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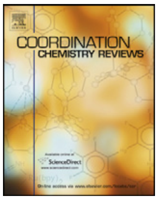

Review

Coordination motifs in modern supramolecular chemistry

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This review is dedicated to 75th birthday of Dr. Sci. Vladimir I. Minkin, Academician of the Russian Academy of Sciences, Professor of the Southern Federal University (Rostov-na-Donu, Russia).

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Self-assembling
Templating

ABSTRACT

In this paper we describe the contribution of coordination chemistry to the creation and development of supramolecular chemistry. Both discrete- and infinite buildups are examined. The first group comprises metal-containing host molecules and organic acceptors for metal cations; the second includes coordination polymers, ionic -and liquid crystals. Their potential- and practical applications are briefly explained.

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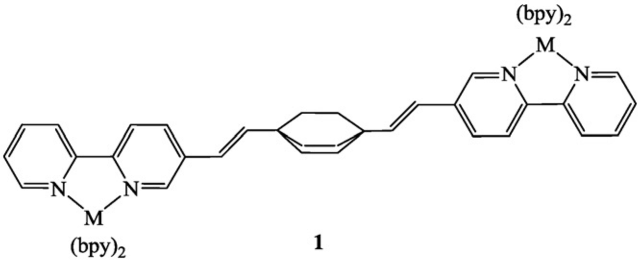

1

Fig. 1.

$[Ru\{(2,3\text{-}dpp)[Ru(2,3\text{-}dpp)Ru\{(2,3\text{-}dpp)Ru(bpy)_2\}_2]_2\}_3]^{44+}$

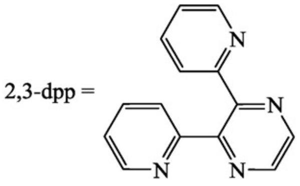

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Fig. 2.

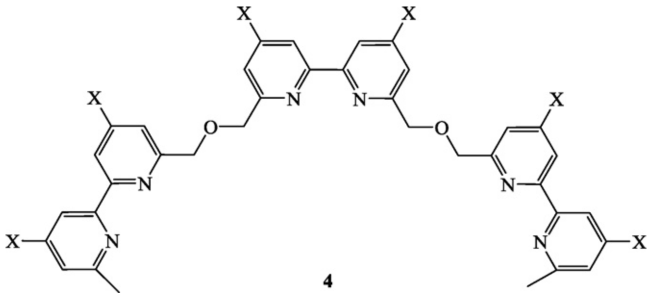
1. Introduction

Supramolecular chemistry owes its nascence, more than 40 years ago, to the coordination motifs of Pedersen and Frensdorff's crown-ethers (coronands) [1] and Lehn's cryptands [2]. This amazing variety of organic molecular structures is based on tetravalent carbon with the diversifying power of structural multiplicity in supramolecular chemistry being considerably enlarged by the inclusion of its sixty metal ions with their valences, coordination numbers, and geometries.

The property of metallosupramolecular structures to self-assemble is frequently coupled with the template effect [3,4,10,11] and is the most common method of preparing these structures [3–9], liberating the chemist from tedious multi-step synthetic procedures. Moreover, thermodynamic aspects [5] too are involved here, since self-assembly occurs by the formation of unstable structures in thermodynamic equilibrium with one another. Since erroneous structures are eliminated, the self-assembled products so formed are thermodynamically maximally stable, generally with high (frequently quantitative) yields.

A wide spectrum of coordination bond energies (10–30 kcal/mol) provides the process route required. Practical applications of the products obtained call for circumventing their thermodynamic character, which is achieved by altering their structures using certain methods [12].

Studies available in the literature referred above focus on only some coordination motifs in the supramolecular chemistry and do not present an overall view of the problem. The present review, we hope, resolves this issue concisely, avoids superfluous details, and achieves the balance required of a review article. The morphological principle, based on dimensionalities of the structures, permits a logical discussion of this important area of the supramolecular chemistry, and was thus chosen as the framework for presentation.



4

Fig. 4.

2. Monodimensional (1D) structures

1D structures are extended polynuclear buildups possessing a large principal axis. Even though they exhibit the least multiplicity, it is possible to derive all the other varieties of coordination supramolecular structures from them.

2.1. Linear polynuclear metal complexes

A comprehensive list of linear polynuclear molecules of the type **1** (Fig. 1) is given in Balzani et al. review [13], where M represents various metals or metals of distinct oxidation numbers.

Superficially, this appears to be simply a large molecule (supermolecule), which does not appear to correspond to the definition of the supramolecule as comprising a complex system of molecular components with distinct individual properties [4,13]. The type **1** structure (Fig. 1) is represented here as A∼B, where "∼" signifies any type of bonding between the components A and B with weak interaction between them, when they behave almost as individual buildups; so a structure of the type **1** (Fig. 1) is a supramolecule. Since this interaction is performed through a spacer "∼", its precise nature determines whether this structure is a supermolecule or supramolecule. Linear supramolecules can be very lengthy, for example, a record-holder — the compound **2** (Fig. 2), which includes 44 ruthenium atoms [13].

Certain less common types are hard linear structures and molecular rods [5,6,14] of the type **3** (Fig. 3), where the coordination sites are connected by a hard spacer.

2.2. Helicates

An unusual capacity of definite linear metal complexes with regular structure is to form spiral supramolecules – known as helicates [15,16] – that result from the tetrahedral coordination of Cu^I, Ag^I cations. This becomes clear from the example of typical ligands **4** (Fig. 4), whose hard bipyridine fragments are connected by flexible spacers, and inter-chain coordination tetrahedrons form as self-assembled double helicates **5** (Fig. 5).

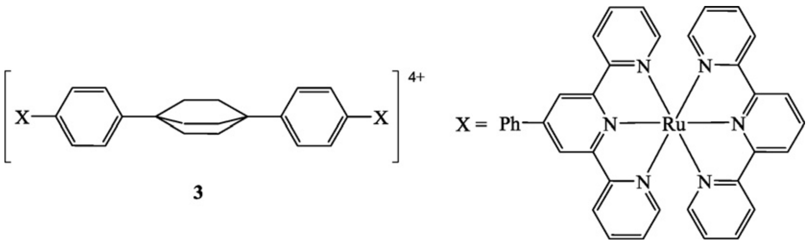


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Fig. 3.

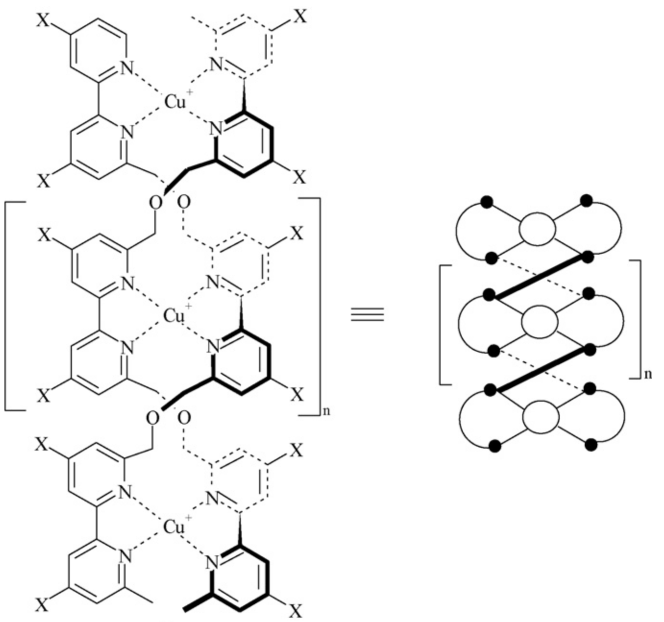

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Fig. 5.

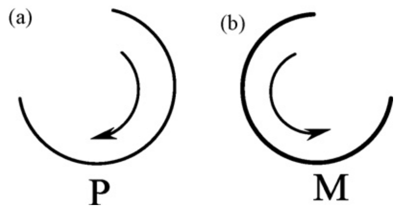

Fig. 6.

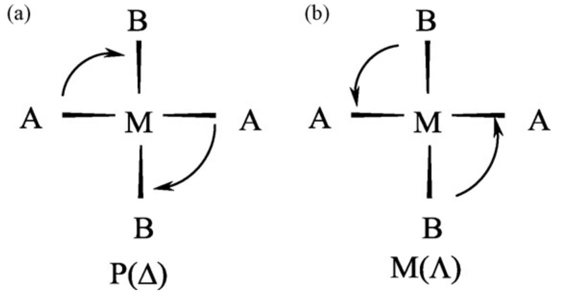

Fig. 7.

The self-assembly of helicates from achiral ligands is a chiral-statistical process resulting in racemic mixtures of right-handed (right-handed) P **6a** (Fig. 6a) and left-handed M **6b** (Fig. 6b) helices, whose chiralities are programmed in P **7a** (Fig. 7a) and M **7b** (Fig. 7b)

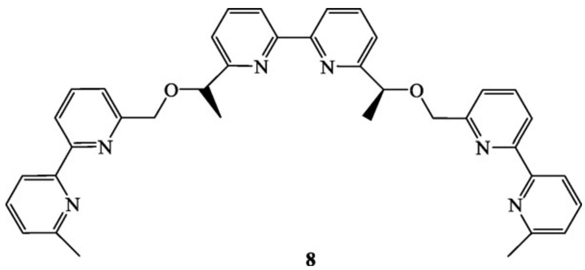

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Fig. 8.

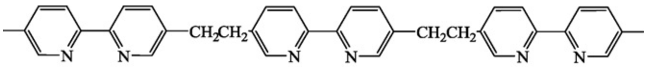

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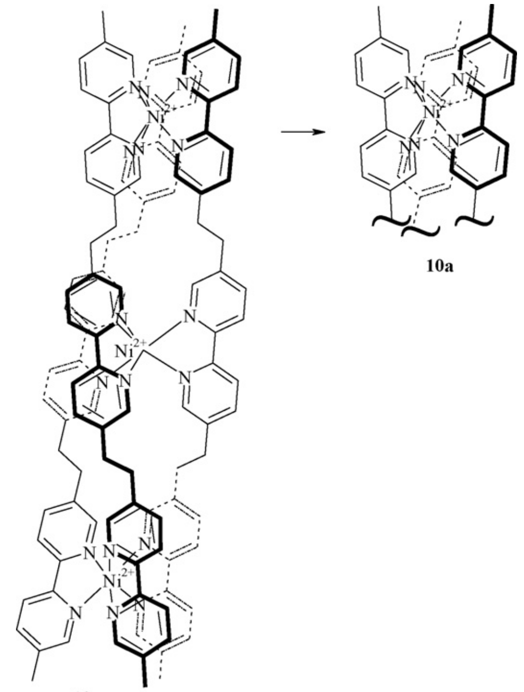
Fig. 9.



10a

10

Fig. 10.

by a spiral chirality of corresponding tetrahedral metal cations. Naturally, in helicates a right-handed helice **6a** (Fig. 6a) all metal cations possess a P(Δ) configuration and in a left-handed helice **6b** (Fig. 6b) M(Λ) configuration [15]. Use of ligands of the type **8** (Fig. 8) with chiral fragments leads to a chiral helicate in a P- or M configuration depending on the chirality of these fragments. Sometimes the racemic mixture spontaneously resolves on crystallization [17].

Oligopyridine ligands are very common; they can contain up to nine pyridine fragments. In the case of metal centers, the exclusive positions of tetrahedrally coordinated Ag^I and Cu^I are diminished by the appearance of octahedrally coordinated Zn^{II}, Fe^{II}, Ni^{II}, Co^{II}, and Cd^{II}.

In ligands of the type **4** (Fig. 4), forming double helicates, the bipyridine fragments are connected by the positions 6,6′. When

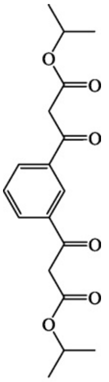


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Fig. 11.

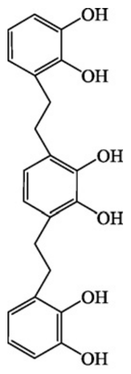

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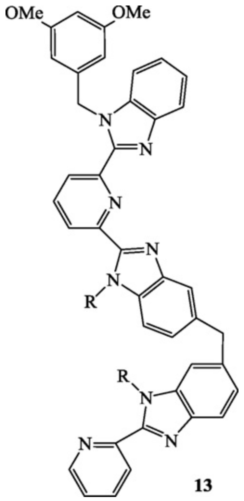
Fig. 12.



13

Fig. 13.

this situation alters to 5,5′-disubstitution, as in the ligand **9** (Fig. 9), a triple helicate **10** (Fig. 10) forms with Ni^{II} [3]. The octahedral coordination of Ni^{II} ion is shown in the fragment **10a** (Fig. 10a).

Although the nitrogen-containing ligands maintain leadership, oxygen-containing ligands [16] are sufficiently widespread, made up mainly of bis(1,3-dicarbonyl) derivatives (for instance **11**, Fig. 11) and linear oligocatechins (for example **12**, Fig. 12), forming double- and triple helicates with oxyphilic metal (Ti^{IV}, V^{I}, V^{III}, Mn^{III}, Ga^{III}, Al^{III}) cations.

Lanthanide ions rarely initiate helicate formation, with the exception of N-containing ligands of the type **13** (Fig. 13), as demonstrated by Bunzli and Piguet and form double- and triple helicates with cations of not only d-, but also f-metals [18].

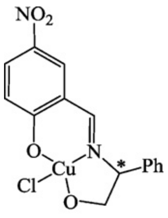


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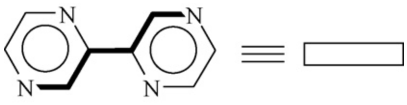
Fig. 15.



16

Fig. 16.

Bis-bidentate azomethinic ligands **14a** (Fig. 14a) with long oligomethylene bridges $\boxed{\quad X \quad}$ form double helicates **14b** (Fig. 14b) by complex-formation with Cu(II) or Ni(II) cations [19].

Finally, we present a further example of another principle of helice-formation by coordination [20], when a copper complex **15** (Fig. 15) of a chiral Schiff base, (s)-2-phenylglycinol, forms a P-monohelix by crystallization at the expense of intermolecular hydrogen bonds O–H···Cl–Cu. This structure illustrates the role of a metal-directed hydrogen bond formed by self-assembled supramolecular structures that has recently provoked lively interest [21].

3. Bidimensional (2D) structures

Generally, the majority of bidimensional supramolecular compounds whose length and width exceed their thickness are macrocycles; in this section we discuss several types of their combinations that lead to certain structures.

3.1. Metallosupramolecular geometric figures

Molecular rods, examined in the previous section, serve as starting material for construction of metallosupramolecular geometric figures [6,8]. Thus, a combination of 2,2′-bipyrazine **16** (Fig. 16) and ethylenediaminoplatinum dinitrate **17** (Fig. 17) results in a molecular triangle **18** (Fig. 18) [22].

Here, metal ions are located in the apexes of triangles; however, they could also be positioned at the sides, as in **19** (Fig. 19), which is an product of interaction of an oligomultidentate ligand **20** (Fig. 20) with iron(II) sulfate [23].

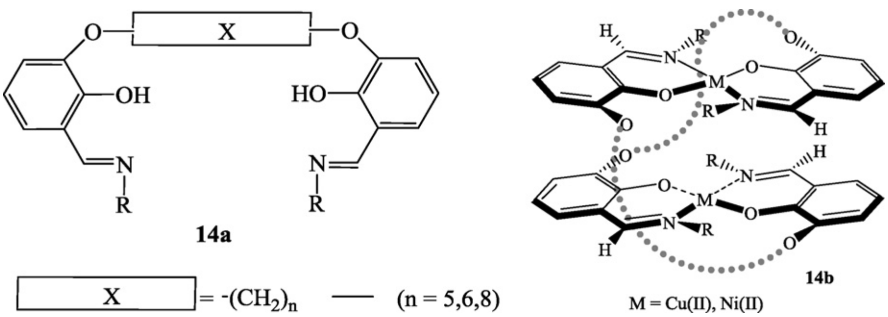
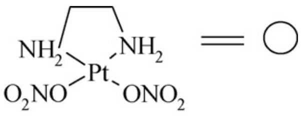


Fig. 14.



17

Fig. 17.

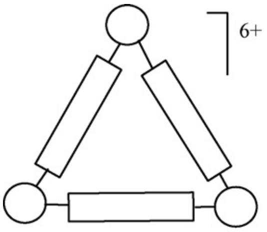


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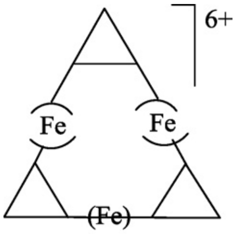
Fig. 18.

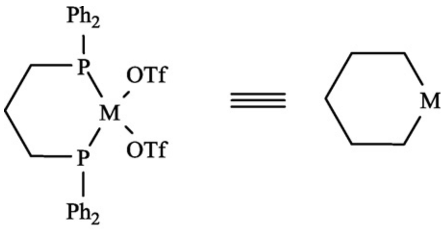


19

Fig. 19.

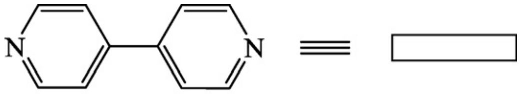
Molecular squares with angular metal atoms are similarly synthesized. Thus, the chelates **21a,b** (Fig. 21a and b) interact with the 4,4′-bipyridine **22** (Fig. 22) resulting in the unexpected self-assembly products **23a,b** (Fig. 23a,b) [24,25]. Such square structures are currently geometric formulae for supramolecular metal chelates.

The only example of formation of a square with metal-containing sides is represented by **26a,b** (Fig. 26a,b) [26], prepared by interaction of 5,10-bispyridilporphyrin **24a** (Fig. 24a) or its zinc complex **24b** (Fig. 24b) with metal complex **25** (Fig. 25). Metal atoms are angular in all other porphyrin-containing squares [5,6].



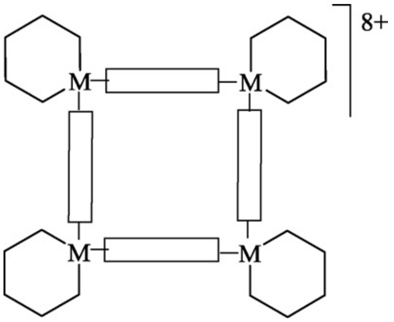
21a,b

Fig. 21.



22

Fig. 22.



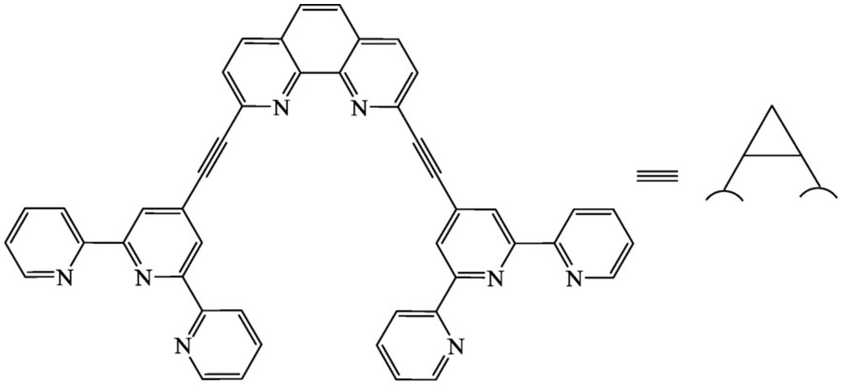
23 a,b

M = a) Pd, b) Pt

Fig. 23.

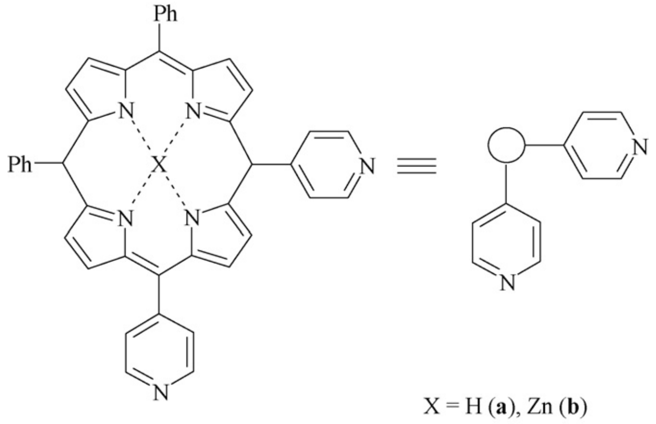
Squares are very frequently mutually converted into triangles resulting in equilibrium mixtures, for example **27** ⇆ **28** (Figs. 27 and 28) [27].

