_3tacn (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) followed by treatment with sodium perchlorate, resulted in the formation of a trinuclear complex, $[(\text{Me}_3\text{tacn})_3\text{Cu}_3(\text{Im-N1,N3})_3](\text{ClO}_4)_3$ [51]. When Me_3tacn was replaced by the smaller 1,4,7-triazacyclononane (tacn) molecule, the same reaction yielded the tetranuclear complex, $[(\text{tacn})_4\text{Cu}_4(\text{Im-N1,N3})_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Fig. 23) [52].

In both complexes, copper is coordinated to N1 and N3 of adjacent imidazoles and three nitrogens of the cyclic amine. The different nuclearity of the metallacalixarenes might be reflected in the higher steric hindrance of Me_3tacn than the tacn amine.

Nevertheless, according to Alessi, these structures cannot be considered to be metallacalixarenes and should be classified as metallasquares with angular linkers instead because of the small size of the aromatic walls defined by the imidazole rings [15]. However, because the classification of metallacalixarenes based on the linker size has not been clearly defined, this structural example is classified as a metallacalixarene. Various metallacalixarenes based on imidazole and benzimidazole rings have been reported and were described in [19]. Among them, metallacalixarenes with the mixed linkers, thpy and benzimidazole [53], and various examples of copper complexes with the multidentate Schiff base ligands, which contain imidazolate moieties, have been reported and are presented in Fig. 24 [23,54–60].

In this review, we highlight interesting examples of metallacalix[4]arenes derived from AlMe_3 or GaMe_3 and benzimidazole ligands [61]. The reaction of an equimolar amount of benzimidazole or 2-methylbenzimidazole (mbzim) with trimethylaluminum (AlMe_3) or trimethylgallium (GaMe_3) in toluene or benzene at room temperature yielded four corresponding metallacalix[4]arenes with the formulas, $[\text{bzimAlMe}_2]_4$, $[\text{bzimGaMe}_2]_4$, $[\text{mbzimAlMe}_2]_4$ and $[\text{mbzimGaMe}_2]_4$ (Fig. 25) [61].

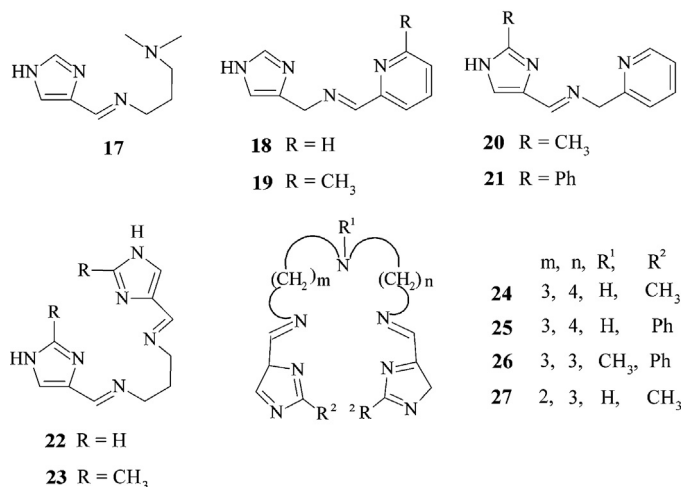


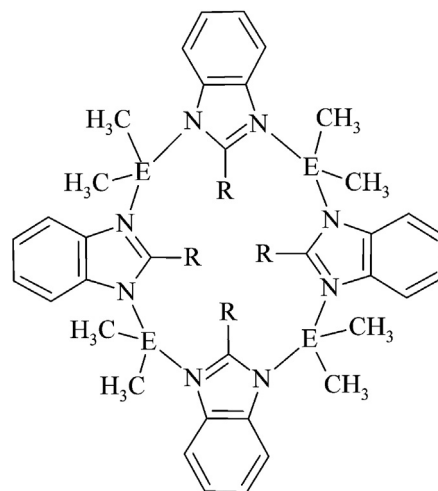
Fig. 24. Chemical structures of the imidazole derivatives used to synthesize metallacalixarenes.

Examples of tri- and tetranuclear metallacalixarenes based on imidazole, 2-phenylimidazole or purine stabilized by tetrafluoropyridyl ligands (Fig. 26) have been reported in [62]. These neutral compounds might be able to host anionic, neutral and cationic guests or can be used as fluorinating agents.

3.3. Phenanthroline-based metallacalixarenes

Yu et al. have communicated the synthesis and anion recognition of a metallacalix[3]arene of the formula, $[(\text{en})\text{M}(4,7\text{-phen})]_3^{6+}$, where $\text{M} = \text{Pd}^{2+}$ or Pt^{2+} . This metallacalixarene adopted a *cone* conformation [63]. Later, the homochiral species, $[(\text{R,R-dach})\text{Pd}(4,7\text{-phen})]_3^{6+}$ and $[(\text{S,S-dach})\text{Pd}(4,7\text{-phen})]_3^{6+}$, were prepared and tested for mononucleotide recognition (Scheme 1) [64].

The phenanthroline-based metallacalix[3]arenes exhibited even stronger interactions with AMP than the pyrimidine-based



- a)** $\text{R} = \text{H}$; $\text{E} = \text{Al}$
- b)** $\text{R} = \text{H}$; $\text{E} = \text{Ga}$
- c)** $\text{R} = \text{CH}_3$; $\text{E} = \text{Al}$
- d)** $\text{R} = \text{CH}_3$; $\text{E} = \text{Ga}$

Fig. 25. Schematic representation of metallacalix[4]arenes derived from AlMe_3 or GaMe_3 and benzimidazole ligands.

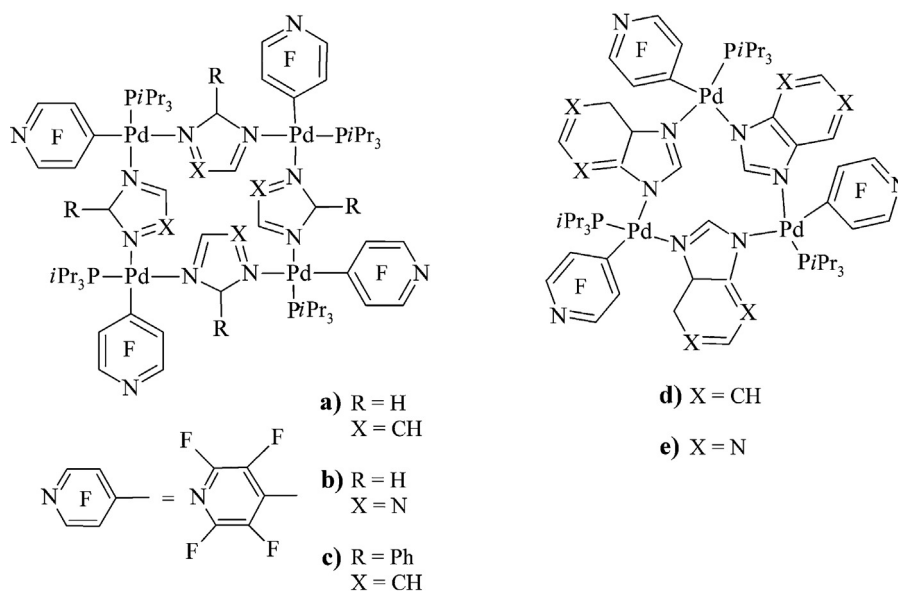


Fig. 26. Tri- and tetranuclear complexes based on tetrafluoropyridyl ligands.

metallacalixarenes. However, in each case, the accommodation of the AMP led to the decomposition of the metallacalixarene.

The combination of two different linkers provides a route to obtain metallacalixarenes of various sizes and with different cavity shapes. The reaction between ethylenediaminepalladium ($[(en)Pd^{2+}]$), pyrimidine and 4,7-phenanthroline (4,7-phen) in a molar ratio of 3:1:2 led to the formation of heterotopic tricyclic metallacalixarenes with the formula, $[Pd_3(en)_3(L-N1,N3)_m(4,7-phen-N4,N7)_2]^{5+}$ ($L = 2-pymo, 2-mpymo$ or $2-dmpymo$) [65]. When $[(en)Pd(phen-N4,N7)]_3(NO_3)_4$ and $[(en)Pd(L)N1,N3]_4(NO_3)_4$ were mixed in a molar ratio of 3:8, a triangle in a *pinched-cone* conformation was formed.

The reaction of a 2:1:1 mixture of ($[(en)Pd^{2+}]$), 2-pymo and 4,7-phen formed the tetranuclear metallacalixarene, $[(en)_4Pd_4(2-pymo-N1,N3)_2(phen-N4,N7)_2]^{6+}$, whereas the reaction between $[(en)Pd(2-pymo-N1,N3)]_4(NO_3)_4$ and $[(en)Pd(phen)]_3(NO_3)_6$ gave the hexanuclear metallacalixarene, $[(en)_6Pd_6(2-pymo-N1,N3)_4(phen-N4,N7)_2]^{8+}$.

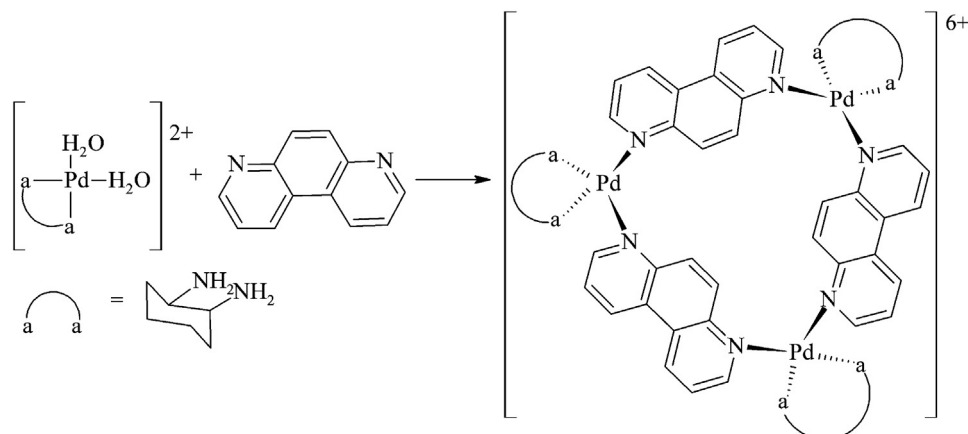
The ability of these species to host mononucleotide guest molecules were studied, and they exhibited weaker interactions with the mononucleotides than $[(en)Pd(4,7-phen)]_3^{6+}$. However, the inclusion of mononucleotides induced the decomposition of the metallacalixarenes.

