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Review
Обзор

Coordination Compounds Based on Metacyclophane Derivatives

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Dedicated to Academician Aslan Yu. Tsivadze on the occasion of his 75th Anniversary

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The solid-state structures of coordination complexes or extended coordination polymers based on the macrocyclic [1.1.1.1]metacyclophane backbone that inherently possesses a blocked 1,3-alternate conformation, have been reviewed. In order to obtain new ligands, N donor coordinating groups like cyano, pyridine, imidazole or pyrazole have been appended to the di or tetrasubstituted macrocycle platform. When combined with transition metals, metallamacrocycles or coordination networks of diverse dimensionalities have been obtained.

Keywords: Metacyclophanes, coordination polymers, coordination networks, metallamacrocycles.

Координационные соединения на основе производных метациклофана

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В обзоре представлены твердофазные структуры металлокомплексов и протяжённых координационных полимеров на основе новых макроциклических лигандов – ди- и тетразамещённых производных [1.1.1.1]мета-циклофана, содержащих нитрильные, пиридильные, имидазолильные и пиразолильные координирующие центры и самопроизвольно принимающие пространственную конфигурацию 1,3-альтернат.

Ключевые слова: Метациклофаны, координационные полимеры, координационные сетки, металломакроциклы.

Introduction

Among the diverse possibilities for the formation of coordination compounds, the use of macrocyclic based ligands always attracted lots of attention. Within the huge family of calixarenes,[1] "classical" calix[4]arenes and thiacalix[4]arenes[2] presenting large cavities and flexible conformations, are candidate of choice for the formation of coordination compounds presenting a wide variety of dimensionalities and topologies.

Along this line, different macrocycles have been already successfully used for the formation of extended coordination networks.[3] Coordination networks based on the use of porphyrines,[4] cyclodextrines,[5] calixarenes[6] or the combination of porphyrines with calixarenes[1] macrocycles have been reported. The coordination abilities of unsubstituted calixarenes[8] in order to obtain multinuclear complexes or cages,[9] have also been extensively explored.

The prediction of the coordination pattern for coordination compounds formation is a difficult task, and it is highly complicated by the use of flexible coordinating ligands. A possible approach to overcome this problem, in the case of calix[4]arenes, is based on the introduction of substituents which disturb the rotational process of the macrocyclic ligands and block the macrocycle platform in an appropriate conformation. For example, compounds derived from calix[4] arene bearing four *endo*-methyl and eight *exo*-methyl groups, and presenting a D_{2d} symmetry in the *1,3-alternate* conformation, appear to be less flexible than their parent compounds. Along this line, mesitylene[1.1.1.1]metacyclophane (**1**, Figure 1a), a conformationally preorganized macrocycle was synthetized decades ago, by bridging the four mesitylene moieties by methylene units.[10] This class of compounds, among them, the well-known mesitol-based calix[4larene or *exo*-calix[4larene derived from 2,4,6-trimethylphenol (**2**, Figure 1b), is remarkable, since their rigid concave surfaces are hold by conformational constraints intrinsic to the macrocyclic architecture. Indeed, owing to the steric hindrance between the different methyl groups, this type of backbone is relatively rigid and still to be blocked in *1,3-alternate* conformation over a wide range of temperature (60 °C to 150 °C).[11] An improved and simple two-step synthesis of this family of compounds bearing one to four OH groups (**2**, Figure 1b) has been reported previously.[12] Starting from **2**, the functionalization with Rn groups (n=1-4, Figure 1c), for the formation of new coordinating ligands is appealing.