In contrast to common self-assemblies of molecular squares and rectangles, pentagons are still represented, to the best of our knowledge, only by the self-assembling product of oligopyridine **29** (Fig. 29) and iron(II) chloride. This structure is an open-work interlacement of five filaments of this ligand forming a lacework-like cyclic aggregate **30** (Fig. 30) [28] with the chloride ion situated at the center of the cavity.



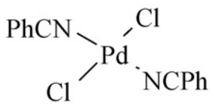
20

Fig. 20.



24 a,b

Fig. 24.



25

Fig. 25.

Surprisingly, the replacement of iron(II) chloride by its sulfate leads to a similar self-assembly of six filaments of the ligand **29** (Fig. 29) into a hexangular cyclic helicate of the type **30** (Fig. 30) containing a sulfate ion at the center of an enlarged cavity [29]. These self-assemblies are vivid examples of the template effect of inorganic anions [6], which is the driving force for self-assembled mechanically coupled structures [30].

Besides those described above, several syntheses of supramolecular hexagons are known [6], for instance, the self-assembled chiral ligand **31** (Fig. 31) forming a sexangular structure of the cyclic monohelicate **32** (Fig. 32) in the presence of silver hexafluorophosphate. Ag^{I} ions are tetrahedrally coordinated by four nitrogen atoms belonging to two independent bipyridine ligands. The external diameter of the hexagon is about 3 nm and the thickness 0.84 nm, *i.e.* it could be considered a 2D buildup. NMR spectra and circular dichroism spectra indicate that the structure **32** (Fig. 32) is conserved in the dissolved state too [31].

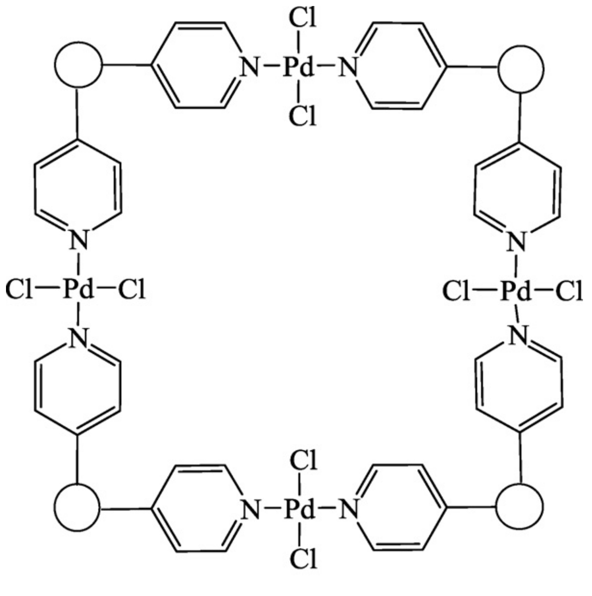


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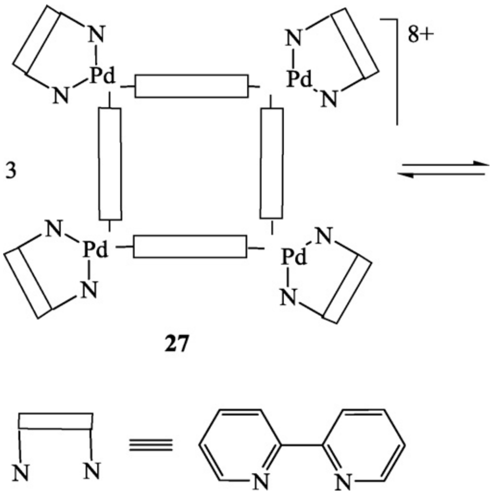
Fig. 26.



27

Fig. 27.

The synthesis of a molecular heptagon is most unusual and hence unique, since it comprises a monoreactor formation of ferrocene fragments coupled with their cyclization on interacting with a dicyclopentadiene derivative **33** (Fig. 33) of iron(II) chloride. The desired product **34** (Fig. 34) is formed but with low yield [32].

The synthesis of a molecular octagon by interaction of bis[3-(2-pyridyl)pyrazole-1-yl] dihydroborate **35** (Fig. 35) with cobalt(II) acetate in the presence of sodium perchlorate, forming a cyclic supramolecular structure **36** (Fig. 36), is also unique [33]. The resulting compound contains eight Co^{II} ions and twelve bridge ligands **35** (Fig. 35) with a perchlorate anion firmly fixed in the cavity.

Binuclear metallocycles [17], formed using a minimal number of reacted particles, are the most simple constructions encountered. Thus, the metallocycle **37** (Fig. 37) results from self-assembly of the complex ion $Cu(NH_3)_4^{2+}$ and bis-β-diketone [34], exhibiting the properties of the host molecule encapsulating such guest molecules as pyrazine, pyridine, quinuclidine, or diazabicyclo[2.2.2]octane (DABO), in the complex **37** (Fig. 37) of the last compound, which possesses the maximal stability constant of 220 L/mol. Where polyhetaryl-substituted arenes are in combination with silver salts,

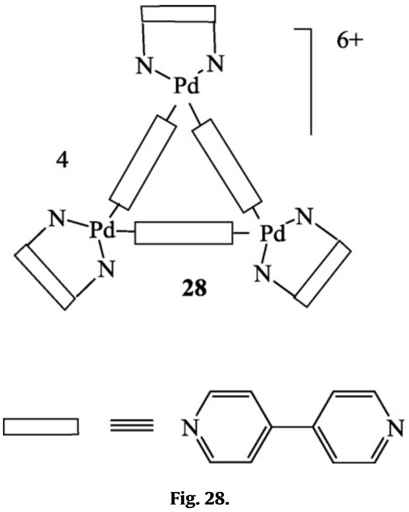


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Fig. 28.

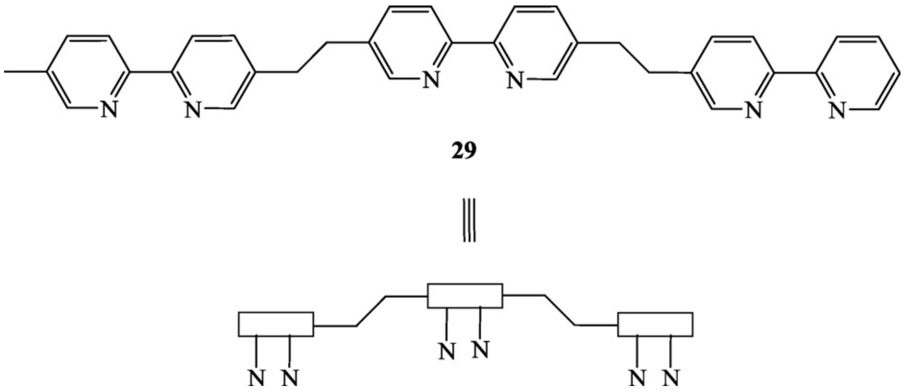

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Fig. 29.

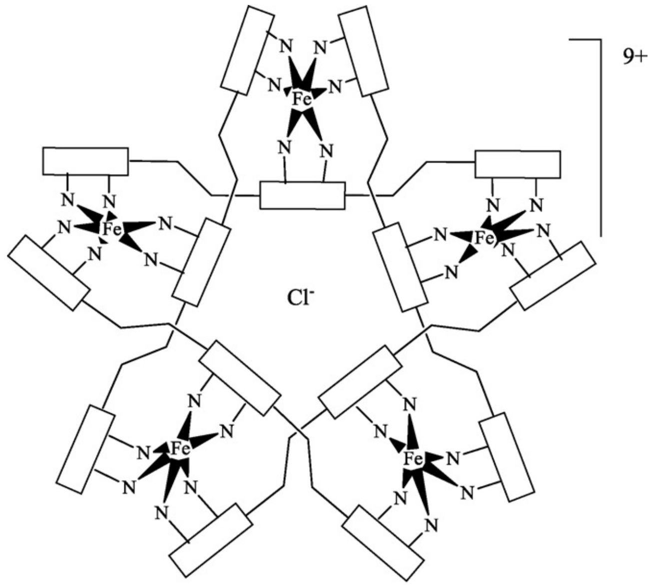

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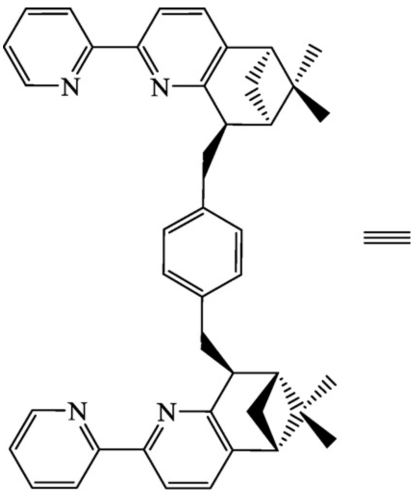
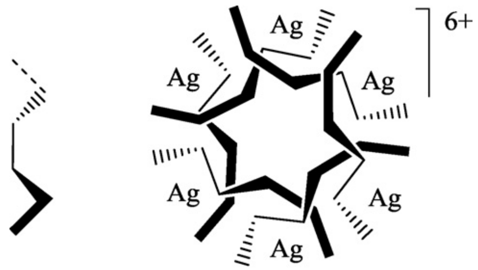
Fig. 30.



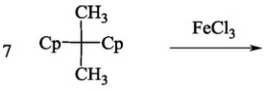
31

Fig. 31.



32

Fig. 32.

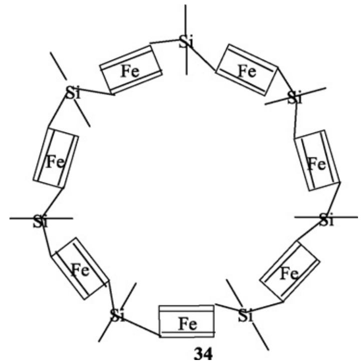


$$7\ \mathrm{Cp}\!-\!\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\!-\!\mathrm{Cp}\ \xrightarrow{\mathrm{FeCl_3}}$$

33

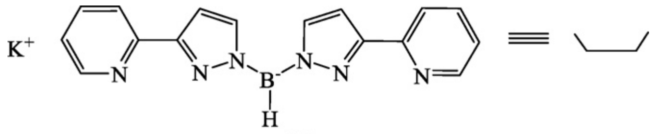
Cp - cyclopentadiene

Fig. 33.



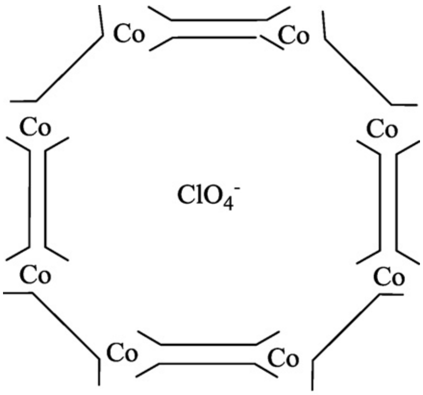
34

Fig. 34.



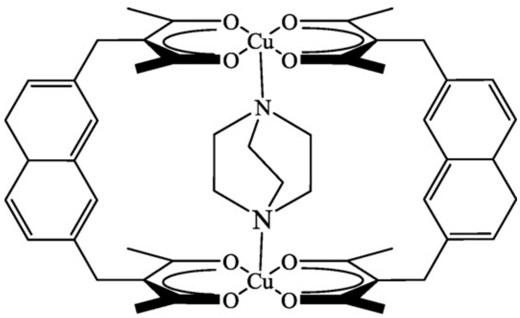
35

Fig. 35.



36

Fig. 36.



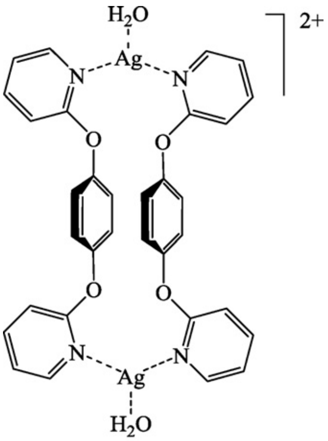
37

Fig. 37.

macrocycles of the type **38** (Fig. 38) [35] are formed. Thus, the benzene rings in this complex are in a state of tightly stacked interaction and add to the stability of the complex.

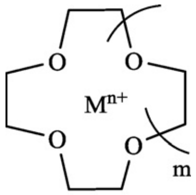
3.2. Cyclic structures with encapsulated metal ions

Metal ions are the structural elements in the supramolecular coordination compounds noted above. Macrocycles, which effectively encapsulate hard metal ions forming such complexes as coronates **39** (Fig. 39) [4,36] and their acyclic analogues, the podates



38

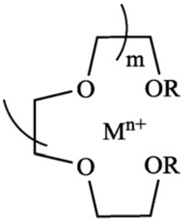
Fig. 38.



39

n = 1,2

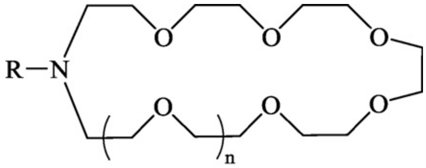
Fig. 39.



40

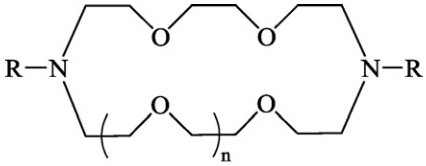
n = 1,2

Fig. 40.



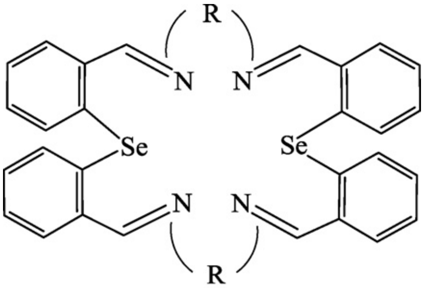
41

Fig. 41.



42

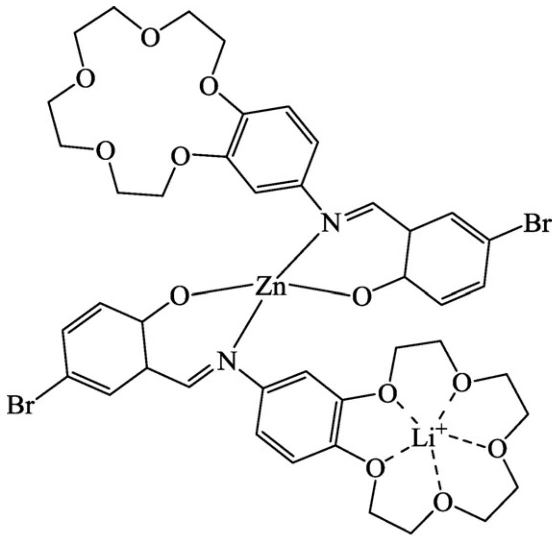
Fig. 42.



43

R = $(CH_2)_n$, n = 2,3

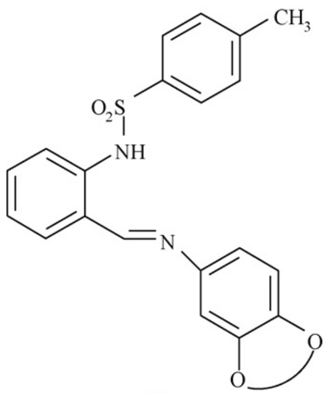
Fig. 43.



44

Fig. 44.

40 (Fig. 40) [4,37], are considerably more well known. Metal complexes of such macrocycles and their numerous chemical modifications have been highlighted in detail [3,4,38]. In addition to s-metal cations, these ligands are capable of coordinating f-metal cations [39].

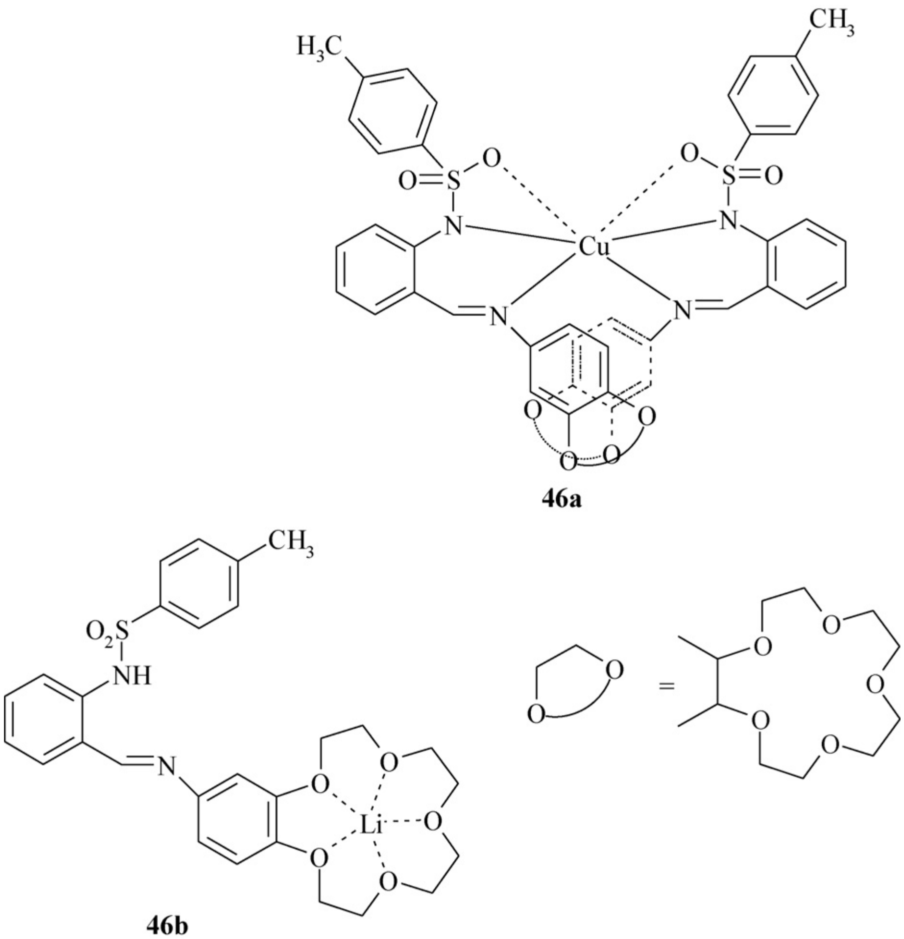


45

Fig. 45.

N-substituted aza- (Fig. 41) (**41**) and diazacoronands (Fig. 42) (**42**) with fluorescent substituents are widely used as fluorescent sensors for metal cations [40–42].

Replacement of donor oxygen atoms by nitrogen- and sulfur atoms leads to a radical change of design [4,43], which implies a transition from acceptors of hard cations to acceptors of soft cations according to the Principle of Hard-Soft Acids and Bases (HSAB) [44]. This is illustrated [45] by selenium-containing azomethine macrocycles **43** (Fig. 43), which coordinate the Pd^{II} ion through the nitrogen atoms, while all donor atoms coordinate the Ni^{II} and Co^{II} ions.



46a

46b

Fig. 46.

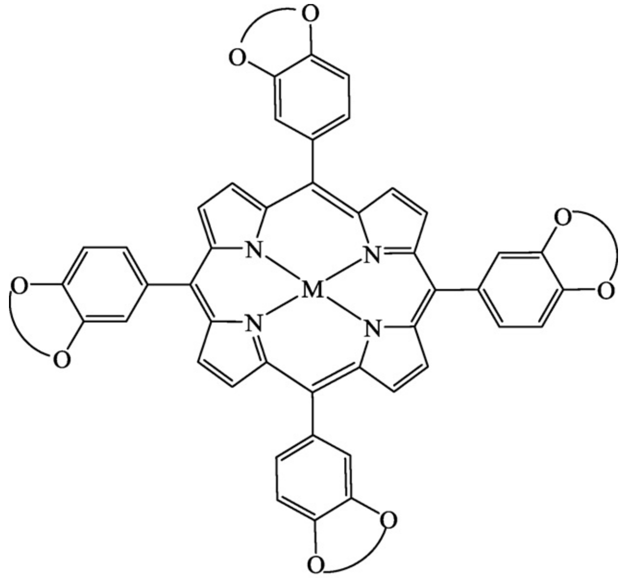
The design of coronands has been made possible by the practically unlimited capacity of modern organic synthesis brought about by the use of both hard and soft metal cation acceptors [46]. This development allows their simultaneous acceptance through distinct donor centers (competitive coordination [44]), for instance in the complex **44** (Fig. 44) [47,48]. The structurally related azomethine ligand **45** (Fig. 45) forms an expected complex **46a** (Fig. 46a) with Cu^{II} ion, while its interaction with the Li^+ ion leads to an open structure **46b** (Fig. 46b) [48].