Subsequently, the synthesis of metallacalix[3]arenes of the general formula, $[(en)_3Pd_3(4,7-phen)_2(Rpymo)]^{5+}$, where ($R = H$, ethynylferrocene or 5-(dimethylamino)-N-(2-propynyl)-1-naphthalene sulfonamide), was announced, and these metallacalixarenes were touted as possible receptors for mononucleotides. The above-mentioned metallacalixarenes were obtained from the ligand exchange reaction between $[(en)_3Pd_3(4,7-phen)_3]^{6+}$ and 5-R-2-hydroxypyrimidine derivatives. In these cases, electro- and photochemical elements were introduced into the structure of the metallacalixarene (Scheme 2) [66]. New materials (b) and (c) (see Scheme 2) were shown to work as sensors for uridine-5'-monophosphate disodium salt with the recognition process occurring inside the cavity of these complexes.

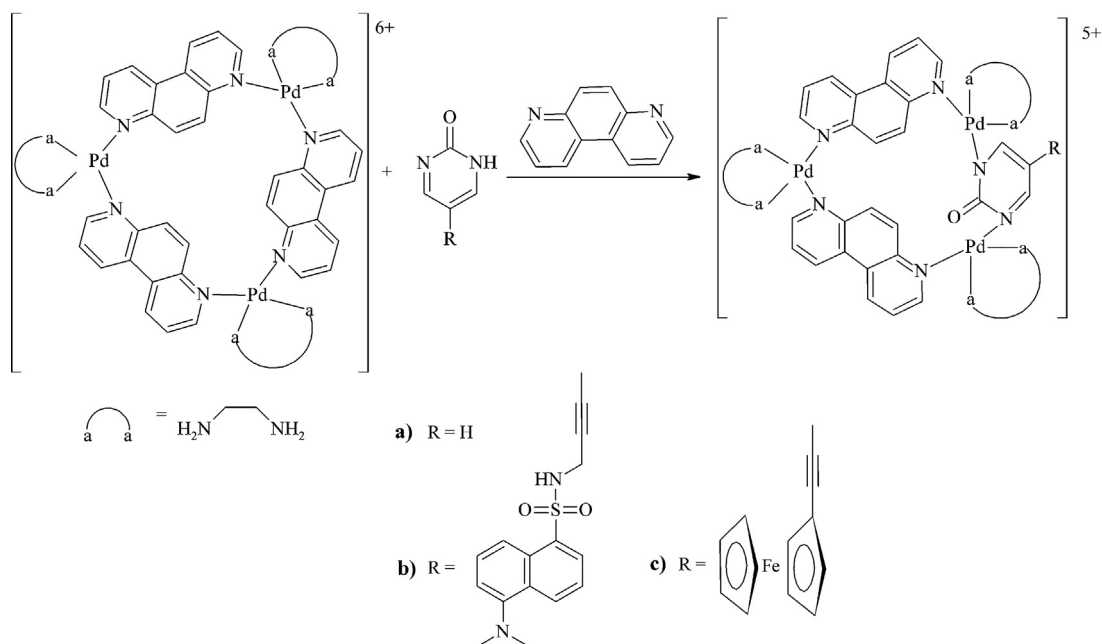
3.4. Bipyrazine-based metallacalixarenes

The heterocyclic ligand, 2,2'-bipyrazine, can coordinate to the metal entity through different bridging modes. In addition to the chelation mode *via* the N1 and N1' atoms, it can also undergo rotation around the C2–C2' bond to give *cis* or *trans* isomers.

The trimeric cyclic compound, *cis*- $[(en)Pt(2,2'-bpz-N4,N4')]_3(NO_3)_6$, was isolated by reacting *cis*-bipyrazine with $(en)Pt^{2+}$. In this structure, three metal atoms were linked through



Scheme 1. Synthesis of a phenanthroline-based trinuclear metallacalixarene.



Scheme 2. Ligand exchange reaction between $[(\text{en})_3\text{Pd}_3(4,7\text{-phen})_3]^{6+}$ and 5-R-2-hydroxypyrimidine derivatives yielding the metallacalix[3]arenes, $[\text{Pd}_3(\text{en})_3(4,7\text{-phen})_2(5\text{-R-pyrimidone-2-olate})]^{5+}$ with R=H (a), ethynylferrocene (b) and 5-(dimethylamino)-N-(2-propynyl)-1-naphthalene sulfonamide (c).

the *N4* atoms, and two pyrazine rings were significantly twisted with respect to each other, allowing for the formation of a cyclic, vase-like triangle [67]. On the other hand, when $(\text{en})\text{Pd}^{2+}$ was mixed with *cis*-bpz, the mononuclear chelate, $[(\text{en})\text{Pd}(\text{bpz-}N1,N1')](\text{ClO}_4)_2$, was formed with the bipyrazine ligands coplanar with the plane of the metal [67].

The formation of two different structures was reported depending on the counterion used [68]. The $[(\text{en})\text{Pt}(\text{trans-bpz-}N4,N4')_3](\text{NO}_3)_2(\text{PF}_6)_4$ structure consisted of a nearly equilateral triangle of three Pt atoms linked through the *N4* atoms (Fig. 27). In the $[(\text{en})\text{Pt}(\text{cis-bpz-}N4,N4')_3](\text{NO}_3)_2(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ structure, one of the bpz ligands was planar, while the other two were more twisted. As a result, a vase-like structure was obtained (Fig. 28).

As a consequence, the structures exhibited different affinities for anions. In the *trans* isomer, PF_6^- was inserted into the cavity, and NO_3^- was located outside the triangle. In the *cis* isomer, both NO_3^- and ClO_4^- were bonded inside the cavity with the NO_3^- and ClO_4^- anions lying in and above the Pt_3 plane, respectively.

The reaction between $[(\text{en})\text{Pt}(\text{bpz-}N4,N4')_3](\text{NO}_3)_6$ and $[(\text{en})\text{Pt}(\text{H}_2\text{O})_2]^{2+}$ gave a Pt_6 vase, whereas a hexanuclear compound, $\{[(\text{en})\text{Pd}(\text{N4,N4'-bpz-}N1,N1')\text{Pd}(\text{en})]_3\}(\text{NO}_3)_4(\text{PF}_6)_8 \cdot 5\text{H}_2\text{O}$, was obtained from the reaction of $[(\text{en})\text{Pd}(\text{H}_2\text{O})_2]^{2+}$ with $[(\text{en})\text{Pd}(\text{bpz-}N1,N1')](\text{ClO}_4)_2$.

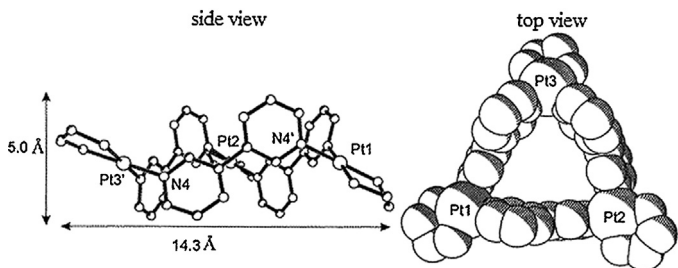


Fig. 27. X-ray crystal structure of the trinuclear complex $[(\text{en})\text{Pt}(\text{bpz-}N4,N4')_3](\text{NO}_3)_2(\text{PF}_6)_4$.

Reprinted with permission from [68], Copyright 2000, American Chemical Society.

Similarly, a $\{[(\text{en})\text{Pd}(\text{N4,N4'-bpz-}N1,N1')\text{Pt}(\text{en})]_3\}(\text{NO}_3)_7(\text{PF}_6)_5 \cdot 9.75\text{H}_2\text{O}$ complex was obtained from the reaction of $[(\text{en})\text{Pt}(\text{bpz-}N1,N1')](\text{NO}_3)_2$ with $[(\text{en})\text{Pd}(\text{H}_2\text{O})_2]^{2+}$ [67].

A hexanuclear Pt_3Pd_3 complex, $[(\text{en})\text{Pt}(\text{N4,N4'-bpz-}N1,N1')\text{Pd}(\text{en})_3](\text{NO}_3)_4(\text{PF}_6)_8$, was obtained from the self-assembly of $[(\text{en})\text{Pt}(\text{bpz-}N4,N4')_3](\text{NO}_3)_6$ and $(\text{en})\text{Pd}^{2+}$ (Fig. 29) [69]. In this structure, three Pt atoms formed an equilateral triangle, whereas the Pd triangle was irregular and larger. The 12+ charge of the hexanuclear cation showed a high affinity for anions. The NO_3^- anions were bound in the center of the Pt_3 triangle, and the PF_6^- anions were located on top of the NO_3^- anions.

^1H NMR studies demonstrated that this complex interacted with other anions, such as SO_4^{2-} and ClO_4^- , as well.

When $[(\text{en})\text{Pd}(\text{bpz-}N1,N1')](\text{ClO}_4)_2$ was reacted with *trans*- $(\text{NH}_3)_2\text{Pt}^{2+}$, an isomeric Pd_3Pt_3 complex, $\{[(\text{en})\text{Pd}]_{2.5}(\text{N,N1'-bpz-}N4,N4')_3\}(\text{NH}_3)_2\text{Pt}_3\}(\text{ClO}_4)_6(\text{NO}_3)_5 \cdot 5\text{H}_2\text{O}$, in which Pt^{2+} coordinates to *N4* and *N4'* and Pd^{2+} binds *N1* and *N1'* was obtained [70].