Different chemical modifications of the [1.1.1.1]metacyclophane backbones have been proposed in the literature: tetrasubstitution with appending chiral[13] and diethylphosphonate[14] groups, formation of doubly crowned metacyclophane[15] and Schiff base[16] derivatives have been reported. Synthesis of nitroxide tetrasubstituted compound presenting some interesting magnetic properties has also been described.[17] In addition, [1.1.1.1]metacyclophane organometallic host for anions has also been previously obtained.[18] Some tetrasubstituted [1.1.1.1]metacyclophanes for specific organic anions recognition, like aminopyridinium[19] imidazolium derivatives have been reported.[20,21] Finally, [1.1.1.1]metacyclophane have also been used as the core for dendrimer-like species formation in combination with classical calix[4]arenes molecules.[22]

Concerning the formation of coordinating species towards transition metals, different chemical modifications of the [1.1.1.1]metacyclophane platform have been performed essentially by Hosseini's group in order to obtain new ligands: tetrasubstitution with thiol,[23] thiomethyl,[24] carboxylic,[24] aldehyde,[24] nitro,[24] amino,[24] diphenylphosphanyl,[24] diphenylphosphoryl,[24] bipyridyl[25] and quinolinyl appended groups.[25] Disubstituted compounds, with coordinating sites located in *syn* fashion, bearing groups like phenol, thiomethyl, *p*-methylthiophenyl, *p*-methoxyphenyl have also been reported.[26]

For all before mentioned macrocyclic compounds based on the [1.1.1.1]metacyclophane, it is important to note that no related coordination compounds were reported to date.

In this contribution, we describe the formation of coordination compounds based on the [1.1.1.1]metacyclophane with other coordinating groups. Twelve di- and tetra-functionalized macrocyclic ligands (**L**1-**L**12) are presented below and their synthesis will be briefly reviewed. Monodentate N donor coordinating groups have been used for the formation of coordination compounds: cyano, pyridine, imidazole or pyrazole. The combination of ligands **L**1-**L**12 with transition metals is reported, leading to crystalline materials that were analysed using X-ray diffraction. Their structures in the solid-state are discussed.

Coordination compounds based on [1.1.1.1]metacyclophane
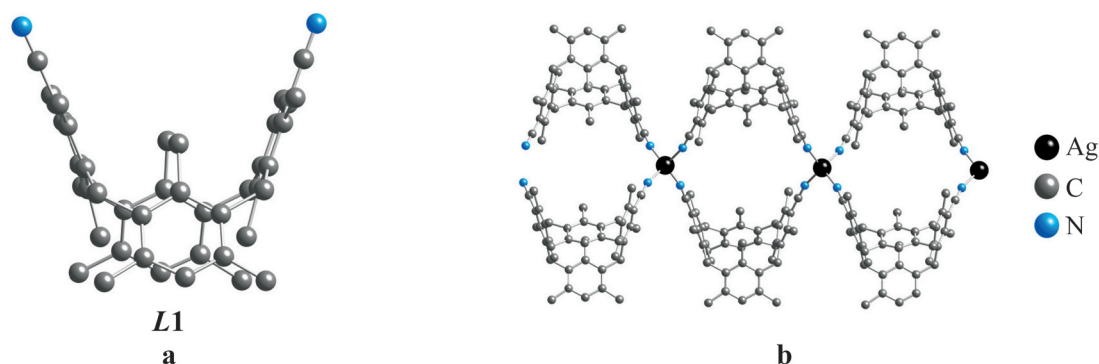
Disubstituted compounds

For the used disubstituted ligands, the coordinating sites are located in *syn* position on the same side of the macrocyclic ring. Four types of different monodentate coordinating groups (cyano, pyridyl, pyrazolyl and imidazolyl) have been used, leading to **L**1-**L**5.

Cyano disubstituted ligands

The disubstitution of the [1.1.1.1]metacyclophane backbone with cyano groups, located in *syn* position,
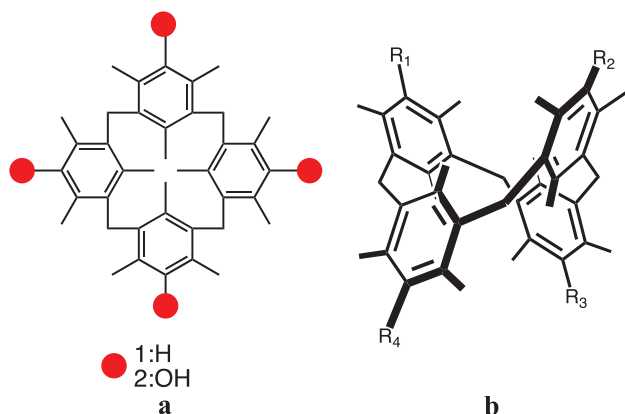
Figure 1. Macrocyclic compounds derived from [1.1.1.1] metacyclophane in *1,3-alternate* conformation. a) Mesitylene [1.1.1.1]metacyclophane **1** and mesitol-based calix[4larene **2**; b) [1.1.1.1]metacyclophane bearing R_n substituants (n=1-4).