Interesting examples of this phenomenon are [46,49] the crown-substituted tetrapyrrols: porphyrinates **47** (Fig. 47) and phthalocyaninates **48** (Fig. 48). If the size of a hard cation (for example, K^+) prevents its encapsulation into a coronand cavity, dimers shown in **49** (Fig. 49) form analogously to the sandwich-type complex by formation of 15-crown-5 with K^+ cation.

The coordination of lanthanide cations in tetracrownphthalocyanines takes place through the ring nitrogen atoms themselves, forming the dimer **50** (Fig. 50) or the trimer **51** (Fig. 51) [49].

Some examples below will provide an idea of modern developments in coronands and cryptand chemistry and their complicated structures that initiate hybrid modifications. Thus, [2 + 3] template condensation of tris(2-aminoethyl)amine with 2,6-diformylpyridine leads [50] to cryptates **52** (Fig. 52). A hybrid structure **53** (Fig. 53) was synthesized [51] using the coordination properties of 12-crown-4 and terpyridine. Lipophilic hybrid molecules **54** (Fig. 54) were found [52] to be effective ditopic carriers of several aminoacids (tryptophan, serotonine) through a liquid membrane. The aminoacids in this case act in zwitterionic forms, where the cationic part $RNH_3{}^+$ is coordinated with crown-ethers and the anionic part $RCOO^-$ — with the Mn^{III} cation.

The structures **47, 48, 54** (Figs. 47, 48 and 54) represent a group of heteroditopic receptors [53], *i.e.* polyfunctional ligands capable of binding cations and anions simultaneously.



47

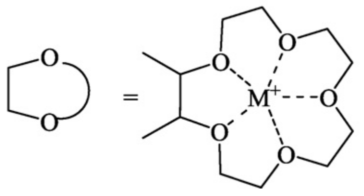
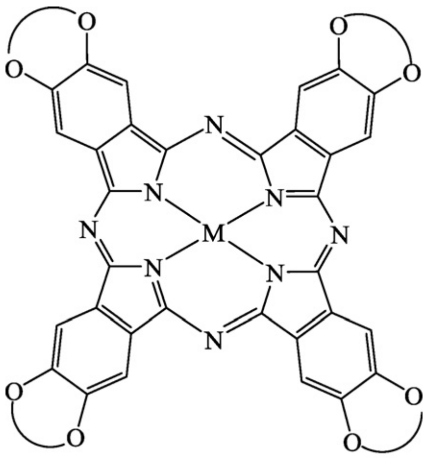


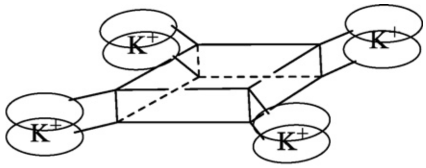
Fig. 47.



48

$M = Co^{II}, Cu^{II}, Zn^{II}, Cu^{II}$
$M^+ = Na^+, Mg^{2+}, Ca^{2+}$

Fig. 48.



49

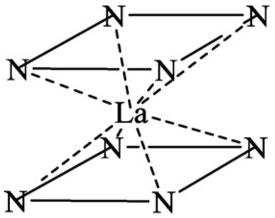
Fig. 49.

The discovery [54] of a molecular assembly – guanosine quartet **55** (Fig. 55), – stabilized with Na^+ or K^+ ions, as a quasi-natural analogue of coronates, turned out to be unexpected and valuable. It was found in the hydrogels of 5′-guanosine monophosphate. The lipophilic analogues, obtained by the lipophilization of hydroxyl groups of the carbohydrate fragment, become selective extractants for metal ions, carriers of liquid-crystal properties, and components in design of molecular electronic nanodevices [54].

Coronands and azocoronands represent important construction materials for the production of artificial ionic channels [55].

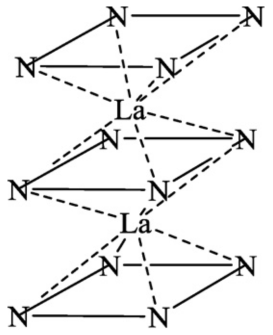
Anti-crowns [4,56,57a], in which oxygen atoms are replaced with metal atoms (for instance, the structures **56a–c** (Fig. 56a–c)), are the original antipodes of crown-ethers. In contraposition to common crown-ethers, these host molecules effectively encapsulate anions.

Over the last decade, many other metal-containing anion receptors have been synthesized with metals included as inert structural elements, as labile structural elements, as part of anion binding



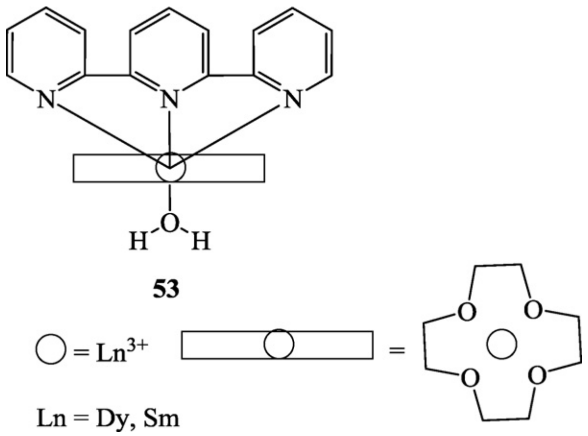
50

Fig. 50.



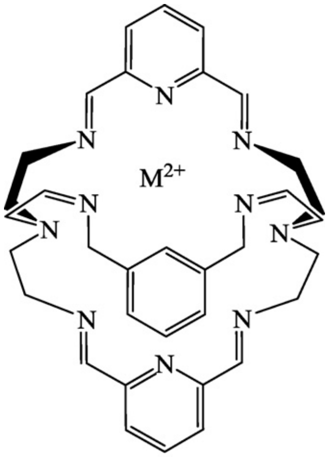
51

Fig. 51.



53

Fig. 53.



52

M = Ca, Sr, Ba

Fig. 52.

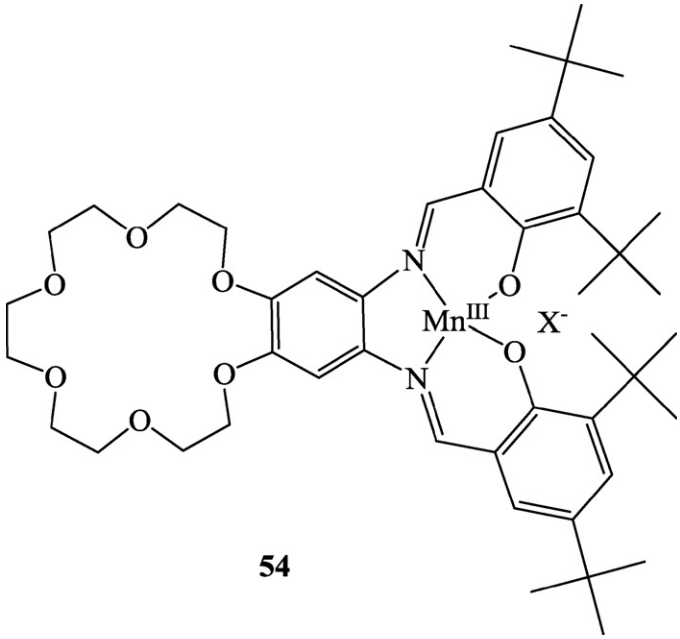
sites, as redox reporter groups, or as luminescent reporter groups [57b,c].

3.3. *"Furniture" structural motifs*

Conformationally hard molecule-rods (Section 2.1) in the presence of definite metal cations are capable of self-assembly into unconventional "furniture" assemblies such as racks (**57a**) (Fig. 57a), ladders (**57b** (Fig. 57b)), and grids (**57c** (Fig. 57c)) [3–5,58].

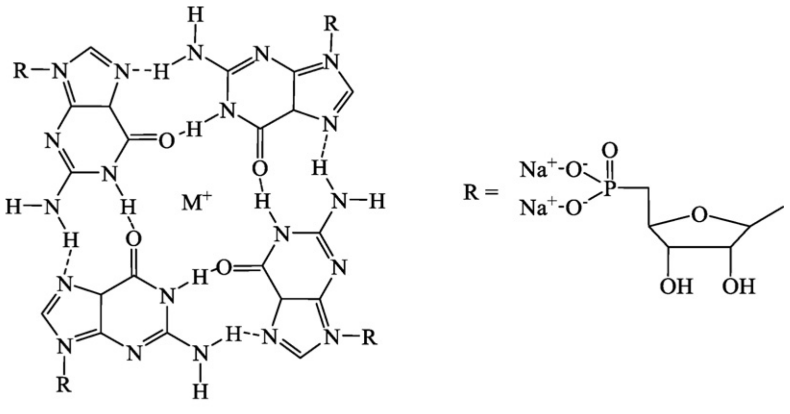
Thus, the ligand **58a** (Fig. 58a) in the presence of Ru(II) can form the rack **59** (Fig. 59) [6,58], and a structurally relative ligand **58b** (Fig. 58a,b) resulting in the ladder **60** (Fig. 60) [3,4,58,59].

In contrast to the types of racks and ladders requiring additional ligands for self-assembly, in grids it is sufficient to have one each of ligand and metal cation [60]. Thus, a comparatively simple ligand **61** (Fig. 61), in the presence of a metal cation with tetrahedral coordination (M = Ag^I, Cu^I), is transformed into the grid **62** (Fig. 62) [61].



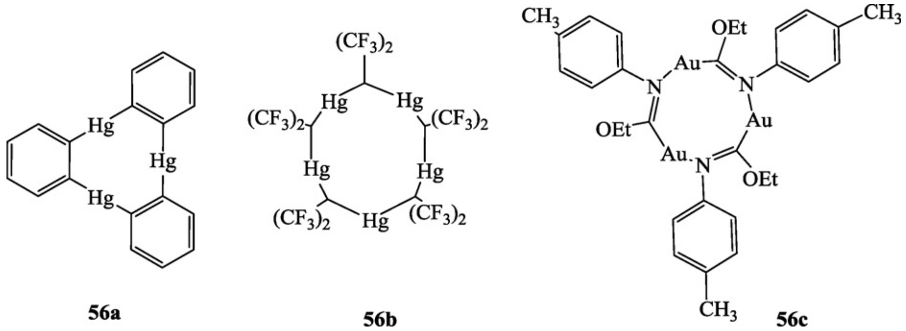
54

Fig. 54.



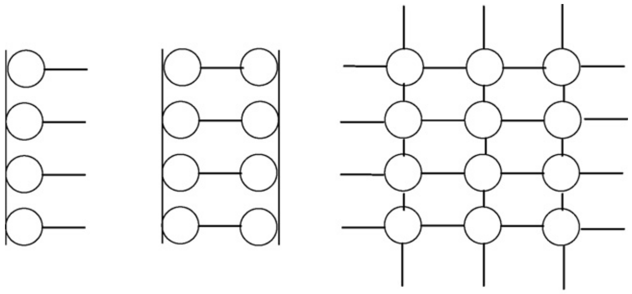
55

Fig. 55.



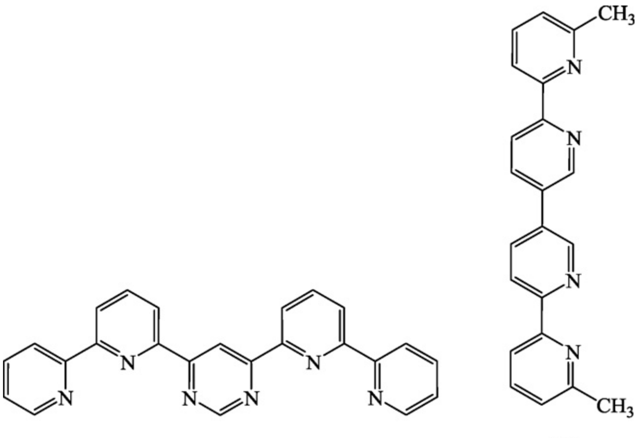
56a **56b** **56c**

Fig. 56.



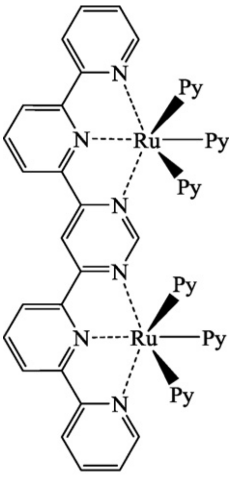
57a **57b** **57c**

Fig. 57.



58a **58b**

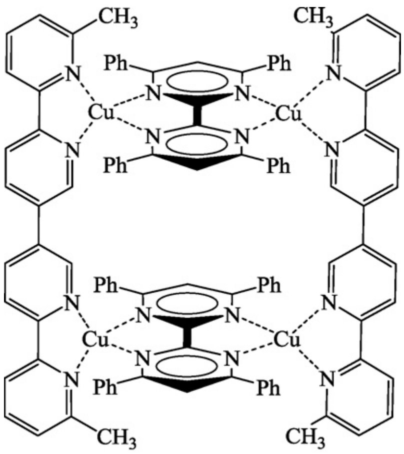
Fig. 58.



59

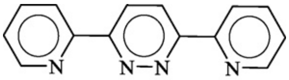
Py = (pyridine ring, N)

Fig. 59.



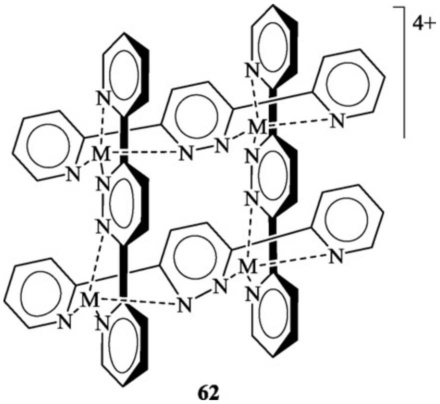
60

Fig. 60.



61

Fig. 61.



62

Fig. 62.

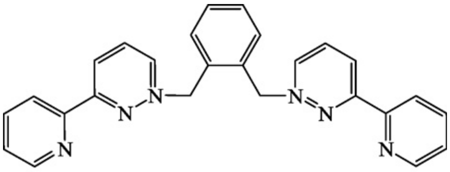
4. Tridimensional (3D) structures

3D structures represent the most widespread and diversified multiplicity of supramolecular coordination compounds. As in the previous section, we commence their study with the most impressive self-assembled products, namely geometric figures.

4.1. Geometric figures

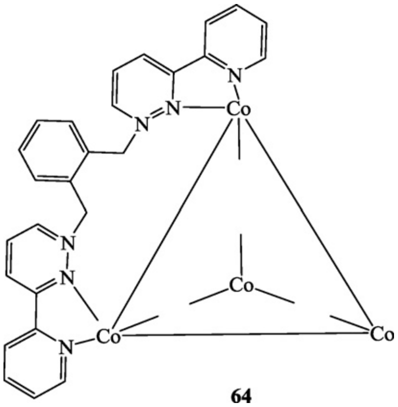
Coordination compounds in the form of tetrahedrons are usually obtained [6,8,58] by interaction of molecular rods with d-metal ions. For instance, a pyridazine–pyridine-containing ligand **63** (Fig. 63) reacts with cobalt(II) acetate in the presence of sodium tetrafluorborate resulting in the tetrahedral structure **64** (Fig. 64), into whose cavity a tetrafluorborate ion is encapsulated [62].

Upbuilding arrangements of cubic structures require additional tridimensional angular metal complexes [6,8,58] of the type **65** (Fig. 65). This compound, in the presence of 4,4′-bipyridine **66** (Fig. 66) and silver triflate, forms the cube **67** (Fig. 67) [63].



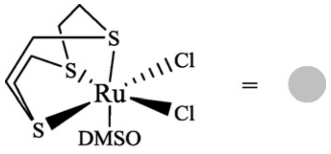
63

Fig. 63.



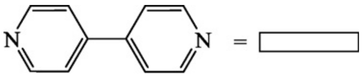
64

Fig. 64.



65

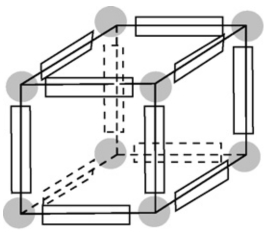
Fig. 65.



66

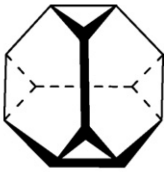
Fig. 66.

More complicated self-assembled products can be obtained, such as octahedrons [8], truncated tetrahedrons **68** (Fig. 68) [6], and cube-octahedrons [6,8]. To produce an octahedron, a plane ligand **69a** (Fig. 69a) and angular complex **70** (Fig. 70) are used, whose self-assembly leads to the expected octahedron **71** (Fig. 71) [64]. Combining an analogous angular complex as in **72** (Fig. 72) and a plane ligand **69b** (Fig. 69b) in the presence of sodium adamantyl carboxylate **73** (Fig. 73) as a template leads to the self-assembly of a truncated tetrahedron **74** (Fig. 74) with high yields [6,65].



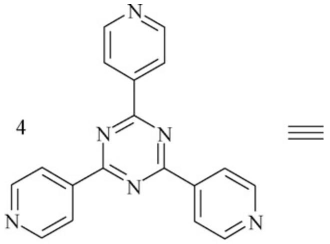
67

Fig. 67.



68

Fig. 68.



69a

Fig. 69.

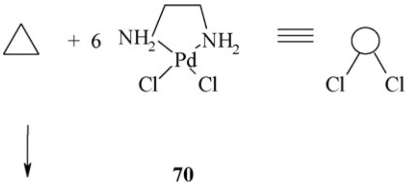
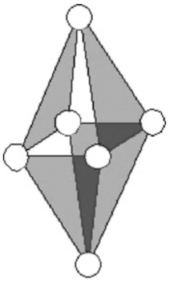


Fig. 70.



71

Fig. 71.

The self-assembly of eight particles of a plane tritopic ligand **75** (Fig. 75) and twelve particles of the complex **76** (Fig. 76) into a complex buildup of a cube-octahedron **77** (Fig. 77) with quantitative yield is also impressive [66].

Combining molecular rods **78a–c** (Fig. 78a–c) with a plane heteroaromatic ligand **79** (Fig. 79) in presence of Cu^I or Ag^I cations leads to molecular cylinders of the type **80** (di-decker cylinder)

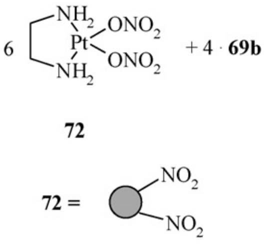


Fig. 72.

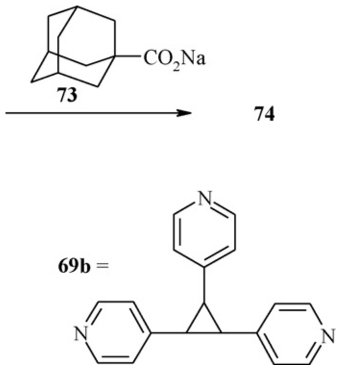
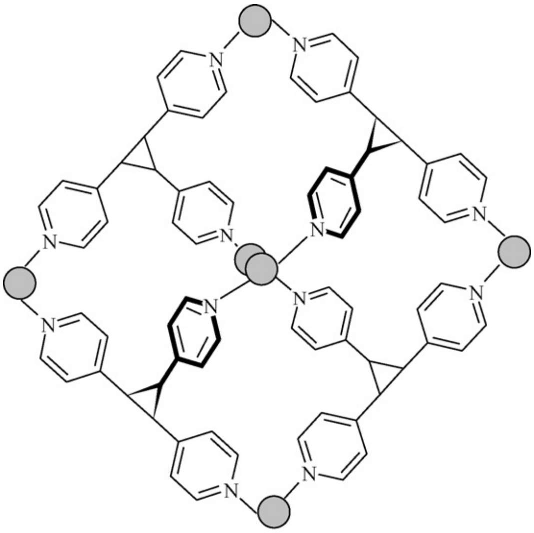


Fig. 73.