A vase-shaped triangular complex of the formula, *cis*- $\{[(\text{NH}_3)_2\text{Pt}(\text{N4,N4'-bpz-}N1,N1')\text{Pd}(\text{en})]_3\}(\text{SO}_4)_6 \cdot 24.5\text{H}_2\text{O}$, obtained upon reaction of *cis*- $\{[(\text{NH}_3)_2\text{Pt}(\text{H}_2\text{O})_2\text{SO}_4]\text{SO}_4$ with bpz and $[(\text{en})\text{Pd}(\text{H}_2\text{O})_2]\text{SO}_4$ provided a rare example of sulfate anion encapsulation *via* anion- π interactions [71]. The host consisted of three

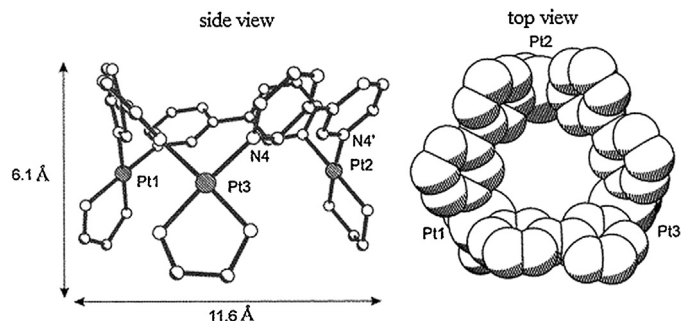


Fig. 28. X-ray crystal structure of $[(\text{en})\text{Pt}(\text{cis-bpz-}N4,N4')_3](\text{NO}_3)_2(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$.

Reprinted with permission from [68], Copyright 2000, American Chemical Society.

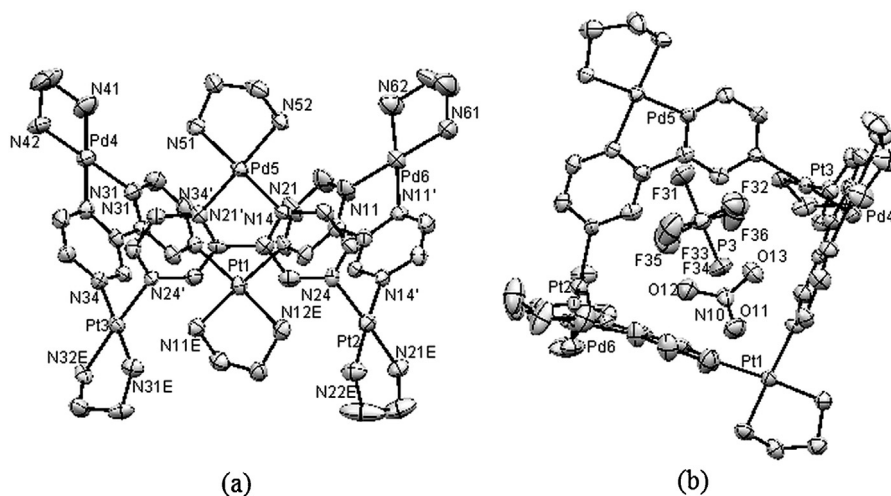


Fig. 29. X-ray crystal structure of $[(en)Pt(N4,N4'-bpz-N1,N1')Pd(en)]_3(NO_3)_4(PF_6)_8$: side view (a) and cavity view showing the simultaneous encapsulation of the PF_6^- and SO_4^{2-} anions (b).

$cis-[(NH_3)_2Pt^{2+}]$ units, three $[(en)Pd^{2+}]$ units and three bridging 2,2'-bipyrazine ligands (Fig. 30), and the structure is analogous to that obtained previously by the authors (Fig. 29) [69].

The X-ray crystal structure revealed that one of the six SO_4^{2-} ions and a water molecule were captured inside the metacalix[3]arene cavity. Three other sulfate anions were located below the plane defined by the six NH_3 ligands and in the same plane as the palladium nodes. The two remaining sulfate ions occupied positions outside the cavity and were hydrogen bonded to the NH_3 and en groups and to the water molecules.

The small difference in the Lewis acidities of $cis-[(NH_3)_2Pt^{2+}]$ and $[(en)Pt^{2+}]$ affected the bpz basicity and, consequently, the hydrogen-bonding properties of the amine ligands. Therefore, attempts to crystallize the SO_4^{2-} salt complex analogous to that in Fig. 31 were unsuccessful.

The compound, $[(en)Pt(2,2'-bpz-N4,N4')]_3(NO_3)_2(SO_4)_2 \cdot 13H_2O$, obtained from the incomplete anion exchange of $cis-[(en)Pt(2,2'-bpz-N4,N4')]_3(NO_3)_6$ [67] has been recently reported [72]. The NO_3^- anion was found to be located inside the cavity in an orientation nearly perpendicular to the Pt_3 plane (Fig. 31).

The cited examples demonstrate that the nitrate binding to the metacalix[3]arenes based on the 2,2'-bpz and Pt^{2+} entities is dependent on the presence of competitive anions. Anions with

low hydration enthalpies, such as ClO_4^- , BF_4^- and PF_6^- , prefer to remain inside the Pt_3 cavity either alone or with an NO_3^- anion.

A series of products obtained from the reaction of 2,2'-bipyrazine and $cis-(NH_3)_2Pt^{2+}$ in water has been recently reported [73]. Among them, two triangular cavity-shaped complexes, $cis-[(NH_3)_2Pt(2,2'-bpz-N4,N4')]_3(NO_3)_6$, were isolated with all three bpz ligands in either a *cis* or a *trans* orientation. Both compounds were able to host anions. In the complex with all three bpz ligands in the *cis* position, the NO_3^- anion was located almost parallel to the metal plane, whereas the PF_6^- anion was encapsulated in the upper rim of the cavity (Fig. 32).

In the second case, the BF_4^- anion and one water molecule were trapped in the cavity.

4. Metacalixarenes based on nucleobases

The pyrimidine nucleobases, such as uracil, thymine and cytosine, are low-symmetry ligands with two non-equivalent nitrogen atoms, *N1* and *N3*. Moreover, metal ions could coordinate to exocyclic oxygen atoms and/or deprotonated exocyclic amino groups. When these ligands react with *cis* square-planar metal entities of the type, $cis-a_2M^{2+}$ (where $M = Pt^{2+}$ or Pd^{2+} and $a = NH_3$, amine or $a_2 =$ diamine), four different connectivity patterns are possible

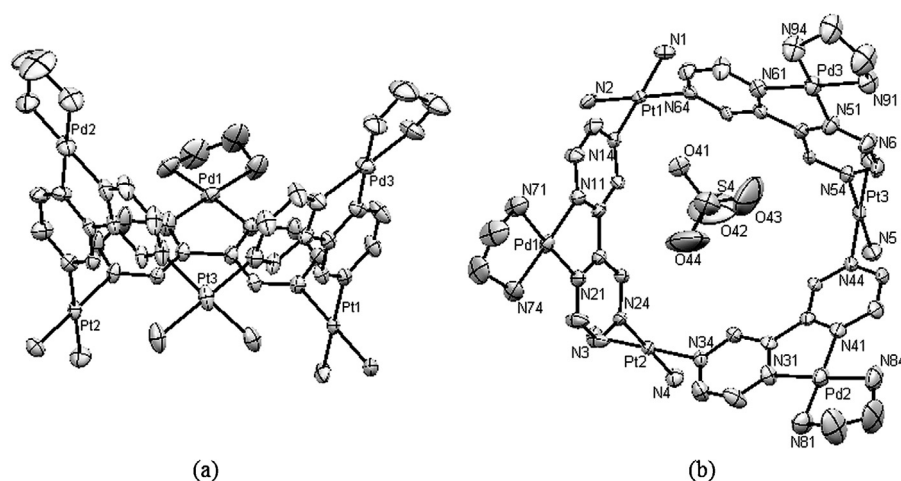


Fig. 30. X-ray crystal structure of $cis-[(NH_3)_2Pt(N4,N4'-bpz-N1,N1')Pd(en)]_3(SO_4)_6 \cdot 24.5H_2O$: side view (a) and cavity view showing the encapsulated SO_4^{2-} anion (b).

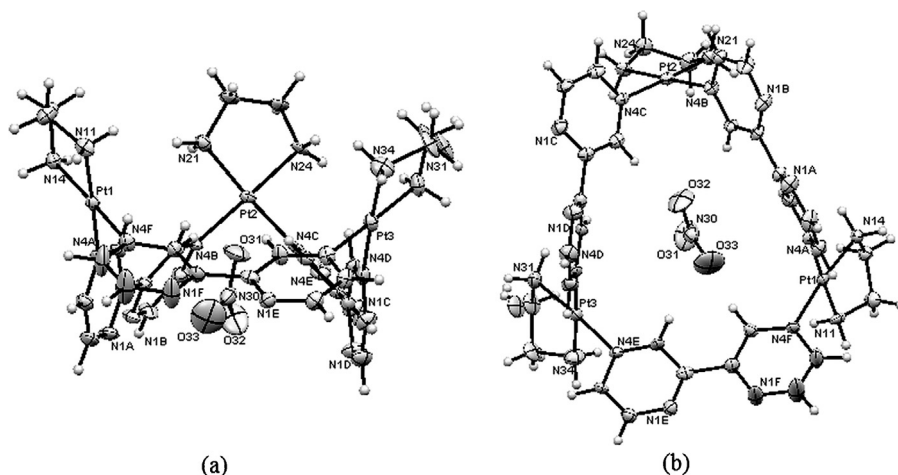


Fig. 31. X-ray crystal structure of $[(en)Pt(2,2'\text{-bpz-N4,N4}')_3](NO_3)_2(SO_4)_2 \cdot 13H_2O$ showing the encapsulated NO_3^- anion: side view (a) and cavity view (b).