L1

a

b

● Ag
● C
● N

Figure 2. A portion of the X-ray structure showing a) the cyano disubstituted *L*1 ligand, and b) the resulting monodimensional coordination compound of formula [(*L*1)$_2$(AgSbF$_6$)]·3H$_2$O·C$_2$H$_5$OH. H atoms, solvent molecules and anions are not presented for sake of clarity. Adapted from Ref.[27]

was achieved by the use of the dibromo intermediate of [1.1.1.1]metacyclophane (Figure 1b, R1=R2=H and R3=R4=Br), treated with CuCN, leading to *L*1 (Figure 2a).[26] Due to the location of the coordinating groups, this *bis*-monodentate ligand displays a «*V*-type» shape. When combined with AgSbF$_6$, it affords a 1-D coordination network in the solid-state (Figure 2b) of formula [(*L*1)$_2$(AgSbF$_6$)]·3H$_2$O·C$_2$H$_5$OH, with a M/L ratio equals to 1/2.[27] This compound can be regarded as the "fusion" of independent metallamacrocycles, since the used metal (Ag⁺) adopts a tetrahedral geometry.
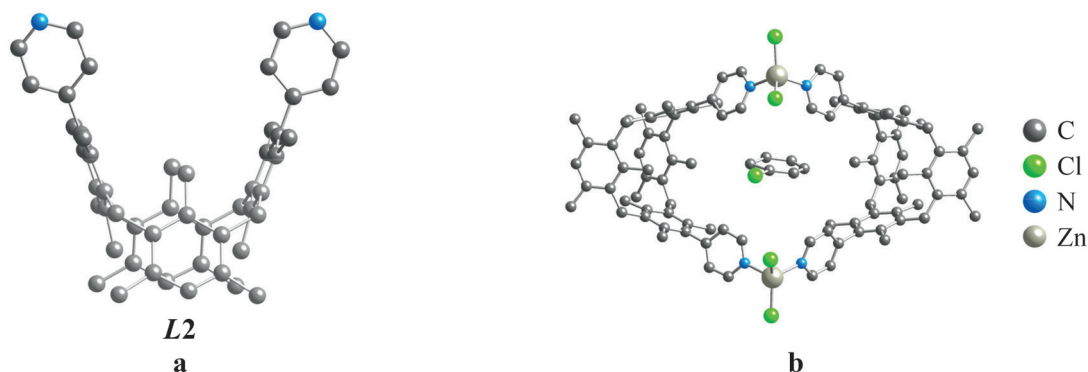
Pyridyl disubstituted ligands

Using the Suzuki reaction between the dibromo derivative (Figure 1b, R1=R2=H and R3=R4=Br) with 4-pyridyneboronic acid pinacol ester, ligand *L*2 has been prepared (Figure 3a).[26] In contrast with the previous case, the combination of the *V*-shaped ligand *L*2 with ZnX$_2$ (X=Cl, Br or I) leads, in the solid-state, to three isostructural neutral metallamacrocycles[28] (Figure 3b) of formula [*L*2(ZnX$_2$)]$_2$S (X=Cl, Br or I) (S=C$_6$H$_5$Cl, C$_6$H$_4$Cl$_2$ or C$_2$H$_5$OH). The binuclear metallamacrocycles possess a roof-shaped geometry, affording a pocket, where different solvent molecules can be located, depending on the nature of the used halide X.