74

Fig. 74.

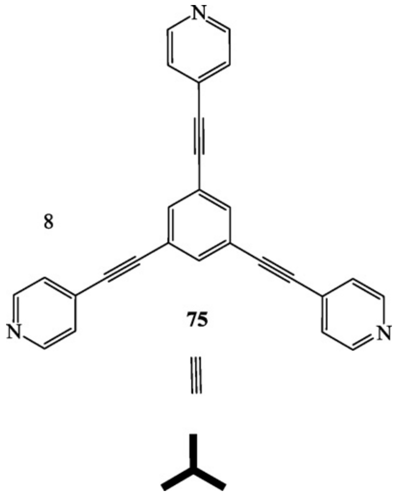
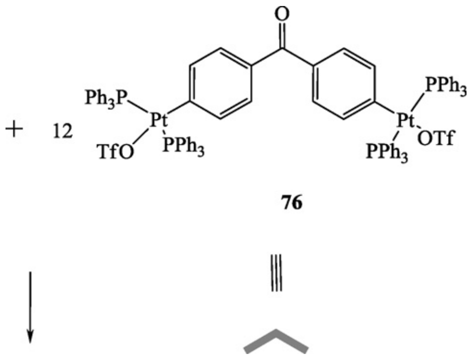


Fig. 75.



76

Fig. 76.

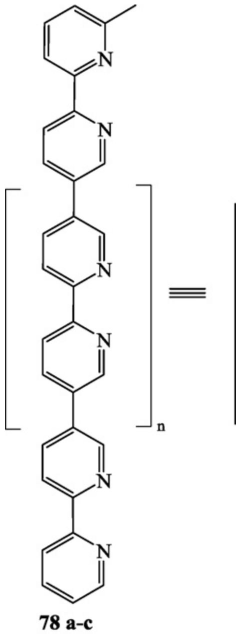
77

Fig. 77.

(Fig. 80) [5,67]. Tri- and tetra-decker cylinders are formed at $n = 1$ and $n = 2$, respectively [5].

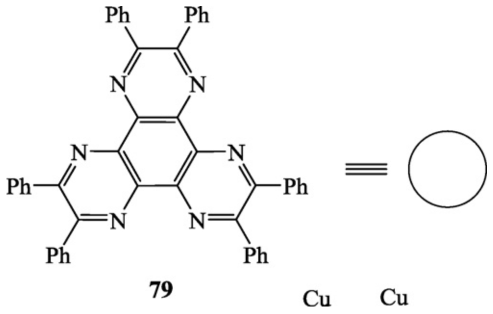
4.2. Metallocyclophanes

Self-assembly of two molecules of a tridentate ligand **81** (Fig. 81) with three molecules of the complex **82** (Fig. 82) in the obligatory presence of a guest molecule (4-methoxyphenyl) acetic acid as a template is finished by the reversible formation of a cyclophane box **83** (Fig. 83) [5,11].



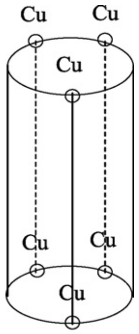
78 a-c
a) n = o
b) n = 1
c) n = 2

Fig. 78.



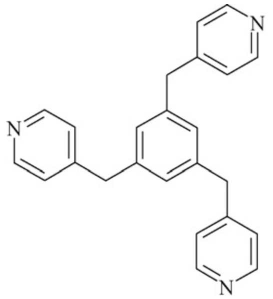
79

Fig. 79.



80

Fig. 80.



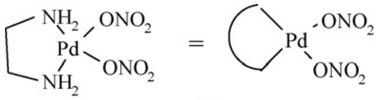
81

Fig. 81.

When zinc porphyrinate derivatives take part in self-assembly, a metallocyclophane as in **84** (Fig. 84) with a large cavity is formed; this cavity is able to complex metal-binding guests such as shown in Fig. 84 [11,45,68].

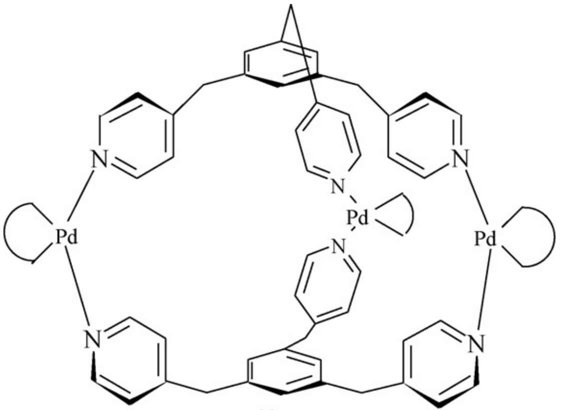
4.3. Interlaced (topologically linked) structures

As described in a series of reviews [69–73], the preparation of interlaced (topologically bounded) structures (pseudo-rotaxanes **85a** (Fig. 85a), rotaxanes **85b** (Fig. 85b), catenanes **85c** (Fig. 85c), and knots **85d** (Fig. 85d)) is related to the transition from invariably



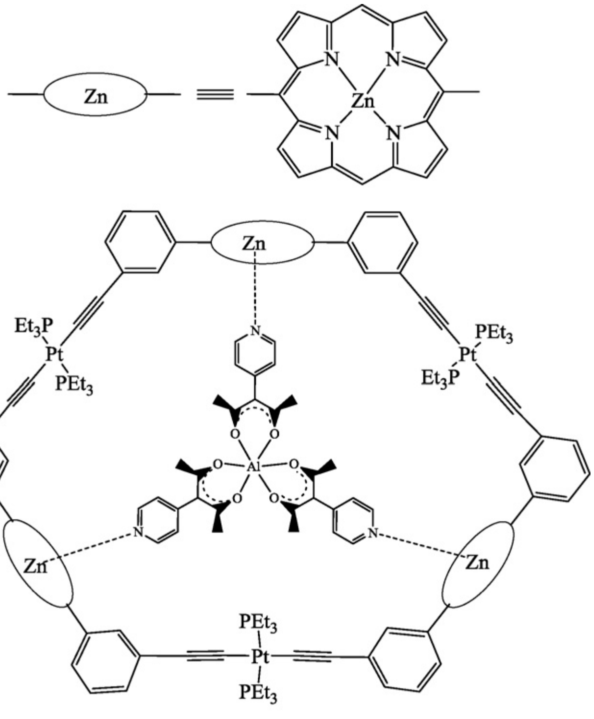
82

Fig. 82.



83

Fig. 83.

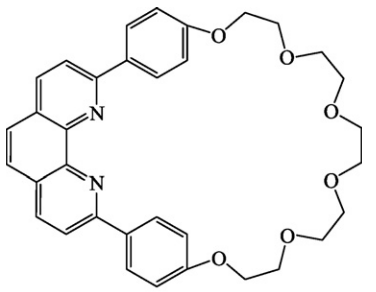


84

Fig. 84.

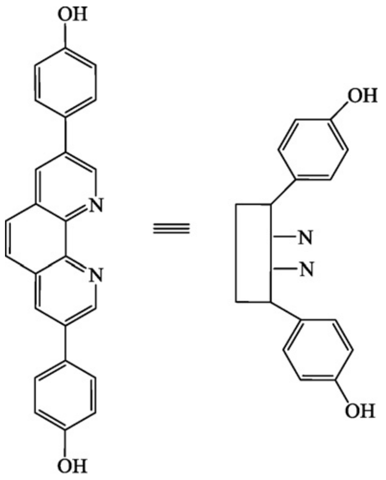
non-productive statistical methods to goal-seeking self-assembly processes in combination with template syntheses, which is the special characteristic of coordination compounds.

Thus, the interaction of the macrocycle **86** (Fig. 86) with the diphenolic phenantroline ligand **87** (Fig. 87) in the presence of a Cu^I ion led to [71,74] the pseudo-rotaxane **88** (Fig. 88), whose structure was safely established by its interaction with spatially



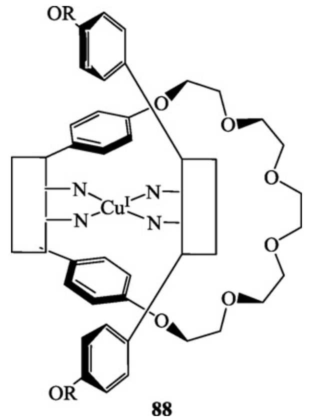
86

Fig. 86.



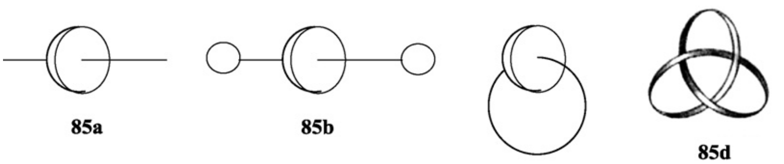
87

Fig. 87.



88

Fig. 88.



85a **85b** **85c** **85d**

M - chirality

Fig. 85.

88 R = H

89

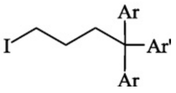


Fig. 89.

90 R =

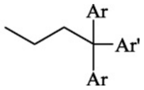


Fig. 90.

91 R,R =

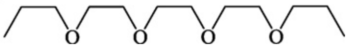
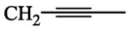


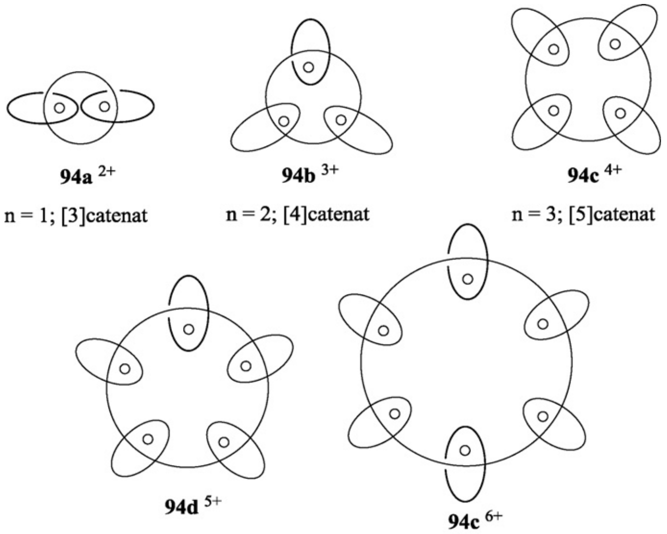
Fig. 91.

92 R =



Ar = p-t-Bu-C_6H_4, Ar' = Ph

Fig. 92.



n = 1; [3]catenat

n = 2; [4]catenat

n = 3; [5]catenat

n = 4; [6]catenat

n = 5; [7]catenat

Fig. 94.

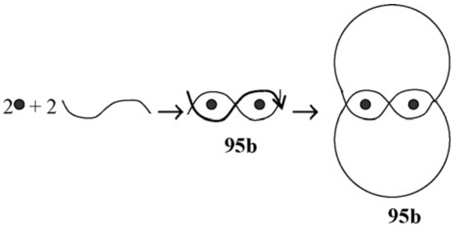


Fig. 95.

voluminous iodide **89** (Fig. 89) as a molecular stopper, that in turn led to the desired [2] rotaxate **90** (Fig. 90) [72,74] (the digit in square parenthesis indicates the number of interlaced structures).

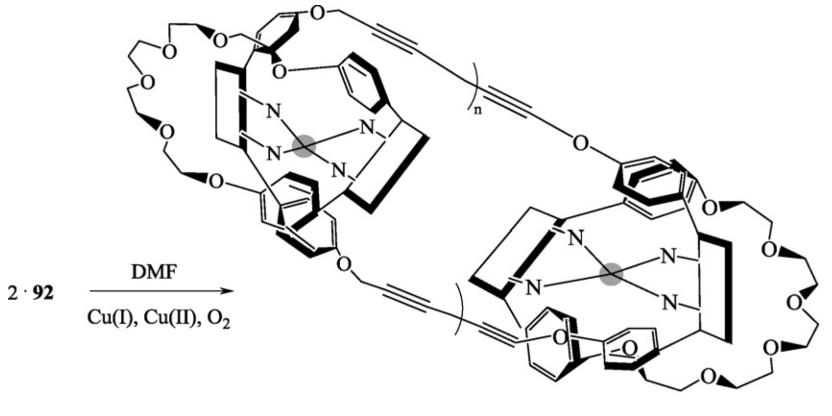
The reaction of pseudo-rotaxate **88** (Fig. 88) with pentaethylene glycol diiodide yields the catenate **91** (Fig. 91) [70,71,75]. Treating it with cyanide ions, the catenate **91** (Fig. 91) is demetallated; the catenane formed is then metallated with d-metal cations [70,76,77].

Diacetylenic pseudo-rotaxane **92** (Fig. 92) under the conditions of Glaser's reaction forms [10,78] the mixture **93** (Fig. 93) of [*n*]catenates, the so-called molecular necklaces shown as in **94a–c** (Fig. 94a–c). This is undoubtedly a remarkable achievement of supramolecular coordination chemistry.

Molecular collars **94a–c** (Fig. 94a–c) were chromatographically isolated in a pure form as tetrafluoroborates whose highest homologues illustrated as in **94c–d** (Fig. 94c–d) were identified in the reaction mixture.

The simplest knot, the trefoil of the type **85** (Fig. 85) can be synthesized in two steps [5]. At the beginning, the self-assembly of two metal ions (·) and two semiflexible ligands (∼) yield the helicate **95a** (Fig. 95) (P-chirality shown), the two opposite ends of which are connected by an appropriate linker in a complex knot **95b** (Fig. 95b) of the same chirality. This strategy was used [79] to self-assemble the ligand **96a** (Fig. 96a) with Cu^I into the helicate **96b** (Fig. 96a) and treated further with hexaethyleneglycol diiodide, at which the desired knot **96c** (Fig. 96c) was obtained with 30% yield.

Polymeric analogues are topologically linked structures — discussed earlier — are also known as pseudo-polyrotaxanes and polyrotaxanes, and are obtained mostly without the participation of coordination compounds [72]. However, there are some exceptions. Thus, the functionalized catenate **97a** (Fig. 97a) was used [72] to prepare the polycatenate **97b** (Fig. 97b) [72,80] and its structural analogues [72,81].



93

Fig. 93.

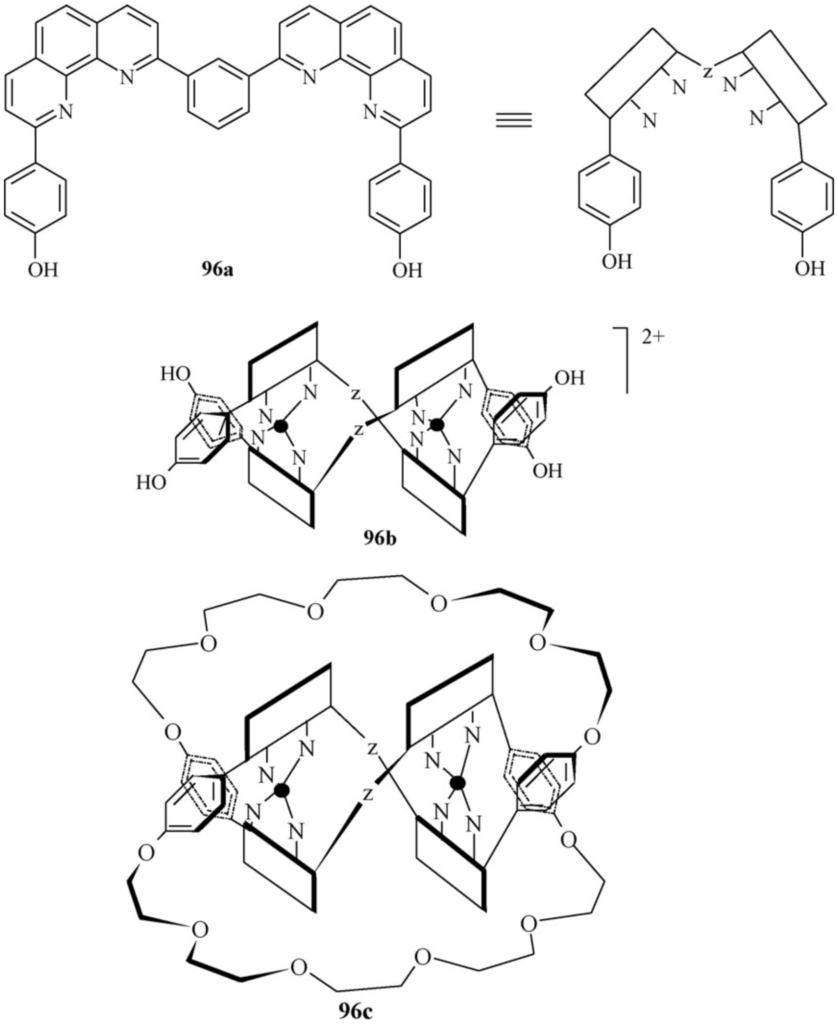


Fig. 96.

The ability of bipyridine fragments to coordinate Ag^+ cation with tetrahedral geometry enables obtaining [72,82] poly[2]catenate **98** (Fig. 98), containing an average of 40 repeated units.

4.4. Metallodendrimers

Dendrimers [4,83] are oligomers possessing highly ramified controlled 3D structures (supersupramolecules), and are obtained by specific methods. Unsurprisingly, modern supramolecular chemistry includes coordination motifs in the study of the synthesis of metallodendrimers and their properties [4,5,13,83–90].

Metallodendrimer types are determined by the functions of the metal atom, which are [84]:

(a) a ramification/branching center;
(b) a bond between building blocks;
(c) a dendrimer core;
(d) a part of the terminator group;
(e) serving as a secondary structural element.

An illustrative example of a metallodendrimer of the type a is a decanuclear polypyridine complex appearing in **99** (Fig. 99) (first metallodendrimer) [12,84–86]. It was synthesized by Balzani group from the trigonal metal complex **100** (Fig. 100) and initially a prepared structural block as in **101** (Fig. 101) [85].

An example of metallodendrimer of the type b is the metal complex **102** (Fig. 102) with alternate ramification/branching centers and Si atoms, connecting the ramifications of Ge atoms [84,86].

A metalloporphyrin complex most often acts as the core in metallodendrimers of the type c, for instance in the metallodendrimer **103** (Fig. 103) [84,87,89]. d- or f-Metal ions can also form cores in such dendrimers [84], as well as with p-metal cations (Si, Ge) [90].

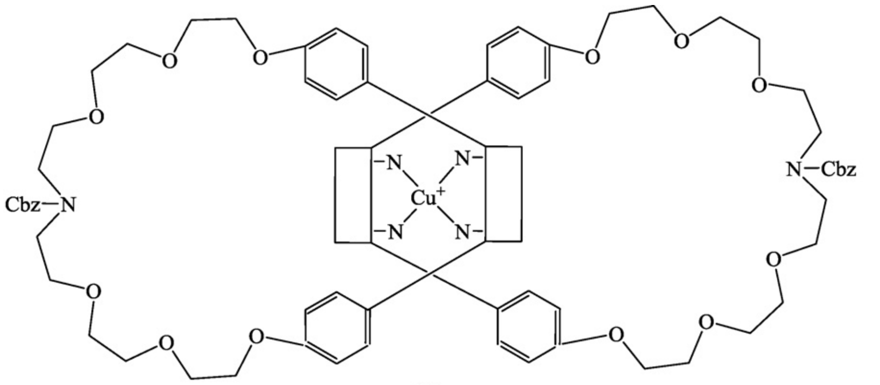
The metallodendrimers of the type d are the most widespread; their metal ions are located on the dendrimer surface as in the complex **104** (Fig. 104) for example [84,88]. Metal carbonyls and chelates function as terminal metal centers [84].

When dendrimers possess reactive sites (a triple bond or chelate fragments), metal centers are introduced as secondary structural elements (type e), as, for example in the transformation **105a** → **105b** (Fig. 105a–b) [70,75].

Platinum nanoparticles, encapsulated with polyamidoamine-dendrimers, could be conditionally attributed to metallodendrimers. The precipitation of such buildups on commercial silica dioxide with highly developed surfaces and their further thermal treatment to eliminate organic dendrimers led [91] to the discovery of active catalysts for oxidation and hydrogenization.