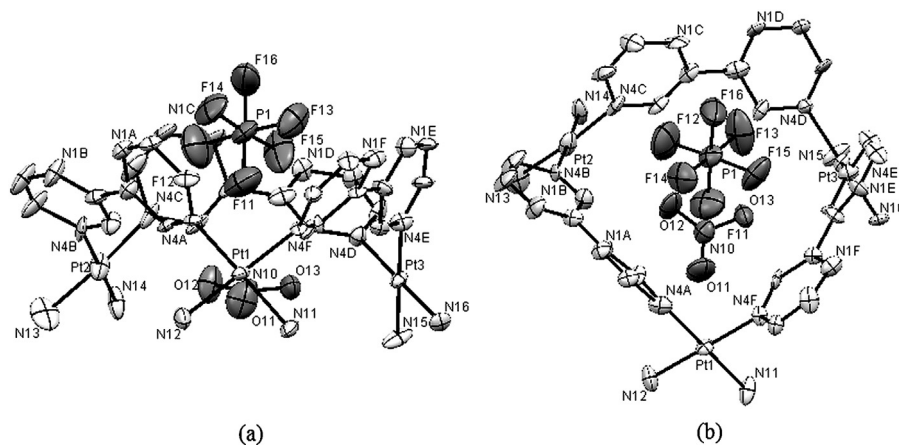


Fig. 32. X-ray crystal structure of $cis\text{-}[(NH_3)_2Pt(2,2'\text{-bpz-N4,N4}')_3](NO_3)_6$ showing the simultaneous encapsulation of two anions, NO_3^- in the lower rim and PF_6^- in the upper rim of the metallacalixarene: side view (a) and cavity view (b).

for the structure of the metallacalix[4]arenes. In addition, various rotameric states for all four nucleobases are possible.

The reaction between $[Pt(en)Cl_2]$ and uracil (UH_2) led to the compound, $cis\text{-}[(en)PtCl(UH-N1)]$, which upon hydrolysis, formed a cyclic tetramer, $[(en)Pt(UH-N1,N3)]_4^{4+}$, similar in structure to calix[4]arenes (Fig. 33) [74].

As with calixarenes, these compounds can adopt different conformations due to the rotation of the flexible uracil moieties. This compound adopted a *1,3-alternate* conformation in the solid state, but in solution and after deprotonation, a second *cone* conformer appeared from the rotation of a uracil group around a Pt–N bond.

The conformation depended not only on the pH of the solution but also on the presence of additional metal ions. For example, Mg^{2+} cations caused 100% of the complexes to be converted to the *cone* conformer, whereas Na^+ cations induced only partial (66%) conversion to the *cone* conformation [74,75].

Navarro et al. have reported that this ligand efficiently complexed various metal ions depending on the nature of the metal cation and the conformation of the metallacalixarene [75].

In the presence of an excess of $AgNO_3$, the *1,3-alternate* conformer formed a complex with the formula, $[(en)Pt(UH)Ag]_4(NO_3)_8 \cdot 4H_2O$, and the conformation changed to a *pinched cone* [76].

Reactions of the *1,3-alternate* conformer with divalent cations led to the formation of the compounds, $[(en)Pt(U-N1,N3,O2,O4)CuCl(H_2O)_2]_4Cl_4$ and $[(en)Pt(U-N1,N3,O2,O4)M^{2+}]_4$.

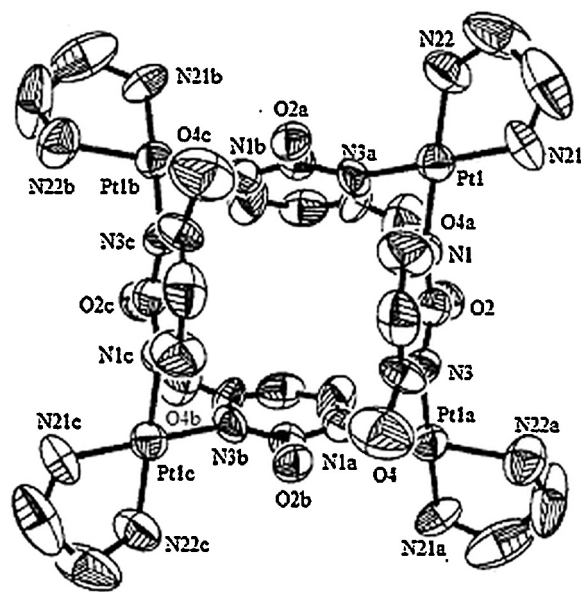


Fig. 33. X-ray crystal structure of the tetranuclear cation, $[(en)Pt(UH-N1,N3)]_4(NO_3)_4$.

Reprinted with permission from [74], Copyright 1994, American Chemical Society.

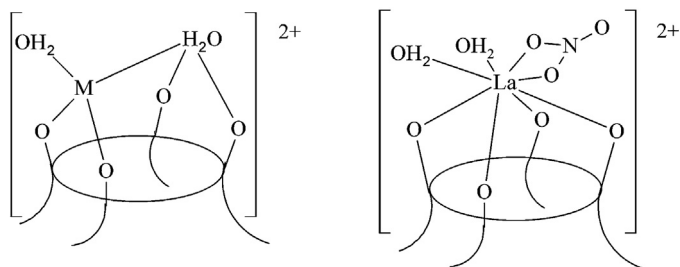


Fig. 34. Schematic representation of the *cone* conformers of the Zn and Be complexes (on the left) and the La complex (on the right).

(H₂O)₃]₄(SO₄)₄ (M = Ni²⁺, Cu²⁺, Co²⁺ or Zn²⁺), where the metals were bonded to the oxygen atoms of the uracil moieties [75].

The compound in its *cone* conformation could incorporate one or four additional metal cations, whereas the *1,3-alternate* conformer always sorbed four cations. Therefore, the *1,3-alternate* conformer was more efficient in the complexation of additional divalent cations.

Upon the addition of one equivalent of Zn²⁺, Be²⁺ or La³⁺ salts, the four uracil units of the *cone* conformer were deprotonated to form {[*(en)*PtU]₄ZnSO₄}, {[*(en)*PtU]₄Be}²⁺ or {[*(en)*PtU]₄La}(NO₃)₃, respectively [77]. In the Zn and Be complexes, the metal cations were bonded to two exocyclic oxygen atoms, and two other oxygen atoms were hydrogen bonded to a coordinated water molecule. In the case of the La³⁺ complex, the additional cation was bonded to four exocyclic oxygen atoms, a nitrate anion and two coordinated water molecules (Fig. 34).

Moreover, the protonated species of the *cone* conformer and the Zn and Be complexes acted as hosts for organic anions in water, whereas no such interactions were observed for the *1,3-alternate* conformer or the La complex.

The self-assembly of K₂PtCl₄ and 2,2'-dipyridylketone (dpk) in the presence of AgNO₃ and subsequent reaction with uracil or thymine led to the formation of the pentanuclear Pt²⁺ complexes, [(dpk)₂(dpkOH₂)₃Pt₅(U)₃](BF₄)(NO₃)₃·8H₂O, [(dpk)₂(dpkOH₂)₃Pt₅(U)₃](PF₆)(NO₃)₃·9H₂O and [(dpk)₂(dpkOH₂)₃Pt₅(T)₃](ClO₄)₂(NO₃)₂·8H₂O [78]. These structures were trinuclear metallacalix[3]arenes with the three nucleobases bridged by three Pt²⁺ centers chelated to (dpkOH₂). The other two Pt²⁺ centers were coordinated to the oxygen atoms of the nucleobases.

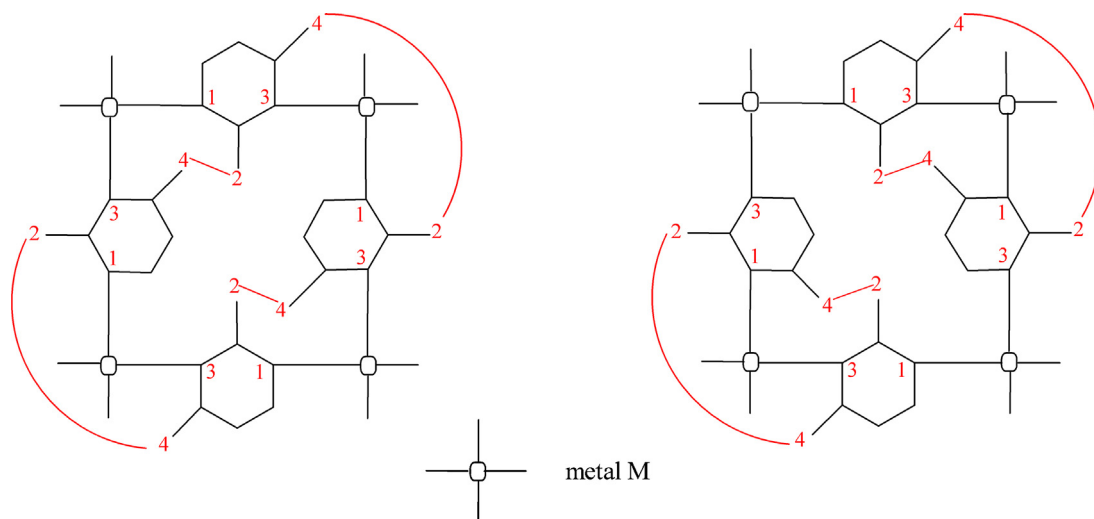


Fig. 35. Schematic representation of the different connectivity patterns leading to the formation of two isomers.

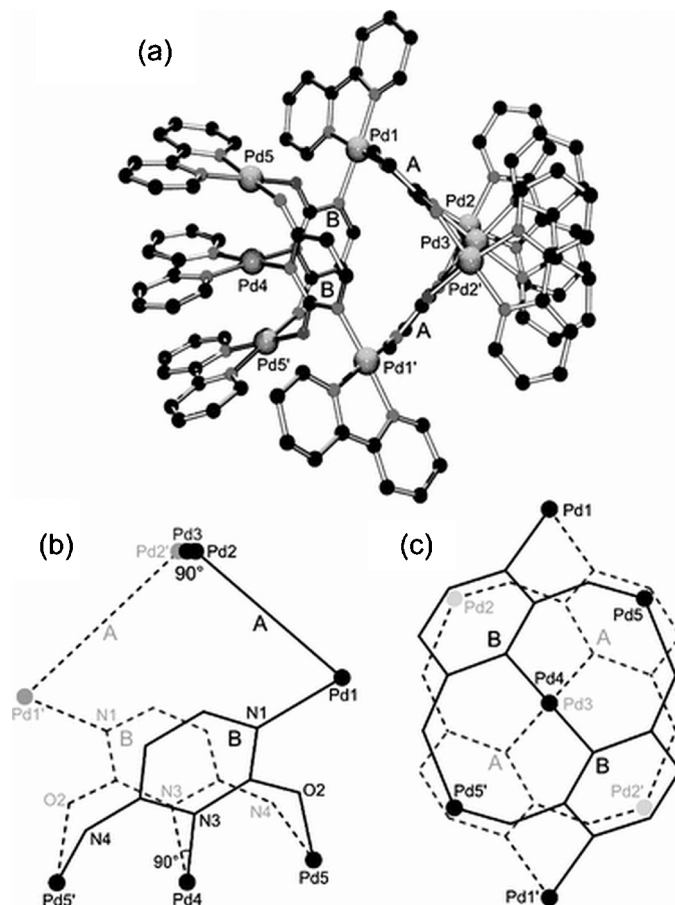


Fig. 36. Full view (a) and schematic views (b and c) of $[\{Pd(bpy)\}_8(C)_4](NO_3)_8 \cdot 25H_2O$.