In contrast, when the *V*-shaped ligand *L*2 is combined with HgCl$_2$, the formation of a 1D zig-zag system is observed in the solid-state (Figure 4).[27] The monodimensionnal compound of formula [*L*2(HgCl$_2$)]C$_2$H$_2$Cl$_4$ presents a M/L ratio equal to 1/1. This arrangement results from the association of a *V*-type bidentate ligand with a pseudo linear connector (metallic complex, HgCl$_2$).

Imidazolyl disubstituted ligands

The disubstitution of the [1.1.1.1]metacyclophane backbone with imidazolyl groups, located in *syn* position, has been performed through a nucleophilic reaction between the dichloromethylene dibromo intermediate (Figure 1b, R1=R2=CH$_2$Cl and R3=R4=Br)[29] and sodium imidazolate, in the presence of a catalytic amounts of NaI, leading to *L*3 (Figure 5a). The combination of *L*3 with different metal halides MX$_2$ (M=Co, Zn, Cu and Hg; X=Cl or Br) affords a series of "metallamacrobicycles" (Figure 5b) that revealed to be isostructural and display a M/L ratio of 1/1. The isolated mononuclear metallamacrocycles present the formula [*L*3MX$_2$]S (M=Co, Zn, Cu and Hg; X=Cl or Br; S=MeOH). The inner cavity of the metallamacrocycle reveals to be very small and no solvent molecules can be trapped inside.

L2

a

b

● C
● Cl
● N
● Zn

Figure 3. A portion of the X-ray structure showing a) the 4-pyridyl disusbtituted *L*2 ligand, and b) a binuclear metallamacrocycle of general formula [*L*2(ZnX$_2$)]$_2$S (X=Cl, Br or I), presenting a C$_6$H$_5$Cl molecule in its cavity. H atoms and other solvent molecules are not presented for sake of clarity. Adapted from Ref.[28]
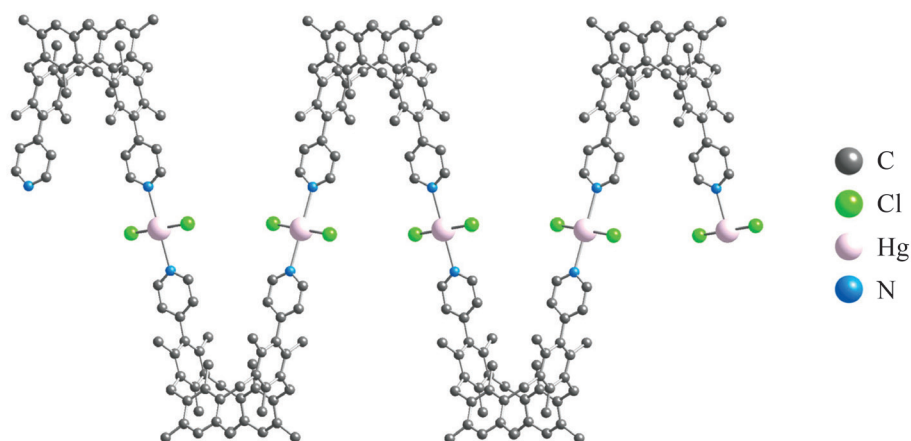
Figure 4. A portion of the X-ray structure of the resulting monodimensional coordination compound of formula [*L*2(HgCl$_2$)]·C$_2$H$_2$Cl$_4$. H atoms and C$_2$H$_2$Cl$_4$ molecules are not presented for sake of clarity. Adapted from Ref.[27]

Pyrazolyl disubstituted ligands

Two types of such ligands were synthetized. They are differentiated by the nature of both substituents located on the opposite side of the macrocyclic ring. We will distinguish the case of bromine substituent (*L*4) from the one of non-coordinating PhSMe chemical group (*L*5).

Disubstituted pyrazolyl ligand *L*4, bearing two pyrazolyl groups located on the same side of the macrocyclic unit, has been synthetized from the dibromo dichloromethyl intermediate (Figure 1b, R1=R2=CH$_2$Cl and R3=R4=Br) and condensed with sodium imidazolate (Figure 6a).[29] Due to flexibility of methylene pyrazolyl moieties, this ligand adopts no specific shape for coordination mode.