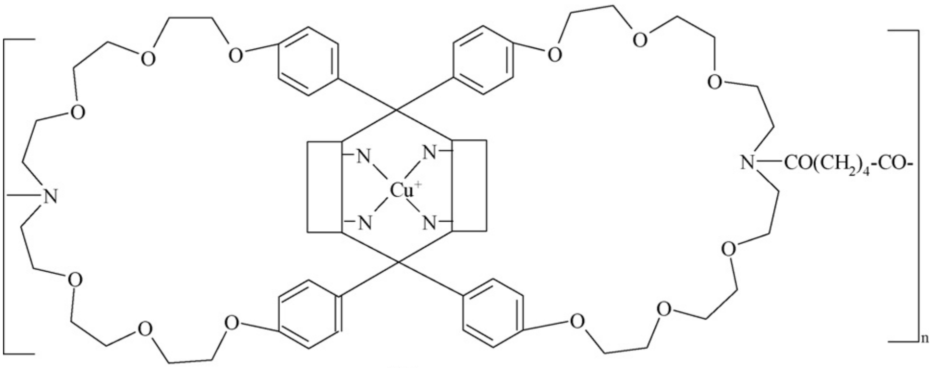
4.5. Coordination polymers

Coordination polymers of the type **106** (Fig. 106) are formed by the polymerization (polycondensation) of monomeric metal



97a

Cbz = Carbobenzoxy group $C_6H_5CH_2OCO$



97b

Fig. 97.

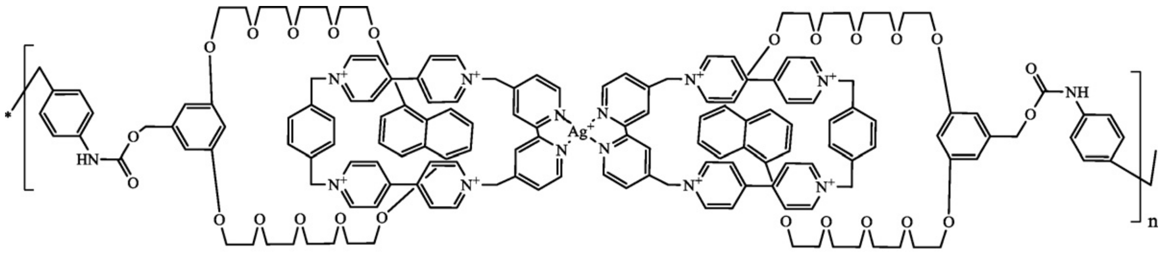
complexes, for instance $[Pt(NH_3)_4]^{2+}$ with bridged particles, or $[Fe(CN)_6]^{3-}$ [58] (where the coordination bonds are inside the polymer chain). So, these compounds should be different from the polymer ligand complexes of the type **107** (Fig. 107) [45] (where the coordination bonds are outside the polymer chain).

Polymers such as in **108** (Fig. 108) with the same bridged cyano groups are relatively complicated structurally and contain an M^{III} ion tetrahedrally coordinated with six cyano groups [92]. The K^+ cation also takes part in the coordination with six cyano groups, which connect M^{III} and K^+ as bridged ligands. Consecutive bonds –M–C–N–K form 3D crystal structures, whose cavities are occupied by plane-square $[Cuen_2]^+$ cations as guests.

At present, lanthanide-containing coordination polymers [18], such as **109** (Fig. 109) [93] with bridged ligands L, are widespread. Among them, mono- and dicarboxylates in combination with bipyridine derivatives are the most well known. Thus, the lanthanum coordination polyhedron $[La(4,4'\text{-bipy})(CHCl_2CO_2^-)_3(H_2O)]_n$ possesses the structure **110** (Fig. 110) [94], in which two dichloroacetates are bidentate (chelate) and the third is monodentate. In the case of fumarate, the coordination polymer $(Sm_2(C_4H_2O_4)_3(2,2'\text{-bipy})_2(H_2O)_2]_n$ with repeated structure **111** (Fig. 111) [95] is constructed from one bridged bidentate and two monodentate fumarates. The dicarboxylate ligand in fumarate coordination polymers could also be monodentate- or bidentate chelates [96].

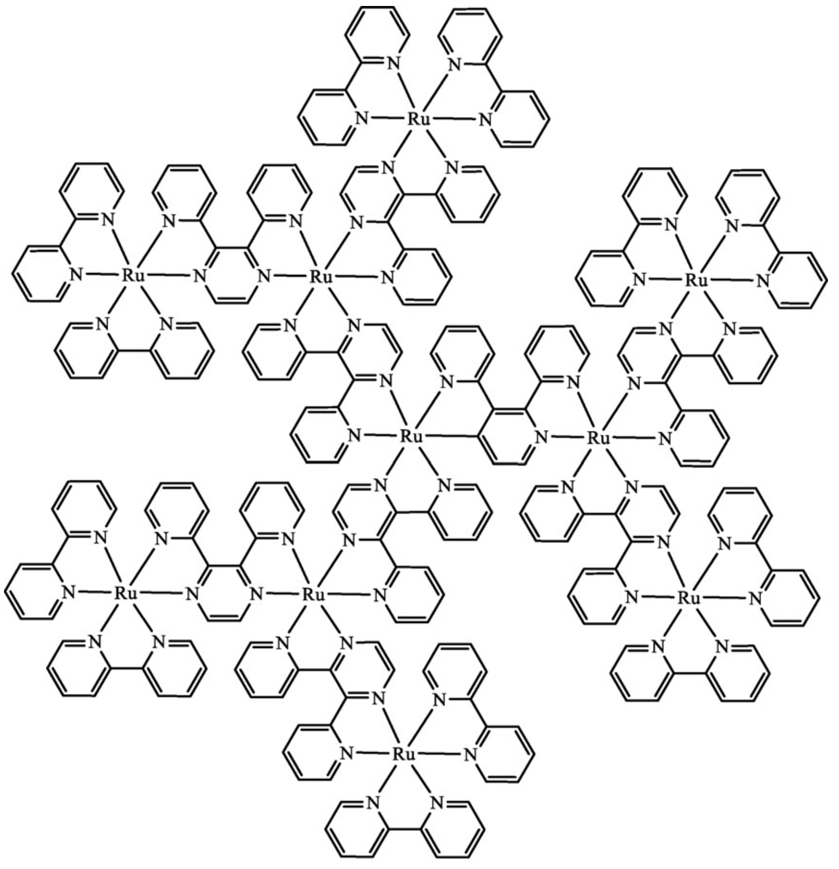
An original copper(II) coordination polymer **112a** (Fig. 112a) [97] consists of thiourea ligands, coordinated with Cu(II) and 2-(2-imino-4-oxo-5-thiazolydinen) acetate ions, which take part exclusively in the form of a *Z*-isomer **112b** (Fig. 112b), *i.e.* the self-assembly here is selective.

Porous networks based on 4,4′-bipyridine are built according to a slightly different principle, such as the diamond lattice of $Cu(bpy)_2{\cdot}PF_6$ **113** (Fig. 113) or the grid of $Cu(bpy)_{1,5}{\cdot}(NO_3)(H_2O)_{1,25}$ **114** (Fig. 114) with mutually penetrated sub-structures [4,78,98].



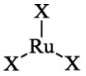
98

Fig. 98.



99

Fig. 99.



100

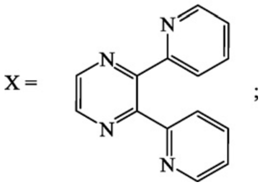
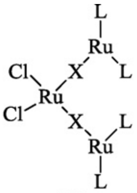


Fig. 100.



101

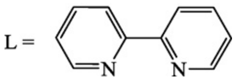


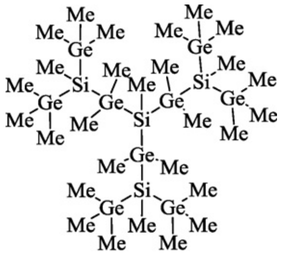
Fig. 101.

4.6. Structures with encapsulated metal ions

The sections above examined supramolecules whose metal ions are of different grades and form integral parts of their structure. The present section is devoted to classic supramolecular host–guest complexes with metal ions as guests, whose synthesis and study were initially the basis of the supramolecular chemistry.

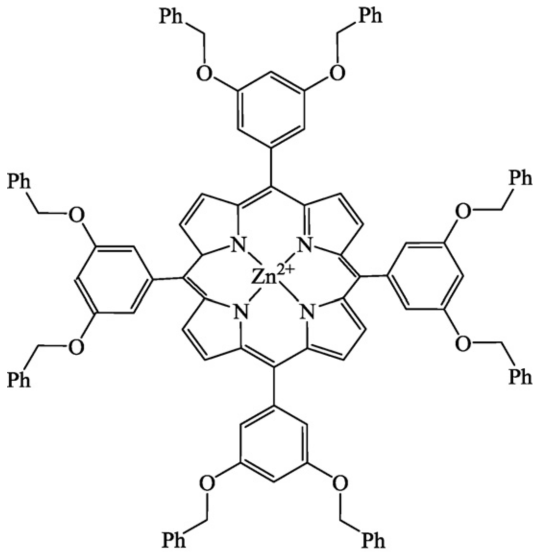
4.6.1. Cryptands (clathrochelates)

This title includes a wide group of suprametallocomplexes, structural relatives of Lehn's cryptates **115** (Fig. 115) [3,4], previously called "clathrochelates" which name is quoted by authors of some titles included in the bibliography [99,100]. Their several names, such as sepulchrates **116** (Fig. 116) [4,99] (lat. *sepulchrum*—tomb) and sarcophaginates **117** (Fig. 117) (Greek *sarcophagus*—coffin, sarcophagus) [4,99], eloquently testify to the extraordinary durability of d-metal binding in their cavities. The



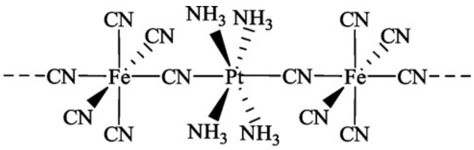
102

Fig. 102.



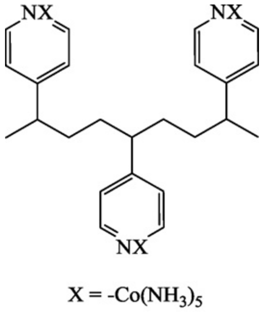
103

Fig. 103.



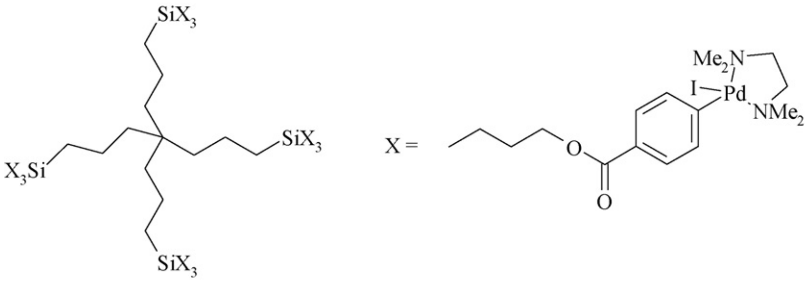
106

Fig. 106.



107

Fig. 107.



104

Fig. 104.

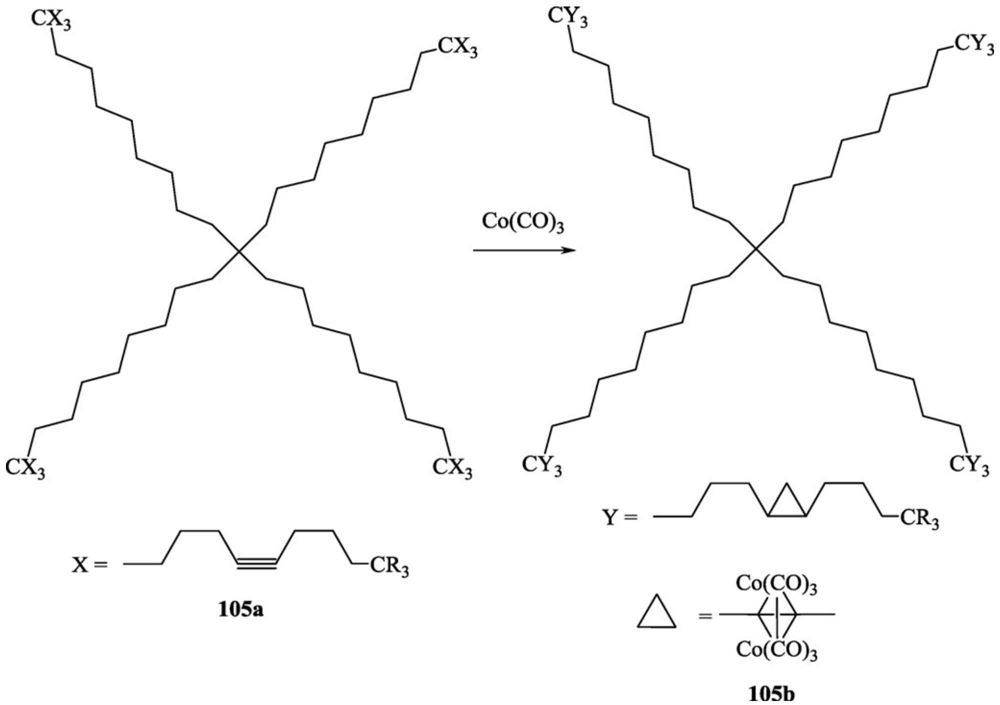


Fig. 105.

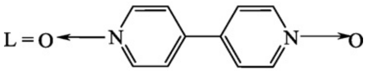
$\{[Cu(en)_2][KM(CN)_6]\}_n$

$M = Cr^{III}, Fe^{III}, Co^{III}$

108

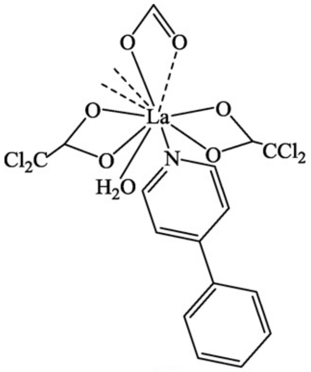
Fig. 108.

$\{[Sm(NH_3)_3L_2] \cdot 0{,}5\ H_2O\}_n$



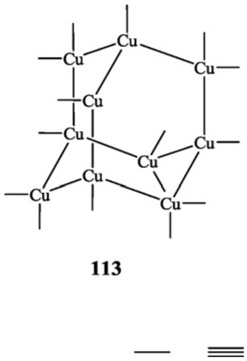
109

Fig. 109.



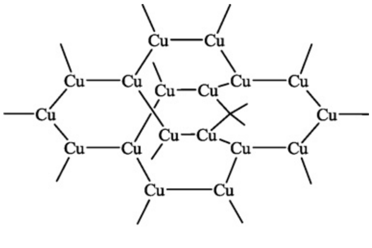
110

Fig. 110.



113

Fig. 113.



114

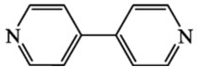
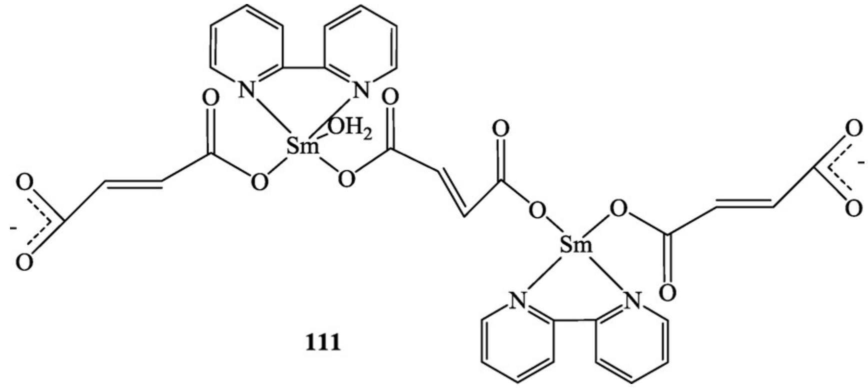
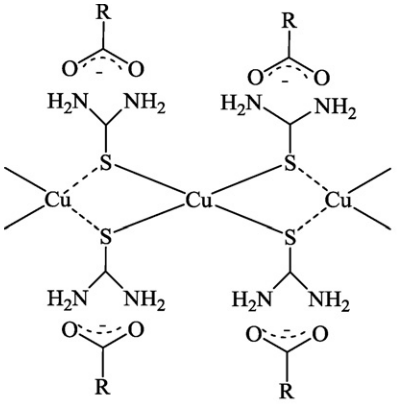


Fig. 114.

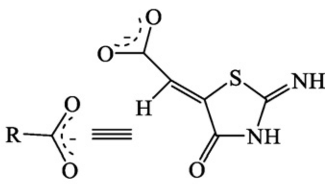


111

Fig. 111.

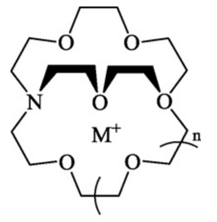


112a



112b

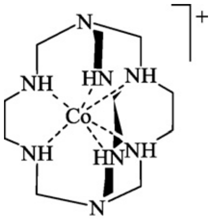
Fig. 112.



M^+- s-cation

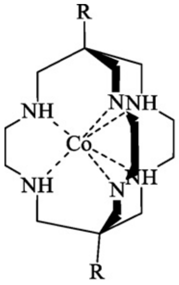
115

Fig. 115.



116

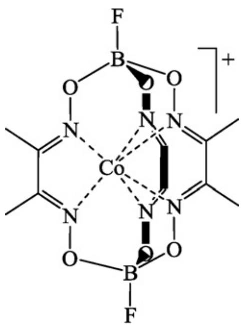
Fig. 116.



117

R = NH_2, NO_2,
CH_2Cl, etc.

Fig. 117.



118

Fig. 118.

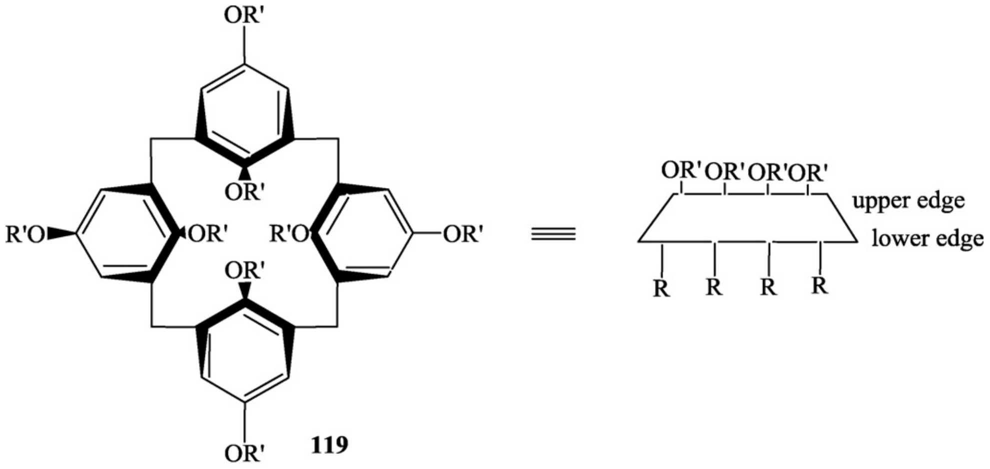
liberation of these enclosed species is made possible by destroying these structures, which form only in the presence of templates [99,100].

The clathrochelates **118** (Fig. 118), obtained from metal glyoximates, are the principal subjects of research in Voloshin's group [99–102]. With metal centers that are virtually wholly insulated from external action, the clathrochelates generate enormous interest in the creation of models for active centers in ferments and siderophores, as subjects of photochemical, magnetochemical, and electrochemical studies, as well as species for boron–neutron capture in cancer therapy and magnetic resonance tomography. Moreover, this synthesis is a springboard for creation of new supramolecular systems [100–102].

4.6.2. Calixarenes

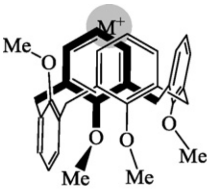
In a variation of noble cryptanoides, the calix[4]arenes **119** are substances of low origin. They appeared as the first industrial plastics because of the curiosity of some meticulous researchers of the very mundane phenol formaldehyde resin [4]. Conformationally, they are molecular-cups (greek *calyx*—bowl), synthesized, of course, not by isolation from the resin mentioned, as before, but by a controlled cyclocondensation of p-alkylphenols with formaldehyde in a basic medium giving **119** (Fig. 119) (R′ = H) [103]. Being hydrophilic and possessing a hydrophobic cavity, with a chemically modified lower edge, these compounds are capable of encapsulating both small neutral organic molecules and metal cations. Further to calix[4]arenes **119** (Fig. 119), calyx[6]- and calyx[8]arenes have been synthesized [104].