Reprinted with permission from [79], Copyright 2010, American Chemical Society.

Two isomeric complexes, $[\{Pd(bpy)\}_8(C)_4](NO_3)_8 \cdot 25H_2O$ and $[\{Pd(bpy)\}_8(C)_4]_2(NO_3)_{16} \cdot Pd(bpy)(NO_3)_2 \cdot 60H_2O$, were synthesized by mixing $[Pd(bpy)(H_2O)_2]^{2+}$ and cytosine (H₂C) in water [79]. Both isomers were obtained because two different connectivity patterns were possible (Fig. 35).

These isomers are presented in Figs. 36 and 37.

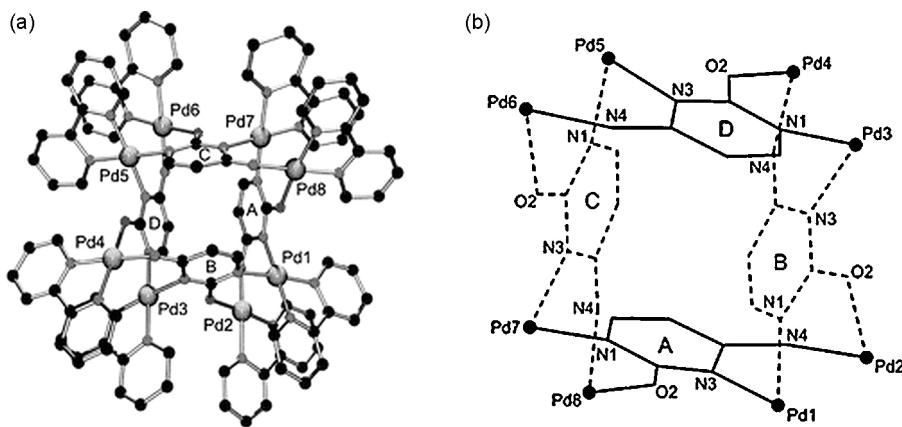


Fig. 37. Top view (a) and schematic view (b) of $[\text{Pd}(\text{bpy})_8(\text{C})_4]_2(\text{NO}_3)_{16} \cdot \text{Pd}(\text{bpy})(\text{NO}_3)_2 \cdot 60\text{H}_2\text{O}$.

Reprinted with permission from [79], Copyright 2010, American Chemical Society.

The situation becomes even more complicated if different metals, such as Pt^{2+} and Pd^{2+} , are employed simultaneously. Extensive work on the synthesis of multinuclear, mixed-metal (Pt^{2+} , Pd^{2+}) and mixed-nucleobase (uracil, cytosine) complexes with different amines (en, 2,2'-bpy) has been reported [80]. In these compounds, various stoichiometries and different connectivities are possible. By reacting $[\text{Pt}(\text{en})(\text{UH}-\text{N}1)(\text{CH}_2-\text{N}3)]^+$ with either $[\text{Pd}^{2+}(2,2'\text{-bpy})]$ or $[\text{Pd}^{2+}(\text{en})]$, a series of multinuclear derivatives of two different metallacalix[4]arenes and metallacalix[8]arenes were isolated. Moreover, penta-, hexa- and octanuclear complexes of Pt_2Pd_3 , Pt_2Pd_4 and Pt_2Pd_6 , respectively, derived from cyclic Pt_2Pd_2 tetramers have been isolated and characterized.

Few papers have appeared in the literature concerning the strategy of directed self-assembly, which prevents the formation of multiple metallacalixarene isomers. Using kinetically inert Pt^{2+} entities as building blocks, it is possible to direct the self-assembly process and obtain the required connectivity while additional Pd^{2+} entities are introduced.

When $\text{cis}-[\text{Pt}(\text{NH}_3)_2(\text{HC}-\text{N}1)_2]$ (HC = monoanion of cytosine = cytosinate) was treated with $(\text{bpy})\text{Pd}^{2+}$ in a 1:1 (or 2:1) molar ratio ($r = \text{Pt}/\text{Pd}$), a cyclic $\text{cis}-[\text{Pt}(\text{NH}_3)_2(\text{N}1-\text{HC}-\text{N}3)_2\text{Pd}(\text{bpy})_2](\text{NO}_3)_4 \cdot 13\text{H}_2\text{O}$ complex was formed with Pt bonded to the N1 sites and Pd bonded to the N3 sites (Fig. 38).

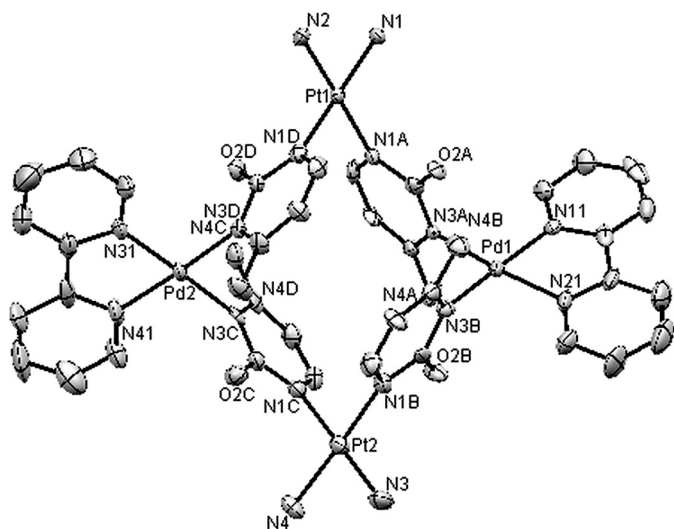


Fig. 38. X-ray crystal structure of the tetranuclear complex, $\text{cis}-[\text{Pt}(\text{NH}_3)_2(\text{N}1-\text{HC}-\text{N}3)_2\text{Pd}(\text{bpy})_2](\text{NO}_3)_4 \cdot 13\text{H}_2\text{O}$.

The complex consisted of four cytosinate ligands in a 1,3-alternate conformation [81].

The same reaction performed using a 1:2 molar ratio resulted in an octanuclear Pd_6Pt_2 complex in which the exocyclic N4H2 of the cytosines coordinated to four more $(\text{bpy})\text{Pd}^{2+}$ entities via the O2 and N4H sites after deprotonation. When the amount of Pd^{2+} was increased (the molar ratio was 1:3 or 1:4), Pt^{2+} was replaced

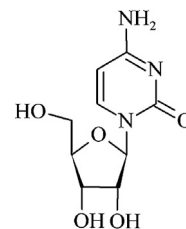


Fig. 39. Chemical structure of cytidine.

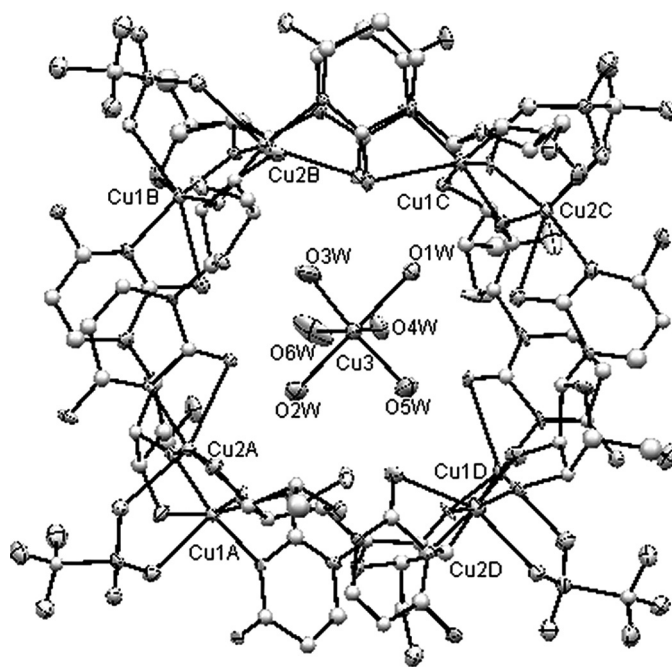
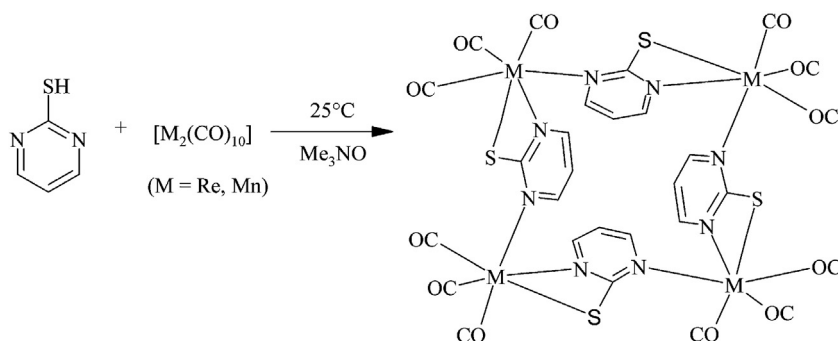
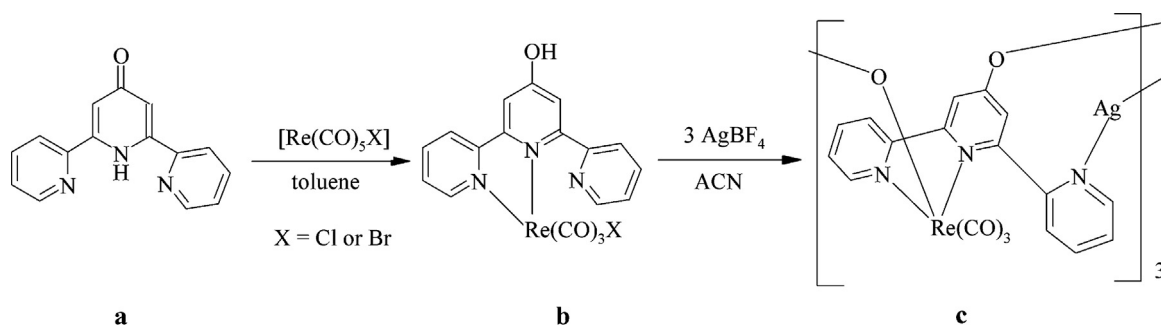


Fig. 40. X-ray crystal structure of $[\text{Cu}_8(\text{Hcyd})_8(\text{CF}_3\text{SO}_3)_4]^{4+}$ showing the mononuclear $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ guest.