The combination of *L*4 with metal halides leads to the formation of four isostructural 1D coordination networks (Figure 6b)[29] of formula [*L*4(MX$_2$)] (M=Co or Zn and X=Cl and Br). The 1D chain results from connection between N atoms from pyrazolyl moieties with MX$_2$ species acting as *V*-shaped connecting nodes, with a M/L ratio of 1/1.

*L*5 was obtained by Suzuki cross-coupling between *L*4 and boronic ester containing PhSMe group using the microwave technique (Figure 7a).[29] Like *L*4, *L*5 doesn't adopt also any specific coordination shape when combined with metal cations.

The reaction of *L*5 bearing two pyrazolyl groups located on the same side of the macrocyclic ring with metal halide complexes CoX$_2$ (X=Cl and Br) produced, in the crystalline phase, a crenel-like 1D coordination network of formula [*L*5(CoX$_2$)] (X=Cl and Br) (Figure 7b),[29] demonstrating the similar connectivity pattern compared to previous described coordination compound based on *L*4, with the same M/L ratio equal to 1/1.

One can observe, that depending on the nature of the nitrogen containing coordinating sites (cyano pyridyl, pyrazolyl, imidazolyl) and also on the nature of the spacer between the coordinating group and the macrocyclic main plane, the combination of bidentate ligands *L*1-*L*5 with MX$_2$ species (M=Co, Zn, Cu, Hg, X=Cl, Br, I) or silver cations, acting as pseudo linear connectors leads either to discrete species (mono- or bi-nuclear metallamacrocycles) or 1D