The diverse conformative properties of calixarenes are discussed in detail in a review [104]. The tetra-O-methyl derivatives (**119** (Fig. 119), R = H, R′ = Me) complex Li^+ and K^+ ions form a native conic conformation by coordination with four methoxy groups, meanwhile the coordination of K^+ and Ag^+ ions takes place in a



R = H, Me, t-Bu, cyclohexyl
R' = H, Me, Pr, etc.

Fig. 119.



120
M = K$^+$, Ag$^+$

Fig. 120.

119 **121**

Fig. 121.

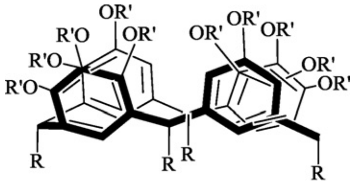
distorted, partially conic conformation, yielding complexes shown in **120** (Fig. 120), by the interaction of these ions with one oxygen atom and two benzene rings [4,104–106].

Interestingly, p-*tert*-butylcalix[n]arenes (n = 4, 6, 8) transport the Cs$^+$ ion from water to chloroform more effectively than they transport other s-metal hydroxides. The Cs$^+$ ion enters the cavity from the upper edge, being situated symmetrically between aromatic rings [106,107].

At present, exploitation of the lower edge of calixarenes by synthesis is a subject of interest [103]. Besides p-*tert*-butylcalix[n]arene **119** (R = *t*-Bu, R′ = H), thiacalix[4]arene **121** (Fig. 121) (R′ = H) (a cyclocondensation product of p-*tert*-butylphenol and sulfur in a basic medium), calix[4]resorcinarene **122** (Fig. 122) (R′ = H), and calix[4]pyrogallolarene **123** (Fig. 123) (R′ = H) (condensation products of resorcinol or pyrogallol with aldehydes in an acidic medium) are products of such chemical transformations [103].

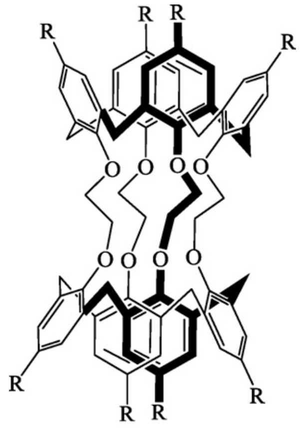
To diversify the ionophoric properties of calixarenes, their hydroxyl groups were alkylated yielding the fragments R′, whereby effective ion-selective extractants of s- and f-metal ions, as well as of some metal complexes, were obtained [103].

The synthesis of molecular bis-calix[4]arene tubes **124** (Fig. 124), as symmetrical- (equal R groups) and asymmetrical (distinct R groups) structures with high selectivity for complexing K$^+$ ions (maximal for the symmetrical structure **124** (Fig. 124) with R = *t*-Bu) [108], is interesting and of high-potential. We also mention the use of ionophoric properties of calixarenes in constructing artificial ionic channels [55].



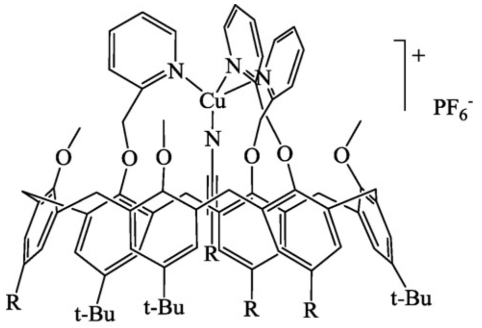
123

Fig. 123.



124

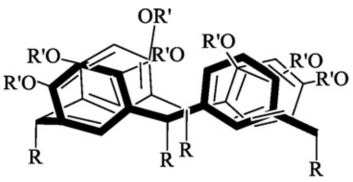
Fig. 124.



125a. R = t-Bu
125b. R = H

Fig. 125.

Copper “funnel-complexes” **125a,b** (Fig. 125a,b) based on calix[6]arenes form stable [109] coordination inclusion compounds with nitriles R′CN (R′ = Me, Et, Ph), penetrating the internal cavity through a molecular door below. In the complex **125b** (Fig. 125b), this door is appreciably expanded by the exchange of a part of

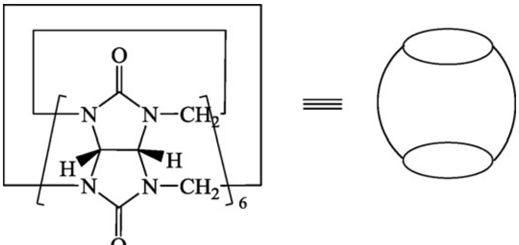


122

R = CH_3, C_9H_{19}, $C_{11}H_{23}$, *p*-OMe-C_6H_3,

R’ = H, CH_2COPh, CH_2COEt, CH_2CONEt, CH_2CO_2H, CH_2SO_3Na, Br, CH_2NMe_2,

Fig. 122.



126

Fig. 126.

the voluminous *tert*-butyl groups for small hydrogen atoms; this increases sharply the rate of exchange of nitrile guests. Thus, the systems **125a,b** (Fig. 125a,b) demonstrably imitate the channel of a hydrophobic substrate, which regulates the access of this one to the active center of the metalloenzyme.

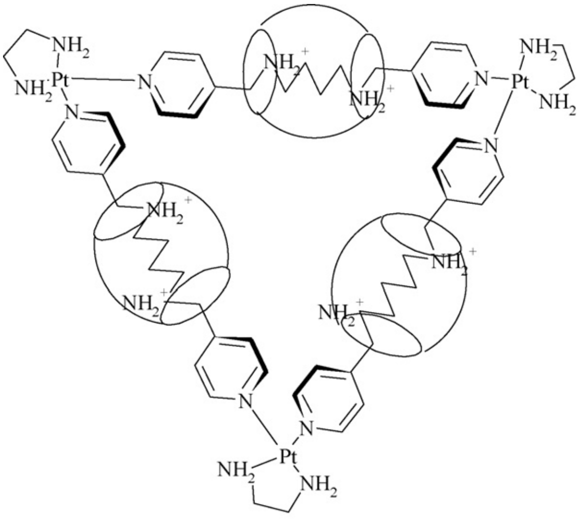
4.6.3. Cucurbiturils

The macrocyclic cavitand cucurbituril **126** (Fig. 126) derives such a strange, undoubtedly non-chemical name because of the similarity of its tubby molecule with a pumpkin belonging to the *Cucurbitaceae* family [4]. Besides the protonated polyamines, it encapsulates a great deal of metal salts [4,110].

The coordination of s- and f-metals with carbonyl groups in cucurbituril is an electrostatic ion–dipole interaction. d-Metal and 13-group metal ions are covalently linked to carbonyls. As regards aqua-ions $[Cr(H_2O)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$, the cucurbituril molecule **126** (Fig. 126) is closed by these ions at the expense of the system of hydrogen bonds formed between the carbonyl groups of cucurbituril and aqua-ligands [111].

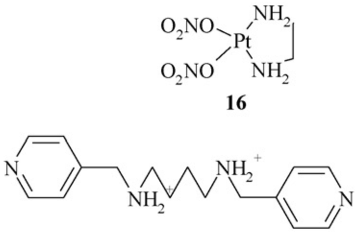
The self-assembled molecular necklace **127** (Fig. 127) with three cucurbituril molecules **126** (Fig. 126) participating as beads, three molecules of diprotonated diamine **128** (Fig. 128) as strings, and three complexes **16** (Fig. 16) as angle connectors with 90% yield is worthy of special attention [5,112].

Besides the structure in **126** (Fig. 126) with six monomeric units ($n = 6$), their homologues with $n = 5$, 7–10 were synthesized. Unprecedented selective encapsulation of the *trans*-$[Coen_2Cl_2]^+$ from a mixture of *cis*- and *trans*-isomers was carried out with cucurbit[8]uril [113]. Cucurbituril highlights the fascinating state-of-the-art science supramolecular chemistry is [114].



127

Fig. 127.



16

128

Fig. 128.

5. Other fundamental coordination motifs

The extreme diversification of coordination supramolecular structures makes their examination within the limits of a unified structural paradigm impossible. The paradigm of dimensionality, applied in the previous sections, is not justified in the examination of other fundamental coordination motifs in supramolecular coordination chemistry and should be modified in the examination of individual structures.

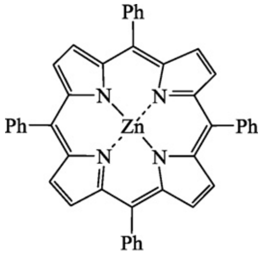
5.1. Porphyrins

Porphyrinic cyclic systems (**24a,b, 47, 48, 103** (Figs. 24a,b, 47, 48, 103)) were occasionally encountered as components of a molecular square and metallocyclophane, Tsivadze's structures [49], and metallodendrimer core, respectively. This circumstance, coupled with the extreme popularity of such construction blocks among metallosupramolecular chemists, merits their separate examination.

The construction paradigm for supramolecular porphyrin metal complexes is the axial coordination of electron-donor ligands by a central metal ion, frequently Zn(II). This ion, commonly disposed to sp^3- or sp^2d^2 hybridization, in the proximity of the plane porphyrin molecule has to accept the sp^2d electronic configuration yielding electron-deficient $4p_z$- and $4d_z{}^2$-orbitals, entering into a donor–acceptor interaction with electron-donor axial ligands. The resulting supramolecular complexes possess sufficiently high binding constants, as, for instance, the complex of piperidine with porphyrin shown in **129** (Fig. 129) ($K_a = 80{,}900\ L\,mol^{-1}$) [115].

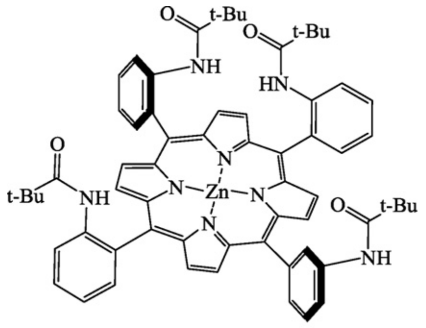
The introduction of hydroxyl-, amino-, amido-, and other donor groups in porphyrin molecules allows an additional binding of the axially coordinated ligand–guest by the tri-center type of interaction. Such modified porphyrins are capable of binding selectively natural compounds (amines, amino acids, sugars, etc.). The capability to identify diastereoisomers of natural compounds appears when chiral groupings, for instance, binaphthyl atropisomers, are introduced into porphyrins [115,116].

Use of picket-fences (for instance **130** (Fig. 130)) and strapped porphyrins [115,117] considerably stabilize the coordination of axial ligands. A strapped porphyrin has two peripheral posi-



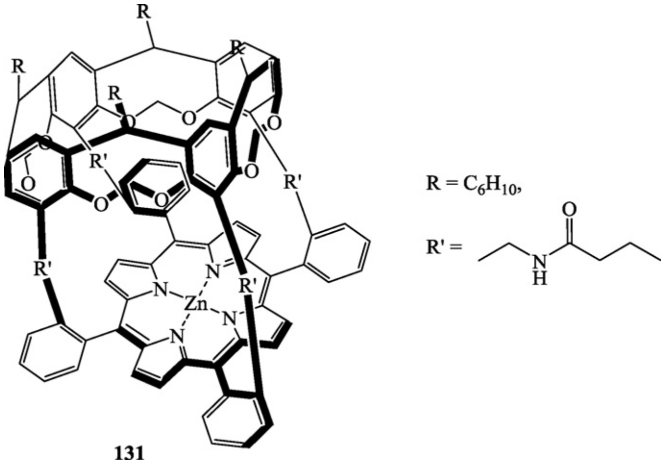
129

Fig. 129.



130

Fig. 130.



131

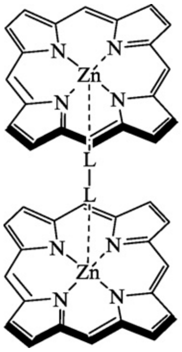
Fig. 131.

tions of the macrocycle linked by bridges of distinct nature. Porphyrins with calix[4]arene bridges [118], for example, the porphyrin **131** (Fig. 131) that forms a stable complex with pyrazole ($K_a = 1 \times 10^6$ L mol^{-1}), are highly effective host molecules.

Bidentate axial ligands form, in this case, the sandwich complexes **132** (Fig. 132) with binding constants $K_a = 1 \times 10^2$–10^6 L mol^{-1} [115,119,120].

The complexes **133** (Fig. 133) of dimers (tweezers) are the developments of this structural type and the dimers **134** (Fig. 134) with two flexible spacers are its completion [115,119,120].

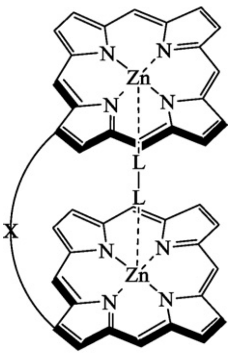
Spacer structures vary greatly [12,115] and serve particularly as calyx[4]arene platforms in tweezers of the type **133** (Fig. 133) [119].



L_2 = pyrazine, 4,4'-bipyridine (bipy), 1,4-diazabicyclo[2.2.2]octane

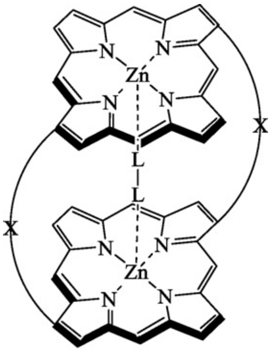
132

Fig. 132.



133

Fig. 133.



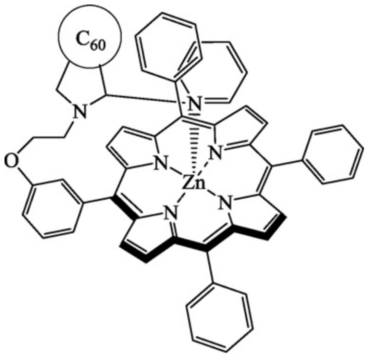
134

Fig. 134.

The covalent binding of the axial ligand through a spacer with a metalloporphyrin platform allows control of the distance “donor-acceptor”, for instance in the complex **135** (Fig. 135) [121], where a fullerene derivative acts as an axial ligand–acceptor for the electron. The axial coordination is broken by heating the system, exchange with a structurally related ligand (competitive axial coordination), or demetallation of the system.

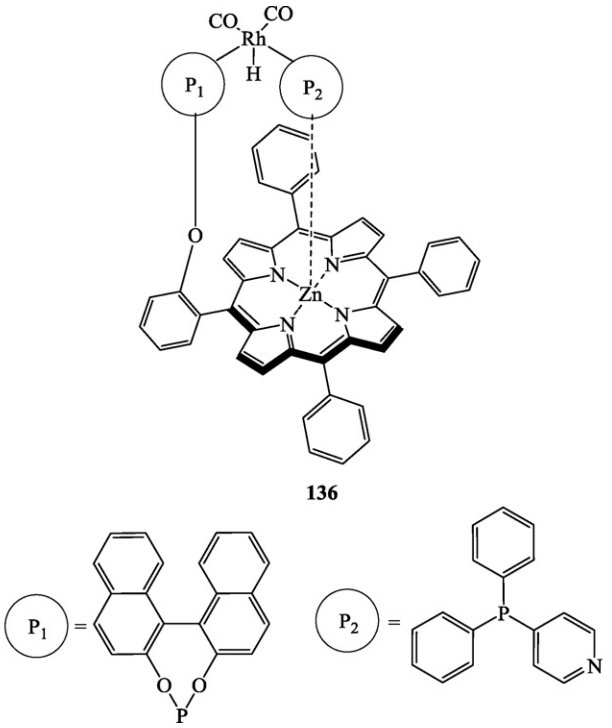
Effective supramolecular porphyrin catalysts of the type **136** (Fig. 136) [122] are similarly designed. Thus, the catalyst **136** (Fig. 136) was the best reagent for the hydrogenation of *N*-(3,4-dihydro-2-naphthalenyl)-acetamide (100% yield with enantiomeric excess of 94%) [122].

Metalloporphyrin hosts of the type **134** (Fig. 134) were successfully employed [123] for fullerene encapsulation. Combining the activity of π-acceptor guests with activity of host π-donors produces more stable complexes than with hosts such as calixarenes, resorcinarenes, and cycloveratrilenes.



135

Fig. 135.



136

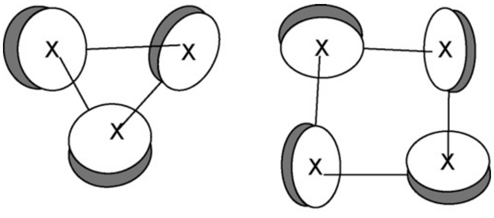
Fig. 136.

Zinc-porphyrin dimers of the type **133** (Fig. 133) turned out [124] to be popular models as they imitate some functional stages of light-harvesting antenna complexes in the photosynthesis apparatus. The species with a weak interaction between the porphyrin fragments (if the spacers X contain triple bonds, aromatic systems, oligomethylene bridges, peptides, systems of paired interactions of nucleobases) belong properly to supramolecular systems, according to Balzani's criterion (Section 2.1). Here, the energy transfer takes place through the spacers.

Zinc-porphyrin monomers **137** (Fig. 137) with a peripheral donor group X are capable of assembling spontaneously in cyclic- (**138 a,b** (Fig. 138a and b)) and open zigzag associates **139** (Fig. 139) at the expense of an axial coordination of the donor X [4,125].

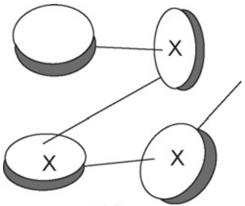
The monoporphyrins with two opposite peripheral donor ligands (structure **140** (Fig. 140)) are self-assembled in dimer supramolecular complexes **141** (Fig. 141) with a dimeric cyclophane architecture [125].

Diversified covalently linked supramolecular porphyrin constructions have become accessible due to an effective technique for their preparation starting from the basic dimer structures **142** (Fig. 142). This route is employed to prepare monodimensional *meso–meso*-linked linear groupings **143** (Fig. 143) with $n \leq 128$, porphyrin belts **144** (Fig. 144), windmills **145** (Fig. 145), lattices **146** (Fig. 146), rings **147** (Fig. 147), and boxes **149** (Fig. 149) (the boxes are formed by self-assembling four diporphyrin molecules **148** (Fig. 148)), and are studied as models of light-harvesting photosynthesis antennae [126].



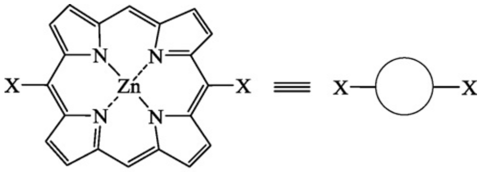
138a 138b

Fig. 138.



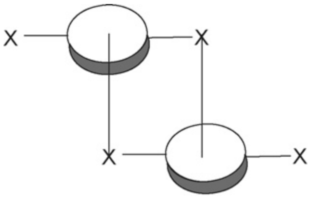
139

Fig. 139.



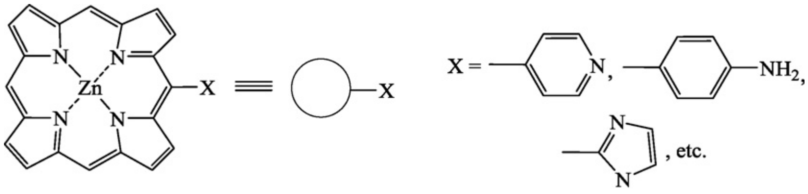
140

Fig. 140.