Reprinted with permission from [83], Copyright 2007, American Chemical Society.



Scheme 3. Reaction between $M_2(CO)_{10}$ ($M = Re, Mn$) and pyrimidine-2-thiol in the presence of Me_3NO leading to a tetranuclear complex consisting of four $M(CO)_3$ units linked by tridentate pyrimidine-2-thiolate ligands.



Scheme 4. Synthesis of a rhenium tricarbonyl 4'-oxo-terpy cyclic trimer (c).

by the more labile Pd^{2+} , yielding the octanuclear $[Pt(en)(H_2C-N3)_2](NO_3)_2 \cdot 2H_2O$ complex [81].

When Pt^{2+} entities such as $[Pt(en)(H_2O)_2]^{2+}$ in water, two complexes, tetranuclear $[Pt(en)(N3-HC-N1)_2Pd(en)_2](NO_3)_4 \cdot 9.5H_2O$ and hexanuclear $[Pt(en)(N3-HC-N1)_2Pd(en)_3](NO_3)_6 \cdot 18H_2O$, were isolated [82]. In both structures, the Pt ions were bonded to the N3 sites, whereas the Pd ions were connected through the N1 sites. The four ligands in the tetranuclear complex adopted a 1,3-alternate conformation.

Another interesting calixarene-like structure was synthesized by mixing an aqueous solution of $Cu(CF_3SO_3)_2$ with cytidine (formed when cytosine is attached to a ribose ring, Fig. 39) in a 1:1 molar ratio, leading to an octanuclear complex consisting of $[Cu_8(Hcyd)_8(CF_3SO_3)_4]^{4+}$ rings.

Despite the high positive charge on the eight copper ion centers, the complex acted as a host for $[Cu(H_2O)_6]^{2+}$ cations (Fig. 40) [83]. Moreover, strong antiferromagnetic interactions were observed.

Metallacalixarenes based on other nucleobases, such as purine, adenine or guanine (Fig. 41) [84–92], have been recently revisited in [19].

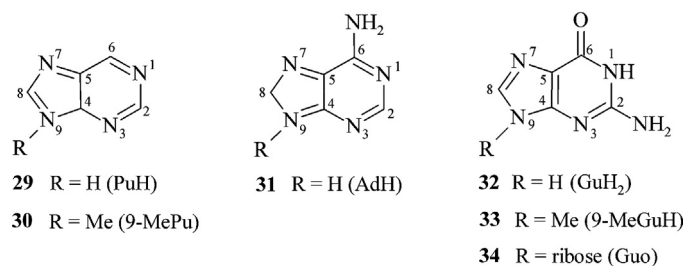


Fig. 41. Chemical structures of purine, adenine and guanine and their derivatives used for the synthesis of metallacalixarenes.

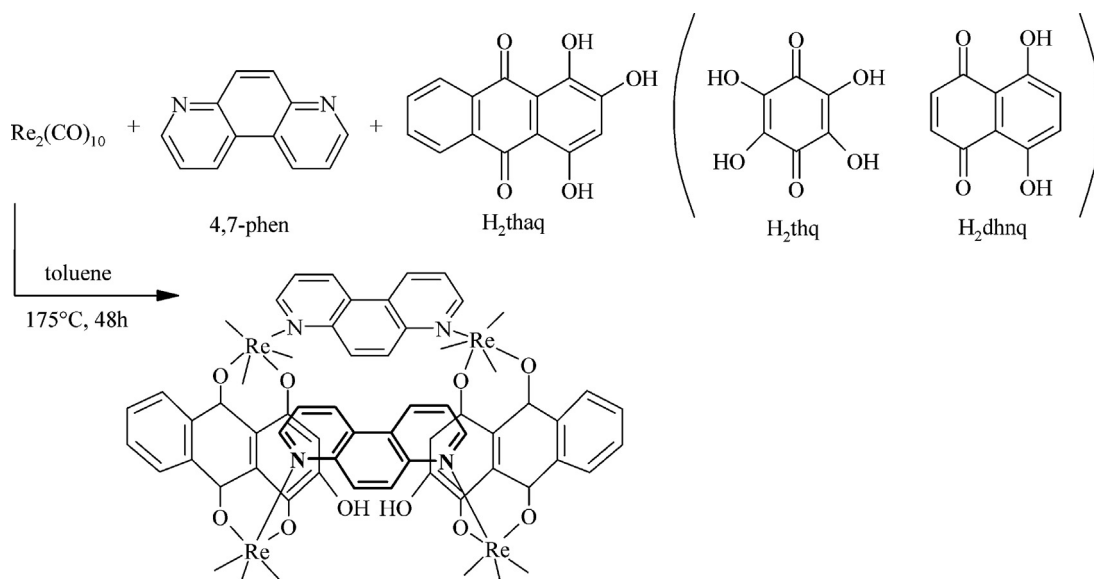
Fish and co-workers have published systematic studies on structures consisting of organometallic complexes and nucleobases [24]. Although, the use of the term “metallacalixarenes” for these structures might be arguable, it was applied later in [93–101]. A few examples of structures containing rhodium, ruthenium and iridium have been discussed in [19].

5. Novel class of metallacalixarenes based on Re carbonyl corners

The $fac-Re(CO)_3$ fragment has frequently been used as a building block for the construction of self-assembled metallamacrocycles. A novel class of metallacalixarenes in which Mn and/or Re carbonyl corners are analogous to the methylene linkers and aromatic ligands mimic the phenol walls of the classical calix[4]arenes has been recently reported [102]. The reaction between $M_2(CO)_{10}$ ($M = Re, Mn$) and pyrimidine-2-thiol in the presence of Me_3NO at $25^\circ C$ afforded tetranuclear complexes consisting of four $M(CO)_3$ units linked by tridentate pyrimidine-2-thiolate ligands (Scheme 3).

The extra nitrogen coordination sites provided by pyrimidine-2-thiol were expected to be capable of binding other atoms while reacting with mono- and bidentate ligands. These reactions led to the decomposition of the metallacalix[4]arene as a result of the weak metal-nitrogen bonds and the formation of sulfur-bound mononuclear species.

Another example of a novel class of metallacalixarenes based on rhenium carbonyl groups has been recently reported [103,104]. The reaction of bispyridylpyridone (a) with rhenium pentacarbonyl halides ($[Re(CO)_5X]$, $X = Cl$ or Br) in toluene gave $[Re(4'-oxo-\eta^2-terpy)-(CO)_3]X$ ($terpy = 2,2',6',2''-terpyridyl$, $X = Cl, Br$) (b) in which one terminal pyridine ring was not coordinated to the ruthenium center. Subsequent reaction with 3 equivalents of $AgBF_4$ in acetonitrile yielded a rhenium tricarbonyl 4'-oxo-terpy cyclic trimer (c) (Scheme 4) [103].



Scheme 5. Synthesis of metallacalixarenes with the formula, $[\{(\text{CO})_3\text{Re}\}_4(\text{L})_2(4,7\text{-phen})_2]\cdot 2\text{C}_7\text{H}_8$ (L = 1,2,4-trihydroxy-9,10-anthraquinone (thaq), tetrahydroxy-1,4-quinone (thq) or 5,8-dihydroxy-1,4-naphthaquinone (dhnq)).

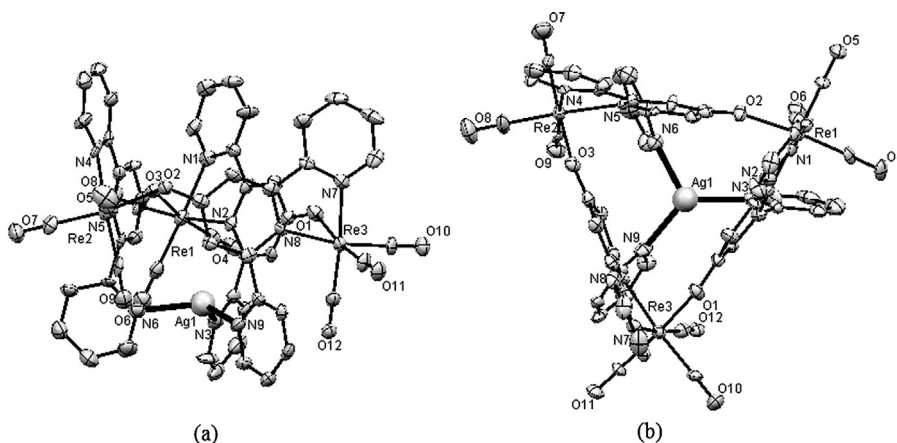


Fig. 42. X-ray crystal structure of the rhenium tricarbonyl 4'-oxo-terpy cyclic trimer: side view (a) and cavity view (b).

The X-ray crystal structure is shown in Fig. 42. The three monomers were bonded through the 4'-oxygen atom to form a pseudo-cylindrical complex in which one remaining pendant pyridine of each unit was bonded to a silver cation, closing one end of the cylinder (Fig. 42).

The complex was unstable in solution upon irradiation with a 405 nm laser, resulting in the loss of the silver cation. Furthermore, the process was reversible, which allowed for the blocking and subsequent unblocking of one end of the cylinder. These complexes not only might act as a host for ions but also the rhenium tricarbonyl pyridine cations are among the most widely studied luminescent metal complexes, and their application in sensors are of great interest [104].