*L*3

a

b
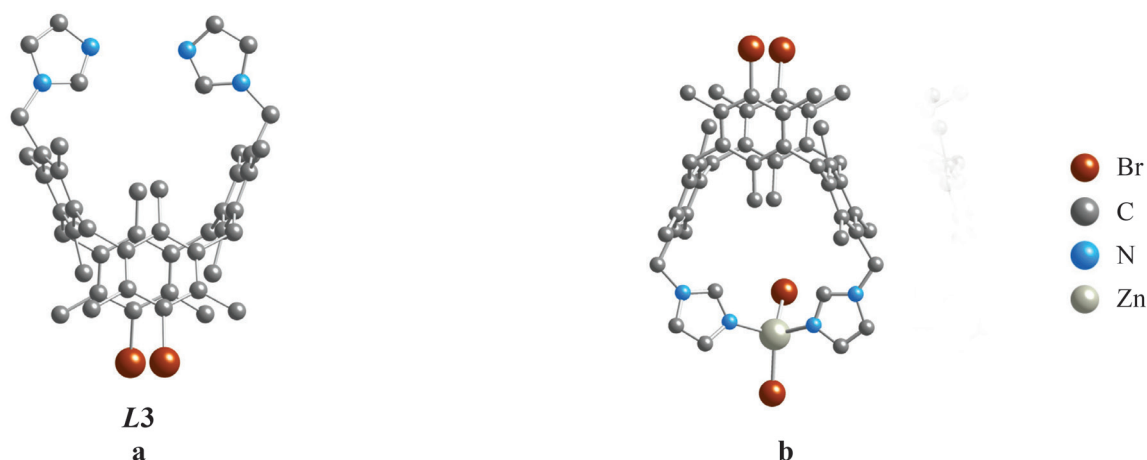
Figure 5. A portion of the X-ray structure showing a) the imidazolyl disusbtituted *L*3 ligand, and b) the metallamacrocycle of general formula [*L*3MX$_2$]S (M=Co, Zn, Cu and Hg; X=Cl or Br). H atoms and solvent molecules are not presented for sake of clarity. Adapted from Ref.[29]
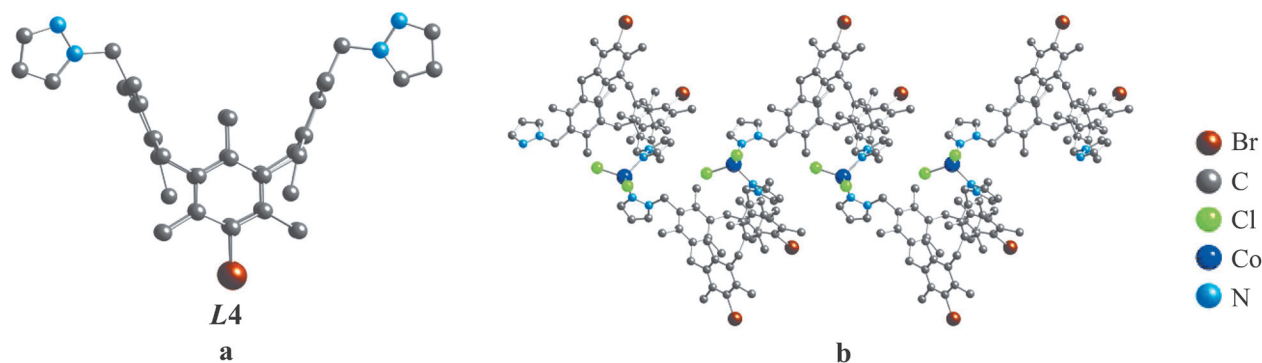
Figure 6. A portion of the X-ray structure showing a) the pyrazolyl disusbtituted *L*4 ligand, and b) the resulting monodimensional coordination compound of formula [*L*4(MX$_2$)] (M=Co or Zn and X=Cl and Br) (here M=Co and X=Cl). H atoms are not presented for sake of clarity. Adapted from Ref.[29]
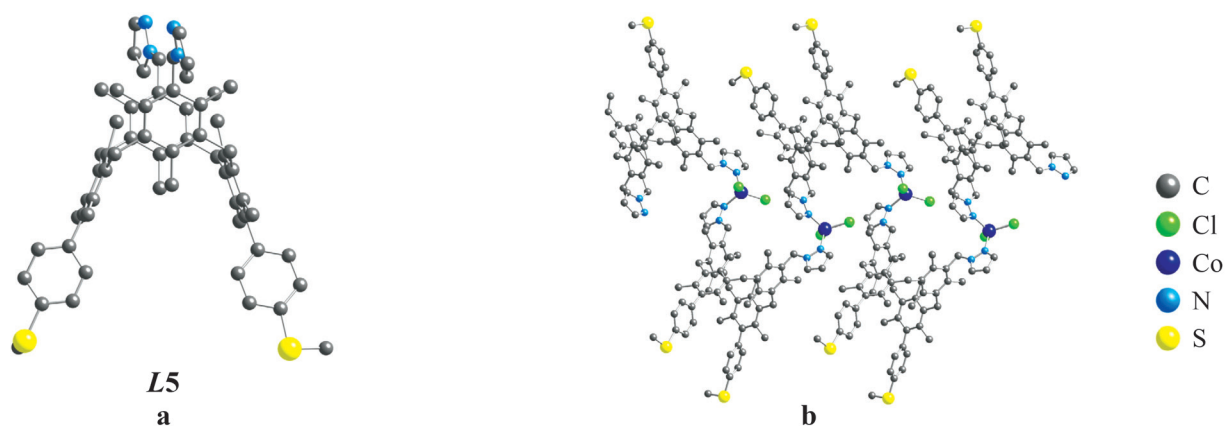
Figure 7. A portion of the X-ray structure showing a) the imidazolyl disusbtituted *L*5 ligand, and b) the resulting monodimensional coordination compound of formula [*L*5(CoX$_2$)] (X=Cl and Br). H atoms are not presented for sake of clarity. Adapted from Ref.[29]

extended coordination polymer. For the formation of coordination polymers of higher dimensionalities, the [1.1.1.1] metacyclophane derivatives bearing four coordinating sites, presenting a higher symmetry, are required.

Tetrasubstituted compounds

The tetrasubstituted ligands *L*6-*L*12, bearing monodentate cyano, pyridyl, imidazolyl or pyrazolyl coordinating groups behave as deformed tetrahedra or deformed rectangles presenting coordinating nitrogen atoms at their vertices. They will be presented below.