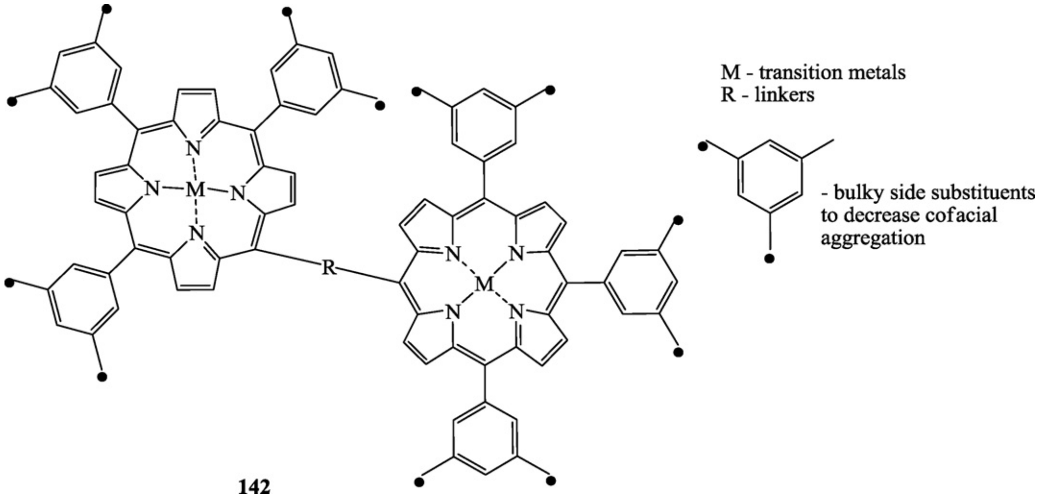
141

Fig. 141.



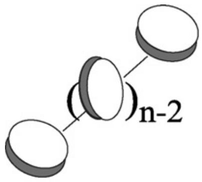
137

Fig. 137.



142

Fig. 142.

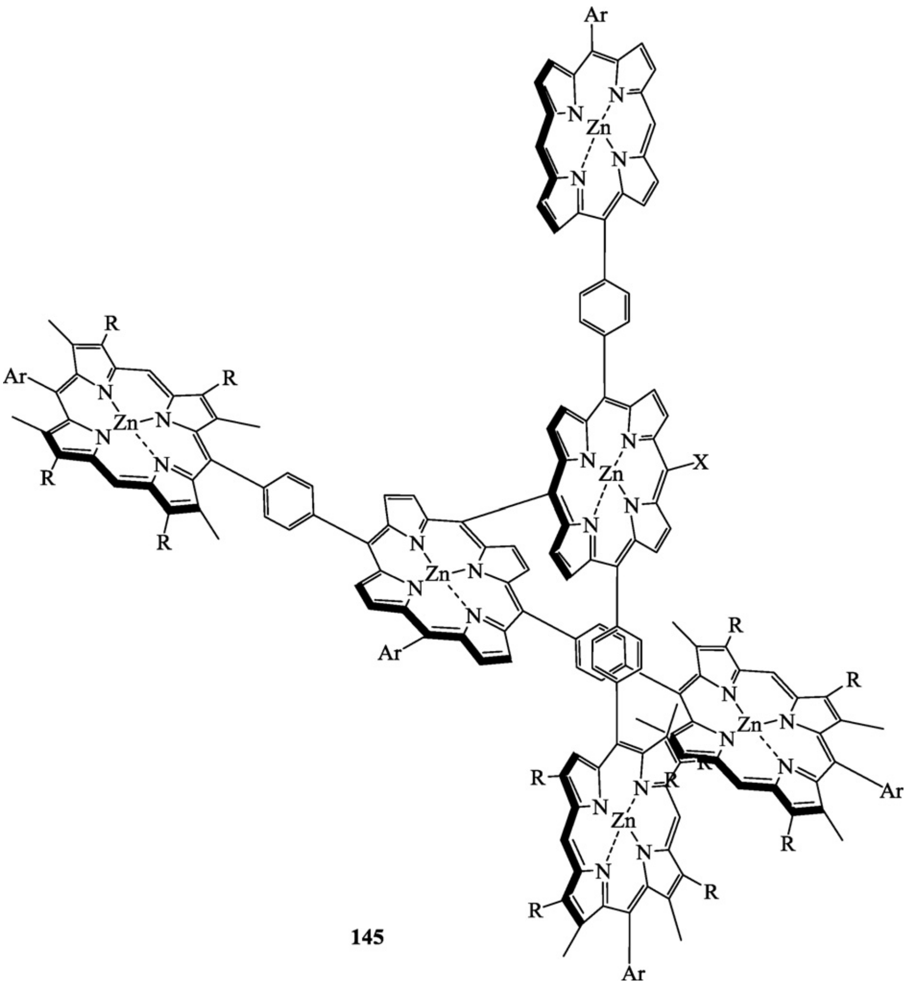


143

Fig. 143.

144

Fig. 144.



145

Fig. 145.

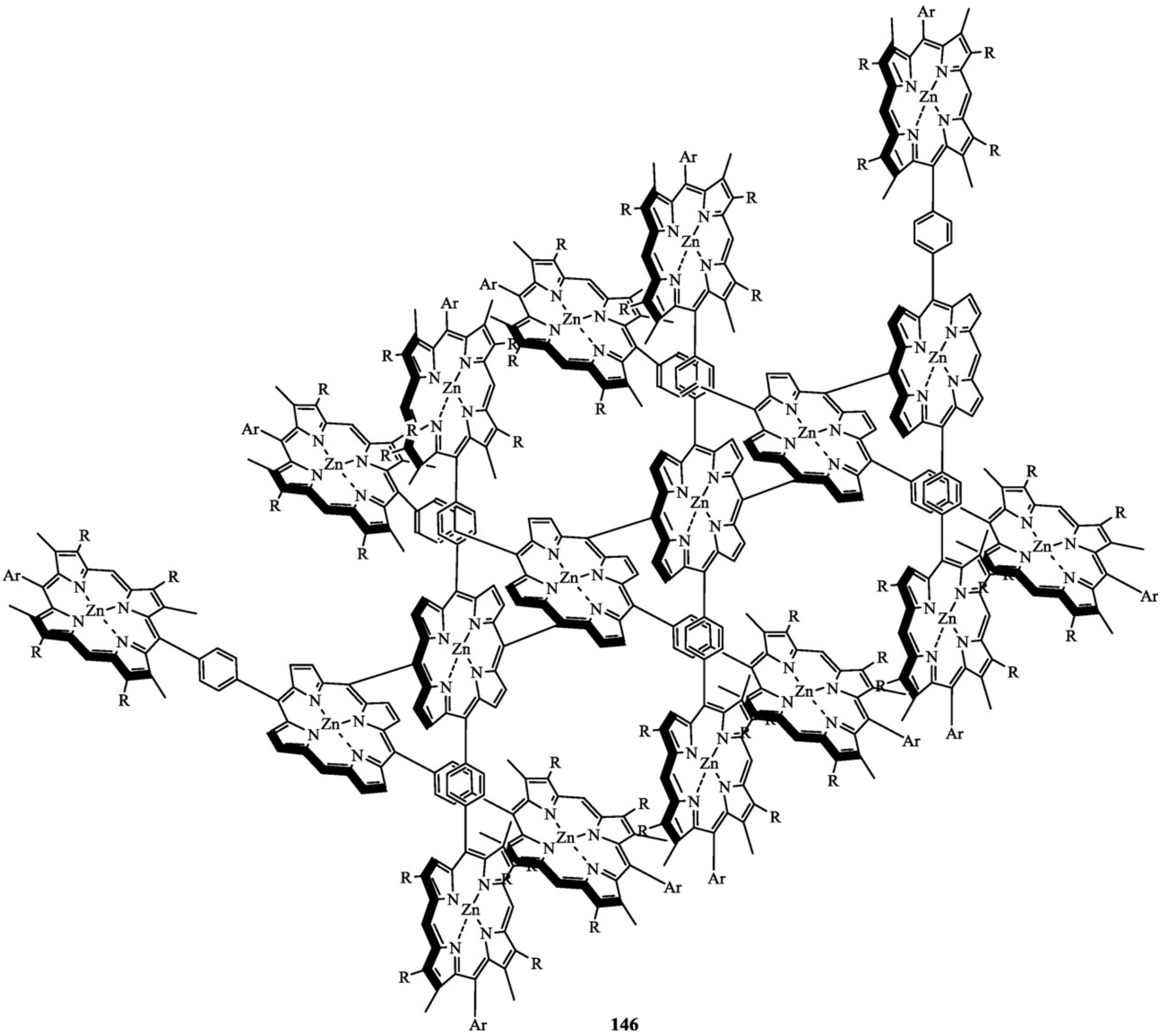

146

Fig. 146.

5.2. Coordination motifs in condensed matter

5.2.1. Liquid crystals

The liquid-crystal state has been associated with coordination compounds only for the last 30 years. The metallomesogens (the molecules forming liquid crystals) represent a considerably extensive area of coordination supramolecular chemistry [58,127–130], which we briefly examine here. The paradigm of this research field is obvious: the use of amphiphilic coordination compounds with polar heads containing metals. As an example, the Schiff base metallomesogens **150** (Fig. 150) [131] are shown; a series of other achievements of this research group in this area is reported in [132–147]. *o*-Cyclopalladates, such as the cyclopalladated azomethines **151** (Fig. 151), belong to a special, most researched group of these compounds [127]. The metallomesogenes [127,132–147] include also the lanthanide complexes of β-ketoenamines **152** (Fig. 152) [148–150].

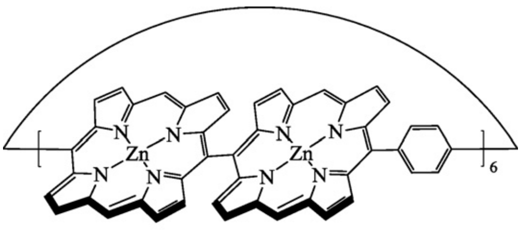

147

Fig. 147.

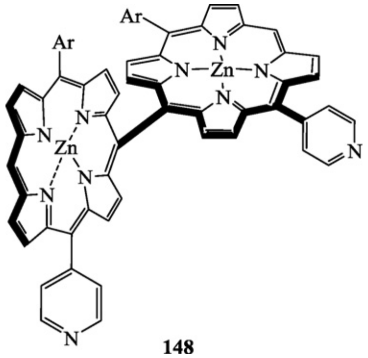
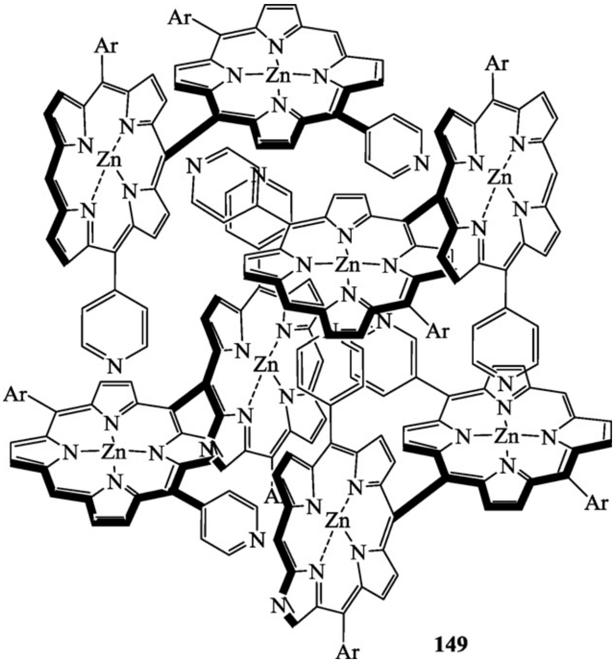
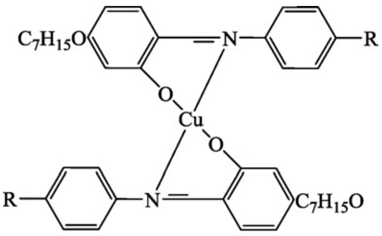

148

Fig. 148.



149

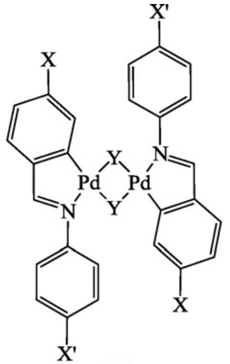
Fig. 149.



150

n = n-OC_6H_{13}, n-OC_7H_{15}, n-OC_8H_{17}

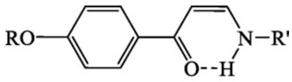
Fig. 150.



151

X = H, Me, OMe, OEt, OC_8H_{17}
X' = H, Me, OMe, OEt, OC_8H_{17}
Y = Cl, CH_3CO_2

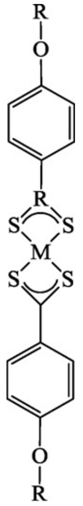
Fig. 151.



152

R = C_7H_{15}, $C_{12}H_{25}$,
R' = $C_{12}H_{25}$, $C_{18}H_{37}$, $C_{16}H_{33}$

Fig. 152.



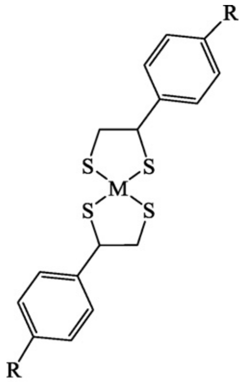
153

Fig. 153.

Dithiobenzoates **153** (Fig. 153), dithiolenes **154** (Fig. 154), and substituted β-diketonates **155** (Fig. 155) [127] have especially interested many researchers.

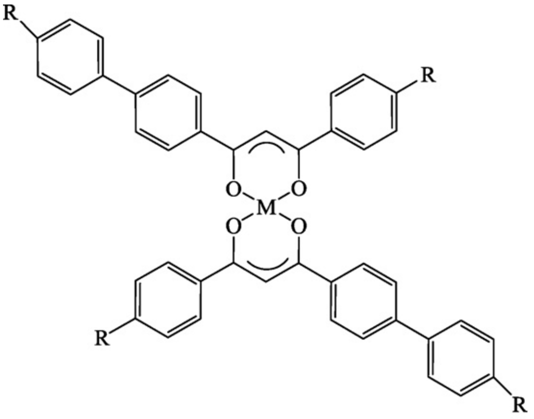
Usually, metallomesogenate ligands also possess liquid-crystal properties, and the introduction of a metal ion only expands the temperature range of the mesophase. Weak axial interactions of metal ions with donor groups of neighboring molecules definitely contribute to the formation of this mesophase [127].

Functional liquid crystals, combining useful properties and supramolecular organization of a mesophase, have attracted the attention of researchers in the last decade of the 20th century. For instance, o-cyclopalladated azomethines **156** (Fig. 156) with a crown-ether fragment [151] form, instead of an expected columnar mesophase, is a smectic phase (see below). The complex formed with potassium ions expands considerably the temperature range



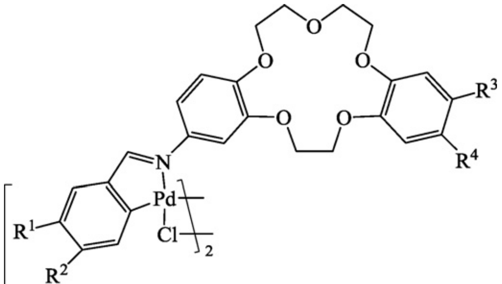
154

Fig. 154.



155

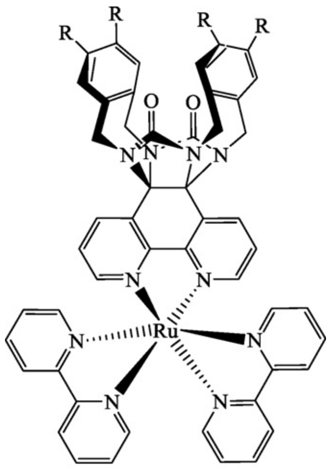
Fig. 155.



R^1- R^4 = $HOC_{10}H_{21}$

156

Fig. 156.



157a R = H

157b R = 

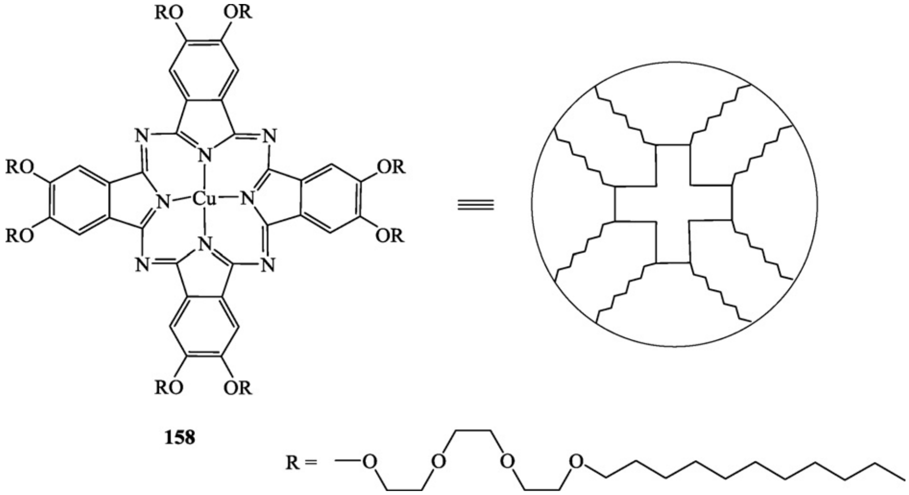
Fig. 157.

of the mesophase and stabilizes it further. It is intriguing that the initial ligands do not form mesophases [151], which are a rare example of the predominance of metal ions.

Amphiphilic metal-containing hosts (metallohosts) **157a,b** (Fig. 157a,b) with receptor cavities [152], which are capable of forming discrete nanostructures in aqueous media and whose character is determined by the size of glycoluril cavity, are a unique case. In the compound **157a** (Fig. 157a), the less spatially hindered part of one of the bipyridine ligands is clipped between the neighboring cavity walls, forming scroll-like aggregates of lengths ranging up to 10 mm and width about 100 nm. In the compounds **157b** (Fig. 157b), the neighboring cavity wall becomes clipped, forming rectangular aggregates of typical size 350 × 150 nm, which are sometimes combined into cigar-like aggregates. No species discussed above has attained nanometric size because of the thermodynamic limits on self-assembly. The smallest species, the metallodecahedron, is of diameter about 8 nm [153].

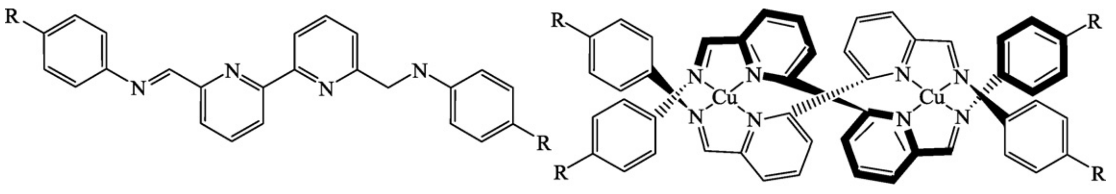
Initially, Ag^I and Hg^{II} (C.N. = 2, linear complexes) or Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II} (C.N. = 4 (square–plane complexes) were used as metal ions. Investigations in the past have indicated the possibility of including octahedral metallocenters (C.N. = 6) in liquid crystals. The next logical step was the use of metallomesogens with C.N. > 6 and the design of liquid crystals with C.N. = 8 or 9, *i.e.* with lanthanide ions [130].

The linear ligands of the azomethine- or β-ketoenamine types generate metallomesogens, forming thermotropic calamitic liquid crystals, including pneumatic (the molecular axes in mesogenes have some existing direction) and smectic phases (the mesogen molecules possess high order and form layers) [4,130].



158

Fig. 158.



159

160

R = $C_{12}H_{25}$

Figs. 159 and 160.

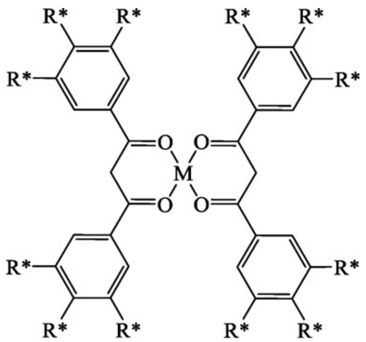
The molecules in the form of a disk are also thermotropic, *i.e.* on heating they form a liquid-crystal phase (mesophase) at the expense of the aggregation in the stacks of various columnar phases [4,130]. The disk-like metallomesogen **158** (Fig. 158) forms liquid-crystal stacks in polar solvents [154], *i.e.* a liotropic liquid-crystal system.