Metallacalixarenes with the formula, $[\{(\text{CO})_3\text{Re}\}_4(\text{L})_2(4,7\text{-phen})_2]\cdot 2\text{C}_7\text{H}_8$ (L = 1,2,4-trihydroxy-9,10-anthraquinone (thaq), tetrahydroxy-1,4-quinone (thq) or 5,8-dihydroxy-1,4-naphthaquinone (dhnq)), were obtained from the reaction of $\text{Re}_2(\text{CO})_{10}$ and 4,7-phen with the appropriate bis-chelating connector, H_2thaq , H_2thq or H_2dhnq , respectively (Scheme 5) [105].

The hydrophobic cavity in these structures was large enough to accommodate and recognize aromatic guest molecules. Fig. 43 presents the X-ray crystal structure of $[\{(\text{CO})_3\text{Re}\}_4(\text{thaq})_2(4,7\text{-phen})_2]\cdot 2\text{C}_7\text{H}_8$

with one toluene guest molecule trapped within the cavity [105].

The interactions between the planar aromatic guest molecule and the ligands of $[\{(\text{CO})_3\text{Re}\}_4(\text{thq})_2(4,7\text{-phen})_2]\cdot 2\text{C}_7\text{H}_8$ were studied with UV-Vis spectrophotometry, and the high stability constants of the 1:1 complexes (8.0×10^4 , 1.7×10^4 , 6.7×10^4 and

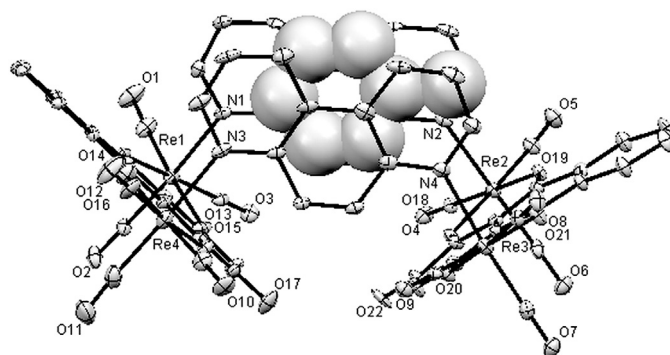


Fig. 43. X-ray crystal structure of $[\{(\text{CO})_3\text{Re}\}_4(\text{thaq})_2(4,7\text{-phen})_2]\cdot 2\text{C}_7\text{H}_8$ with one toluene guest molecule trapped within the cavity.

8.4×10^4 with naphthalene, anthracene, phenanthrene and pyrene, respectively) demonstrated that these compounds have potential for use as molecular receptors for aromatic molecules.

6. Conclusions

In this paper, an organic–inorganic class of materials called metallacalixarenes is reviewed, and their interesting properties are summarized. They can be either discrete cyclic oligomers based on heterocyclic linkers or part of a polymeric network when the metallacalixarenes are derived from 1,3-benzenedicarboxylates, which makes them particularly interesting in terms of their potential applications.

The biggest advantage of metallacalixarenes based on 1,3-benzenedicarboxylates over other coordination polymers is the presence of bowl-shaped cavities, which can accommodate different types of guest molecules. These metallacalixarenes also have unique hourglass-shaped channels, the size of which is dependent on the solvent used in the synthesis. The unique channels can block appropriately sized guest molecules, making them useful for the design of highly selective receptors. These materials possess N_2 and/or H_2 sorption properties and can also adsorb methanol/benzene vapors in some cases.

As with classical calixarenes, metallacalixarenes might serve as promising cation or anion receptors, and we summarized examples of this application in this paper. Highly positively charged metallacalixarenes based on heterocycles and nucleobases, which are able to bind up to two anions simultaneously, are promising candidates for hosting anions. Moreover, some of them exhibit affinities for mononucleotides, demonstrating their potential for use as selective DNA-binding drugs.

We hope that this review will be helpful in the rational design of new metallacalixarenes with interesting and desirable properties.

Acknowledgements

The authors thank Conselho Nacional de Pesquisa (CNPq) and Rede Nanobiotec Brasil/Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support.

References

- [1] C.D. Gutsche, in: J.F. Stoddart (Ed.), *The Royal Society of Chemistry*, Cambridge, UK, 1998.
- [2] Z. Asfari, V. Bohmer, J. Harrowfield, J. Vicens, *Calixarenes*, Kluwer Academic Publishers, Dordrecht, 2001.
- [3] X. Fang, B.L. Scott, J.G. Watkin, Ch A.G. Carter, G.J. Kubas, *Inorg. Chim. Acta* 317 (2001) 276.
- [4] E. Brenner, D. Matt, M. Henrion, M. Teci, L. Toupet, *Dalton Trans.* 40 (2011) 9889.
- [5] M. Frank, G. Maas, J. Schatz, *Eur. J. Org. Chem.* (2004) 607.
- [6] I. Dinarès, C.G. Miguel, M. Font-Bardia, X. Solans, E. Alcalde, *Organometallics* 26 (2007) 5127.
- [7] T. Fahlbusch, M. Frank, G. Maas, J. Schatz, *Organometallics* 28 (2009) 6183.
- [8] R. Ludwig, *Fresenius J. Anal. Chem.* 367 (2000) 103.
- [9] H. Rauter, E.C. Hillgeris, B. Lippert, *J. Chem. Soc. – Chem. Commun.* 19 (1992) 1385.
- [10] C. Gagnon, J. Hubert, R. Rivest, A.L. Beauchamp, *Inorg. Chem.* 16 (1977) 2469.
- [11] A. Terzis, A.L. Beauchamp, R. Rivest, *Inorg. Chem.* 12 (1973) 1166.
- [12] E. Sletten, *Acta Crystallogr.* B25 (1969) 1480.
- [13] P.D. Meester, A.C. Skapski, *J. Chem. Soc. A* (1971) 2167.
- [14] C.H. Wei, K.B. Jacobson, *Inorg. Chem.* 20 (1981) 356.
- [15] E. Zangrando, M. Casanova, E. Alessio, *Chem. Rev.* 108 (2008) 4979.
- [16] S.A. Bourne, J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko, *Angew. Chem. Int. Ed.* 40 (2001) 2111.
- [17] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O’Keeffe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319.
- [18] H. Abourahma, G.J. Bodwell, J. Lu, B. Moulton, I.R. Pottier, R. Bailey Walsh, M.J. Zaworotko, *Cryst. Growth Des.* 3 (2003) 513.
- [19] S. Kumar, N. Kaur, H. Singh, *Adv. Heterocycl. Chem.* 96 (2008) 123.
- [20] J.A.R. Navarro, B. Lippert, *Coord. Chem. Rev.* 222 (2001) 219.
- [21] J.A.R. Navarro, B. Lippert, *Coord. Chem. Rev.* 185–186 (1999) 653.
- [22] J.A.R. Navarro, E. Barea, M.A. Galindo, J.M. Salas, M.A. Romero, M. Quirós, N. Masciocchi, S. Galli, A. Sironi, B. Lippert, *J. Solid State Chem.* 178 (2005) 2436.
- [23] Y. Sunatsuki, Y. Motoda, N. Matsumoto, *Coord. Chem. Rev.* 226 (2002) 199.
- [24] R.H. Fish, G. Jaouen, *Organometallics* 22 (2003) 2166.
- [25] B. Lippert, P.J.S. Miguel, *Chem. Soc. Rev.* 40 (2011) 4475.
- [26] D.-S. Zhou, F.-K. Wang, S.-Y. Yang, Z.-X. Xie, R.-B. Huang, *Cryst. Eng. Commun.* 11 (2009) 2548.
- [27] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629.
- [28] S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* 34 (2005) 109.
- [29] K. Uemura, R. Matsuda, S. Kitagawa, *J. Solid State Chem.* 178 (2005) 2420.
- [30] Z. Wang, V. Ch Kravtsov, R.B. Walsh, M.J. Zaworotko, *Cryst. Growth Des.* 7 (2007) 1154.
- [31] D.-X. Xue, Y.-Y. Lin, X.-N. Cheng, X.-M. Chen, *Cryst. Growth Des.* 7 (2007) 1332.
- [32] L. Gao, B. Zhao, G. Li, Z. Shi, S. Feng, *Inorg. Chem. Commun.* 6 (2003) 1249.
- [33] H.K. Lee, D. Min, B.-Y. Cho, S.W. Lee, *Bull. Korean Chem. Soc.* 25 (2004) 1955.
- [34] R.-Q. Zhong, R.-Q. Zouab, Q. Xu, *Cryst. Eng. Commun.* 13 (2011) 577.
- [35] E.A. Nytko, J.S. Helton, P.D. Muller, G. Nocera, *J. Am. Chem. Soc.* 130 (2008) 2922.
- [36] C.D. Ene, A.M. Madalan, C. Maxim, B. Jurca, N. Avarvari, M. Andruh, *J. Am. Chem. Soc.* 131 (2009) 4586.
- [37] H. Abourahma, G.J. McManus, B. Moulton, R.D.B. Walsh, M.J. Zaworotko, *Macromol. Symp.* 196 (2003) 213.
- [38] H. Chun, *J. Chem. Crystallogr.* 41 (2011) 537.
- [39] J.A.R. Navarro, J.M. Salas, *Chem. Commun.* (2000) 235.
- [40] N. Masciocchi, E. Corradi, M. Moret, G.A. Ardizzoia, A. Maspero, G. LaMonica, A. Sironi, *Inorg. Chem.* 36 (1997) 5648.
- [41] C.V.K. Sharma, S.T. Griffin, R.D. Rogers, *Chem. Commun.* (1998) 215.
- [42] L.C. Tabares, J.A.R. Navarro, J.M. Salas, *J. Am. Chem. Soc.* 123 (2001) 383.
- [43] E. Barea, J.A.R. Navarro, J.M. Salas, N. Masciocchi, S. Galli, A. Sironi, *J. Am. Chem. Soc.* 125 (2004) 3014.
- [44] E. Barea, J.A.R. Navarro, J.M. Salas, N. Masciocchi, S. Galli, A. Sironi, *Polyhedron* 22 (2003) 3051.
- [45] Z. Qin, M.C. Jennings, R.J. Puddephatt, *Inorg. Chem.* 41 (2002) 3967.
- [46] J.A.R. Navarro, E. Freisinger, B. Lippert, *Inorg. Chem.* 39 (2000) 2301.
- [47] M.A. Galindo, D. Olea, M.A. Romero, J. Gómez, P. Castillo, M.J. Hannon, A. Rodger, F. Zamora, J.A.R. Navarro, *Chem. Eur. J.* 13 (2007) 5075.
- [48] E. Barea, J.A.R. Navarro, J.M. Salas, M. Quirós, M. Willermann, B. Lippert, *Chem. Eur. J.* 9 (2003) 4414.
- [49] M. Maekawa, H. Konaka, T. Minematsu, T. Kuroda-Sowa, M. Munakata, S. Kitagawa, *Chem. Commun.* (2007) 5179.
- [50] M. Maekawa, T. Tominaga, K. Sugimoto, T. Okubo, T. Kuroda-Sowa, M. Munakata, S. Kitagawa, *Cryst. Eng. Commun.* 14 (2012) 1345.
- [51] P. Chaudhuri, I. Karpenstein, M. Winter, C. Butzlaff, E. Bill, A.X. Trautwein, U. Flörke, H.-J. Haupt, *J. Chem. Soc. – Chem. Commun.* (1992) 321.
- [52] P. Chaudhuri, I. Karpenstein, M. Winter, M. Lengen, C. Butzlaff, E. Bill, A.X. Trautwein, U. Flörke, H.J. Haupt, *Inorg. Chem.* 32 (1993) 888.
- [53] S.-W. Lai, M.C.-W. Chan, S.-M. Peng, C.-M. Che, *Angew. Chem. Int. Ed.* 38 (1999) 669.
- [54] N. Matsumoto, M. Ohba, M. Mitsumi, K. Inoue, Y. Hashimoto, H. Ôkawa, *Mol. Cryst. Liq. Cryst.* 233 (1993) 299.
- [55] N. Matsumoto, Y. Mizuguchi, G. Mago, S. Eguchi, H. Miyasaka, T. Nakashima, J.-P. Tuchagues, *Angew. Chem. Int. Ed.* 36 (1997) 1860.
- [56] N. Matsumoto, Y. Motoda, T. Matsuo, T. Nakashima, N. Re, F. Dahan, J.P. Tuchagues, *Inorg. Chem.* 38 (1999) 1165.
- [57] M. Mimura, T. Matsuo, T. Nakashima, N. Matsumoto, *Inorg. Chem.* 37 (1998) 3553.
- [58] Y. Shii, Y. Motoda, T. Matsuo, F. Kai, T. Nakashima, J.-P. Tuchagues, N. Matsumoto, *Inorg. Chem.* 38 (1999) 3513.
- [59] M.-L. Lehaire, R. Scopelliti, L. Herdeis, K. Polborn, P. Mayer, K. Severin, *Inorg. Chem.* 43 (2004) 1609.
- [60] G. Kolks, C.R. Frihart, P.K. Coughlin, S.J. Lippard, *Inorg. Chem.* 20 (1981) 2933.
- [61] E. Rufino-Felipe, M.-A. Munoz-Hernández, *Chem. Commun.* 47 (2011) 3210.
- [62] A. Steffen, T. Braun, B. Neumann, H.-G. Stammer, *Angew. Chem. Int. Ed.* 46 (2007) 8674.
- [63] S.-Y. Yu, H. Huang, H.-B. Liu, Z.-N. Chen, R. Zhang, M. Fujita, *Angew. Chem. Int. Ed.* 42 (2003) 686.
- [64] M.A. Galindo, J.A.R. Navarro, M.A. Romero, M. Quirós, *Dalton Trans.* (2004) 1563.
- [65] M.A. Galindo, S. Galli, J.A.R. Navarro, M.A. Romero, *Dalton Trans.* (2004) 2780.
- [66] M.A. Galindo, A. Houlton, W. Clegg, R.W. Harrington, J. Dobado, F. Santoyo-Gonzalez, F. Linares, M.A. Romero, J.A.R. Navarro, *Chem. Commun.* (2008) 3735.
- [67] R.-D. Schnebeck, L. Randaccio, E. Zangrando, B. Lippert, *Angew. Chem. Int. Ed.* 37 (1998) 119.
- [68] R.-D. Schnebeck, E. Freisinger, F. Glahé, B. Lippert, *J. Am. Chem. Soc.* 122 (2000) 1381.
- [69] R.-D. Schnebeck, E. Freisinger, B. Lippert, *Angew. Chem. Int. Ed.* 38 (1999) 168.
- [70] R.-D. Schnebeck, E. Freisinger, B. Lippert, *Chem. Commun.* (1999) 675.
- [71] A. Galstyan, P.J. Sanz Miguel, B. Lippert, *Chem. Eur. J.* 16 (2010) 5577.
- [72] A. Galstyan, P.J. Sanz Miguel, B. Lippert, *Dalton Trans.* 39 (2010) 6386.
- [73] A. Galstyan, W.-Z. Shen, E. Freisinger, H. Alkam, W. Hiller, P.J. Sanz Miguel, M. Schurmann, B. Lippert, *Chem. Eur. J.* 17 (2011) 10771.
- [74] H. Rauter, E.C. Hillgeris, A. Erxleben, B. Lippert, *J. Am. Chem. Soc.* 116 (1994) 616.
- [75] J.A.R. Navarro, E. Freisinger, B. Lippert, *Eur. J. Inorg. Chem.* 147 (2000) 147.