The progress in the area of metallomesogens is illustrated by two characteristic examples. Using a simple organization strategy for non-mesomeric, but lipid 1D bipyridines **159** (Fig. 159) of the azomethinic type around d-metal cations became [155] an effective synthesis method for earlier unavailable mesohelicates of the type **160** (Fig. 160). The formation of such structures has become possible due to the balance achieved between the rigidity of the central helicate core and the flexibility of paraffin chains.

The other example of self-assembling metallomesogens is [156] the formation of spiral supramolecular liquid-crystal structures from chiral plane β-diketonates of the type **161** (Fig. 161), possessing mesomeric properties at room temperature, which are stable in a wide temperature range. In its columnar mesophase, the columns are composed of plane mesogene disks, forming a herringbone-type 2D rectangular grouping **162** (Fig. 162) [156].

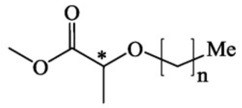
Octahedral chiral β-diketonate complexes **163** (Fig. 163), exist as propeller structures **164** (Fig. 164), form [156] liquid-crystal columns shown as homochiral stacks **165** (Fig. 165) (the Δ-configuration is shown), whose absolute configuration is determined by chirality of the initial ligand.

Plane homochiral oxazoline complexes **166** (Fig. 166) with two stereogenic centers form [156] rectangular columnar mesophases. However, a mixture of S,S and R,R diastereomers {M = Pd(II)} forms a hexagonal columnar mesophase [156].



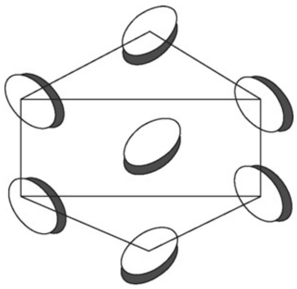
161

R* = D or L



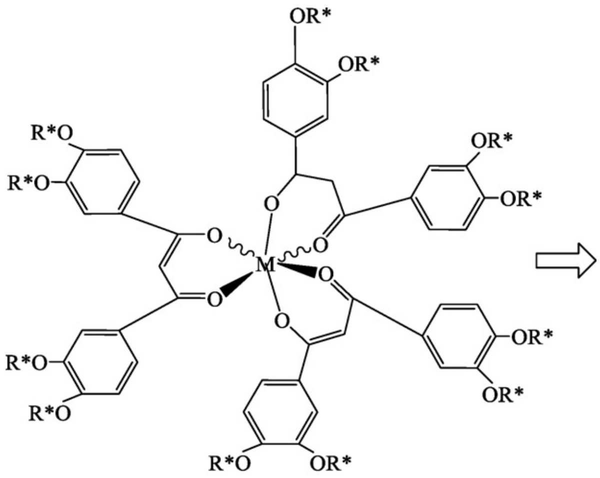
n = 5,6
M = Pd(II), Cu(II), VO(IV)

Fig. 161.



162

Fig. 162.

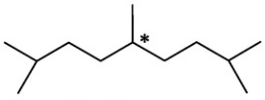


163

Fig. 163.

164

R* =



D or L
M = Fe(III), Co(III)

Fig. 164.

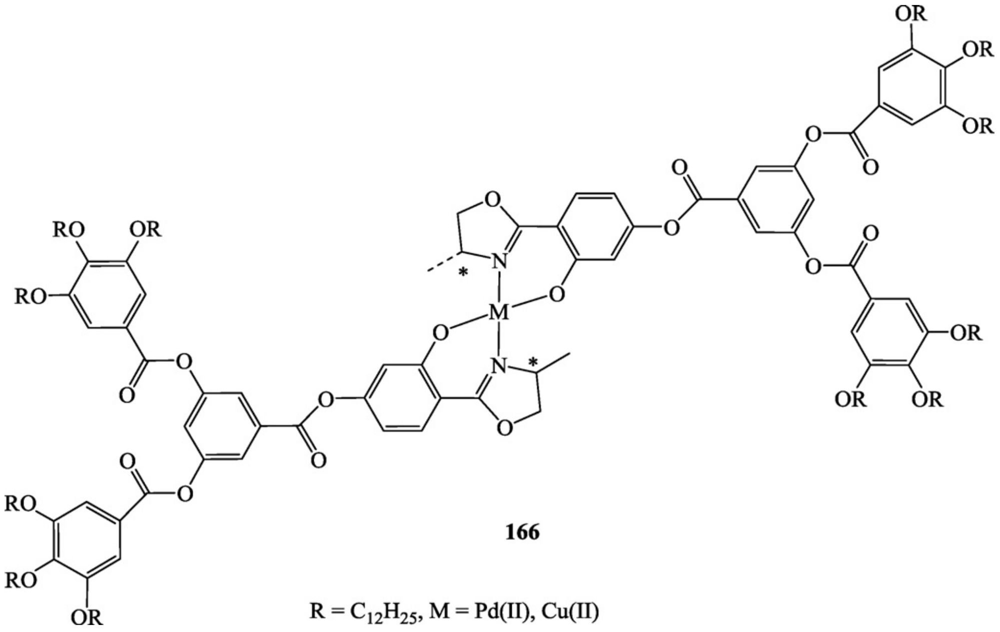
165

Fig. 165.

The complexes **160**, **161**, **163**, and **166** (Figs. 160, 161, 163 and 166) of columnar mesophases form helical heterostructures [156], and introducing stereogene centers into their initial ligands initiate optical activity in all the systems. These results are still of an academic character However, if functional molecules having optical or other useful properties as a part of their spiral structures, are synthesized, new molecular devices should be forthcoming from these materials [156].

5.2.2. Molecular crystals

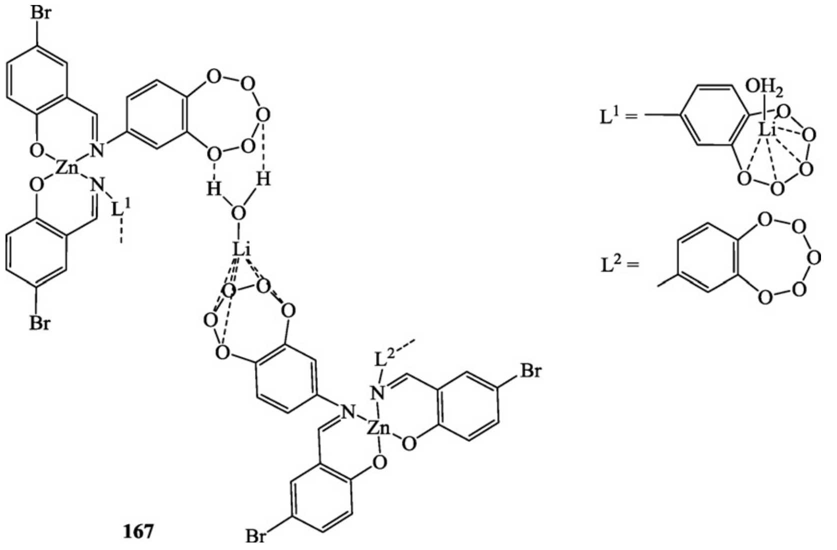
Since the crystals, including the molecular ones, are formed via self-assembly, they can also be considered supramolecular systems [4]. The driving forces for their self-assembly are non-covalent intermolecular interactions, to begin with the hydrogen bonds, besides the interactions between ion and ion, ion and dipole, dipole and dipole, and π and cation, π–π and stacking, and van der Waals forces [4]. Supramolecular engineering of crystals is achieved, basically, by coordination complexes [157–162] containing the sites capable of carrying out the intermolecular interactions described above and forming crystal structures such as adamantoides, cubic stairs, combs, helical stairs or brick-wall structures [161].



166

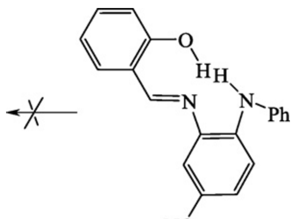
$R = C_{12}H_{25}$, M = Pd(II), Cu(II)

Fig. 166.



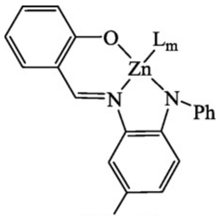
167

Fig. 167.



168

Fig. 168.



169

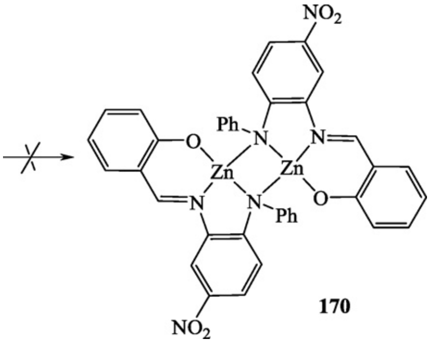
Fig. 169.

The sequence of creation of supramolecular metallolattices can be described first as the formation of 1D structures, 2D layers next, and their final unification in 3D lattices [157]. This can be informatively demonstrated by the example of Schiff base metal complexes, whose ligands belong to the most fundamental chelating systems in coordination chemistry [44,163]. Thus, the metal complex **44** (Fig. 44) yields a 1D structure **167** (Fig. 167) [47].

When the dibasic azomethine ligand **168** (Fig. 168) interacts with zinc acetate in methanol and potassium methylate, as a deprotonator, it leads to the formation of the trinuclear complex **171** (Fig. 171) [164] instead of the expected complexes **169** (Fig. 169) or **170** (Fig. 170).

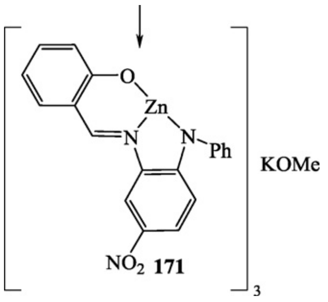
Single-crystal X-ray diffraction data showed that the complex **171** (Fig. 171) possesses the structure **172** (Fig. 172); the unitary layer in the crystal corresponds to the self-assembly **173** (Fig. 173) of such structures, unusually connected by K$^+$ cations of neighboring layers through the nitro groups [164]. Searches made for such structures in the Cambridge Crystallographic Database Center (CCDC) before publication of the cited work proved unsuccessful.

The zinc analogue of copper complex **46a** (Fig. 46a) on crystallization forms [48] bidimensional ribbons **174** (Fig. 174) at the expense of π–π-stacking between the neighboring aromatic fragments that carry the azomethinic- or macrocyclic groupings the short intermolecular distance of 3.650(5) Å between them. These ribbons are further merged in tridimensional structures at the expense of protruding macrocycles.



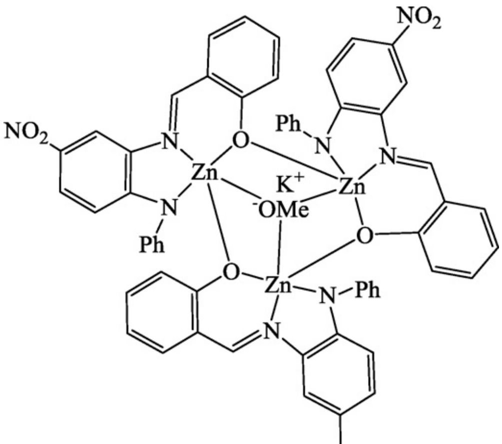
170

Fig. 170.



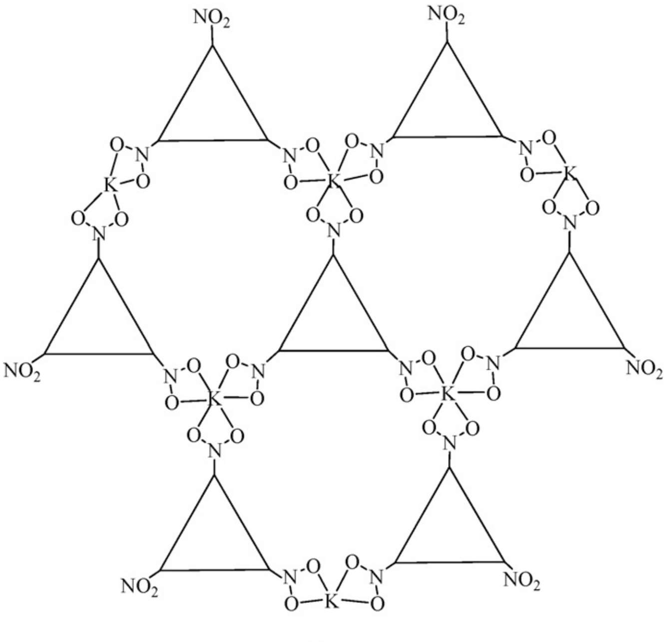
171

Fig. 171.



172

Fig. 172.



173

Fig. 173.

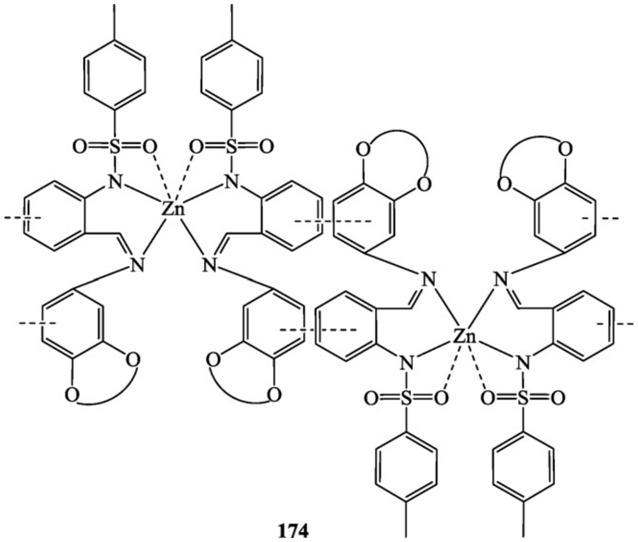


Fig. 174.

6. Conclusion

In this review, we have attempted to recount how coordination- and supramolecular motifs have gradually merged into an integral unit — supramolecular coordination chemistry, a new vast area of chemical science. This field relates to aesthetically imaginative metallosupramolecular templated and self-assembled constructions from a comparatively small number of basic molecular elements (rods, angles, etc.) similar to molecular LEGO [4,165] or a molecular library [166]. To all these, we could add the material kit of standard molecular blocks of bis-aminoacids used to synthesize nanostructures [167] and the concept of modular chemistry [168] — for the construction of specific species from molecular building blocks (modules), which are especially useful for obtaining microporous resistant materials, potential absorbents, chemical sensors, molecular sieves, and catalysts [169]. It is possible to functionalize the internal surfaces of the mesopores of mesoporous materials and use them for molecular linking, recognition, sensors, catalysis, and controlled delivery [170]. Molecular imprinting takes place when, during polymerization, cavities complementary to guest molecules form in a matrix-host [58,171,172]. For effective interaction with low-molecular guests, it is not obligatory for the polymer to possess cavities. DNA carries out such interaction by π–π-stacking or partially including (intercalating) a planar guest. Planar metal complexes [4,173,174] are successful intercalators and are capable of probing DNA, introducing luminescent sites into this molecule, to control its splicing.

The award in 2007 of the Nobel Prize in chemistry to Gerhard Ertl for his studies on chemical processes of solid surfaces confirms that the branch of supramolecular coordination chemistry has not been overlooked. Structural studies of Langmuir films (monolayers) and Langmuir–Blodgett films (multilayers), formed by metalloamphiphiles on the air–liquid interphase revealed [175] the prospects for their use as effective catalysts and sources of quantum dots. A technique for forming bidimensional metallolattices on Langmuir layers and their eventual transformation to Langmuir–Blodgett layers was developed [176]. Mono- and multilayers on solid surfaces have been studied in depth. Self-assembled monolayers (SAMs) have gained popularity, in particular, the chemo-assembly of products of *n*-alkanethiols on the surfaces of Au(1 1 1) and Ag(1 1 1) crystals [177], enabling control of their chemical properties and surface structure, which are important from both scientific- and technological points of view. *N*-alkanethiols, functionalized with diacyldiaminopyridine and chemosorbed on the gold nanoparticles, are capable of selectively recognizing flavin molecules at the expense of intermolecular hydrogen bonds [178]. Complex monolayers can be constructed by insertion of certain organic molecules (for instance, conjugated organic oligomers [179] or mercaptopropionic acid [180]) into SAMs, as well as by chemically modifying alkanethiolate components and adding the desired fragments, for example, fullerene derivatives (the supramolecular chemistry of fullerenes on surfaces [181]). SAMs are already among substances in nanotechnology form [182].

The elaboration of a series of construction methods of self-assembling templating structures, including those discussed in [183] has brought about these achievements in the area of bidimensional metallosupramolecular chemistry.

Organic crystal surfaces structurally resemble the Langmuir and Langmuir–Blodgett surfaces [184]. By adopting a conceptually new approach, namely surface-assisted self-assembly [185,186], a molecular beam of a ligand is deposited on the surface of metallic crystals. Metal atoms, liberated by electron beam bombardment, are then directed to form a ligand layer. Further annealing causes the metal atoms to interact with the ligand monolayer to form the desired metallocomplexes. These processes are performed under ultrahigh-vacuum conditions.

Ionophores (podands, coronands, cryptands or calixarenes) are utilized as components for recognizing systems in chemosensors [41,187–189], some of them are employed in commercial devices. However, the modern supramolecular designer's dream is to construct, on molecular scale, superminiature devices, which under the influence of external chemical-, electric-, or photonic impetus, are capable of dynamic conformative reconstructions. Such innovations are inspired by the discovery of dynamic biological systems, such as motor proteins, which control movements that carry out important biological functions (for example, ATP-synthase used as a rotatory motor and the actin-myosin complex as a linear motor [190]). d-Metal complexes (specifically cathenates and rotaxanes) have become especially essential for design and synthesis of artificial molecular motors or molecular cars [73,191]. Noteworthy success has been also achieved in the construction of immobile components for metallosupramolecular devices of the future, such as molecular wires [192–194], rectifiers [195,196], and switches [197]. Some ionophores were utilized [198] to carry out logistics operations; supramolecular bipyramidal Ru(II) complexes were capable of [199] photostable memory storage.

Intensive development in calixarene chemistry over the last two decades has led to the creation of a series of supramolecular systems possessing such fundamental properties as molecular recognition, membrane transport, self-assembly, and supramolecular catalysis [200]. Finally, we mention synthetically modified cyclodextrines, where a combination of hydrophobic cavities and metallochelate fragments converts these compounds to mimic enzymes (synzimes), siderophores, and ferredoxines [201].

A glance at the monographs, reviews, and original articles in this area is akin to the examination of a kaleidoscope with fascinating templated molecular self-assemblies. Thanks to the remarkable advances achieved in organic synthesis, these fantastic molecular metalloconstructions, capable of creating complex ligands, as many as desired, are to a greater or lesser degree preorganized for templating and self-assembly. Diversified polypyridine ligands [202–204], on repeated occasions noted above, testify to this fact. Also, the aesthetic desires of the many researchers, as driving forces in the creation of metallosupramolecular arabesques blending the splendid with the rational, cannot be ignored.

Brief information on supramolecular metalloconstructions is presented in the review [205]. Other state-of-the art accounts of supramolecular coordination chemistry are available in a special issue of the D.I. Mendeleev *Journal of Russian Chemical Society* [206].

The review [207] describes crown-containing chemosensor structures. Chemical modification of high-spin coordination polymers enhances considerably their diversifying capacity [208]. Templating uranylsilicates with various organic molecules [209] creates nanoclusters, which are a new group of organo-inorganic composite systems. Termolysis of certain metal complexes has become [210] a useful source of important nanocomposites with practical applications. The last two publications, together with the review [211], show clearly the relationship between supramolecular chemistry and nanochemistry and on their potential to direct/guide the creation of molecules and molecular assemblies with controlled dimensionality. Polyoxametallates [212a–c] and metal clusters [212d] could be considered precursors of supramolecular coordination structures such as coordination polymers [212d] and organic–inorganic hybrid materials [212e].

Vigorous development of supramolecular chemistry and, in particular, its coordination aspects, has aroused appreciation of the significance of chemistry and its place in modern natural sciences. According to Lehn, one of the founders of supramolecular chemistry, it is due to the self-assembly phenomenon that self-organization becomes dynamic to a greater degree, acquiring the fifth dimension in addition to the three spatial dimensions (structure) and time (kinetics) leading to the conception of a chemistry of five-dimensions [213]. This prophesy of one of the most authoritative chemist–thinkers has every chance to become a reality.

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