- [76] I. Mutikainen, C.J.L. Lock, L. Randaccio, E. Zangrando, E. Chiarparin, B. Lippert, H. Rauter, P. Amo-Ochoa, E. Freisinger, M. Blomberg, *Angew. Chem. Int. Ed.* 36 (1997) 1296.
- [77] J.A.R. Navarro, M.B.L. Janik, E. Freisinger, B. Lippert, *Inorg. Chem.* 38 (1999) 426.
- [78] M.J. Rauterkus, B. Krebs, *Angew. Chem. Int. Ed.* 43 (2004) 1300.
- [79] A. Khutia, P.J.S. Miguel, B. Lippert, *Inorg. Chem.* 49 (2010) 7635.
- [80] E.G. Bardaji, E. Freisinger, B. Costisella, C.A. Schalley, W. Bruning, M. Sabat, B. Lippert, *Chem. Eur. J.* 13 (2007) 6019.
- [81] A. Khutia, P.J. Sanz Miguel, B. Lippert, *Chem. Eur. J.* 17 (2011) 4205.
- [82] A. Khutia, P.J.S. Miguel, B. Lippert, *Chem. Eur. J.* 17 (2011) 4195.
- [83] D. Armentano, T.F. Mastropietro, M. Julve, R. Rossi, P. Rossi, G. Munno, *J. Am. Chem. Soc.* 129 (2007) 2740.
- [84] M. Roitzsch, B. Lippert, *Angew. Chem. Int. Ed.* 45 (2006) 147.
- [85] C.S. Purohit, S. Verma, *J. Am. Chem. Soc.* 128 (2006) 400.
- [86] B. Longato, G. Bandoli, G. Trovo, E. Marasciulo, G. Valle, *Inorg. Chem.* (1995) 1745.
- [87] M.S. Luth, E. Freisinger, F. Glahé, B. Lippert, *Inorg. Chem.* 37 (1998) 5044.
- [88] I.B. Rother, M. Willermann, B. Lippert, *Supramol. Chem.* 14 (2002) 189.
- [89] E. Sletten, *Acta Crystallogr. B* 26 (1970) 1609.
- [90] N.H. Agnew, T.G. Appleton, J.R. Hall, G.F. Kilmister, I.J. McMahon, *J. Chem. Soc. – Chem. Commun.* (1979) 324.
- [91] B.J. Lorberth, W. Massa, M.E. Essawi, L. Labib, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 1160.
- [92] K. Yamanari, I. Fukuda, T. Kawamoto, Y. Kushi, A. Fuyuhiko, N. Kubota, T. Fukuo, R. Arakawa, *Inorg. Chem.* 37 (1998) 5611.
- [93] D.P. Smith, E. Baralt, B. Morales, M.M. Olmstead, M.F. Maestre, R.H. Fish, *J. Am. Chem. Soc.* 114 (1992) 10647.
- [94] H. Chen, S. Ogo, R.H. Fish, *J. Am. Chem. Soc.* 118 (1996) 4993.
- [95] D.P. Smith, E. Kohen, M.F. Maestre, R.H. Fish, *Inorg. Chem.* 32 (1993) 4119.
- [96] K. Yamanari, S. Yamamoto, R. Ito, Y. Kushi, A. Fuyuhiko, N. Kubota, T. Fukuo, R. Arakawa, *Angew. Chem. Int. Ed.* 40 (2001) 2268.
- [97] H. Chen, M.M. Olmstead, D.P. Smith, M.F. Maestre, R.H. Fish, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1514.
- [98] W.S. Sheldrick, H.S. Hagen-Eckhard, S. Heeb, *Inorg. Chim. Acta* 206 (1993) 15.
- [99] S. Korn, W.S. Sheldrick, *Inorg. Chim. Acta* 254 (1997) 85.
- [100] S. Korn, W.S. Sheldrick, *J. Chem. Soc. – Dalton Trans.* (1997) 2191.
- [101] P. Annen, S. Schildberg, W.S. Sheldrick, *Inorg. Chim. Acta* 307 (2000) 115.
- [102] S.E. Kabir, J. Alam, S. Ghosh, K. Kundu, G. Hogarth, D.A. Tocher, G.M.G. Hos-sainc, H.W. Roesky, *Dalton Trans.* (2009) 4458.
- [103] M.P. Coogan, V. Fernandez-Moreira, B.M. Kariuki, S.J.A. Pope, F.L. Thorp-Greenwood, *Angew. Chem. Int. Ed.* 48 (2009) 4965.
- [104] P. Thanasekaran, Ch-Ch. Lee, K.-L. Lu, *Acc. Chem. Res.* 45 (2012) 1403.
- [105] Ch.-Ch. Tsai, P. Thanasekaran, T.-T. Luo, Ch.-I. Yang, G.-H. Lee, S.-M. Peng, K.-L. Lu, *Chem. Eur. J.* 17 (2011) 3343.