Cyano tetrasubstituted compounds

Two different ligands with appended cyano and cyanomethylene coordinating groups (*L*6 and *L*7, respectively) have been obtained. *L*6 was synthesised using the tetrabromo derivative (Figure 1b, R1=R2=R3=R4=Br, obtained using the already described strategy)[24] and CuCN as a source of CN anions (Figure 8a).[30]

Combination of *L*6 with AgPF$_6$ under self-assembly conditions leads to a 1D tubular coordination polymer, of formula [*L*6(AgPF$_6$)$_2$]2MeOH 1.5CH$_2$Cl$_2$, with a M/L

ratio equal to 2/1. It is formed by double bridging of consecutive rings, assembled by linearly coordinated metal centres and macrocyclic species presenting coordinating sites located at the vertices of a tetrahedron (Figure 8b).[30]

*L*7 differs from *L*6 by the presence of the methylene junction between the cyano coordinating sites and macrocyclic platform. *L*7 was obtained using the treatment of the tetrachloromethylene derivative (Figure 1c, R1=R2=R3=R4=CH$_2$Cl, obtained using the already described strategy)[24] with KCN in DMF (Figure 9a).[31]

It was established, that a slight modification of the stoichiometry between *L*7 and silver salts during the synthesis, leads to the formation of different coordination compounds. Indeed, the binuclear metallamacrocycle of formula [*L*7(AgNO$_3$)$_3$]$_2$·6CHCl$_3$(Figure 9b) has been prepared when the 4-fold excess of silver nitrate was used with respect to *L*7.[31] The size of the inner cavity of the metallamacrocycle doesn't allow any interaction with solvent molecules. In the present case, one of the four coordinating cyano groups of *L*7 remains non-coordinating which allows the nitrate anion to enter in the coordination sphere of the silver cation (Figure 9b).

As already mentioned, the enhanced flexibility of *L*7 respecting to *L*6, when combined with silver cations in two-
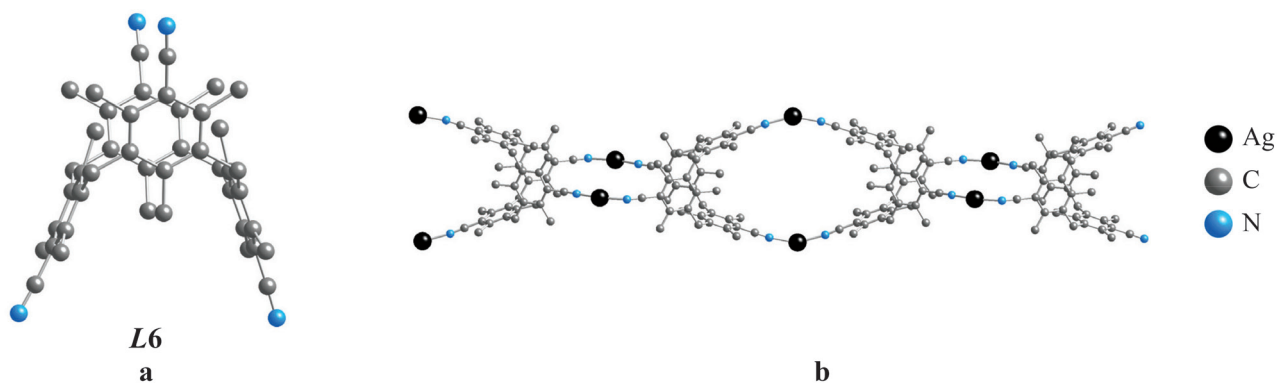
Figure 8. A portion of the X-ray structure showing a) the cyano tetrasusbtituted **L**6 ligand, and b) the resulting monodimensional coordination compounds of formula [**L**6(AgPF$_6$)$_2$]·2MeOH·1.5CH$_2$Cl$_2$. H atoms, anions and solvents are not presented for sake of clarity. Adapted from Ref.[30]
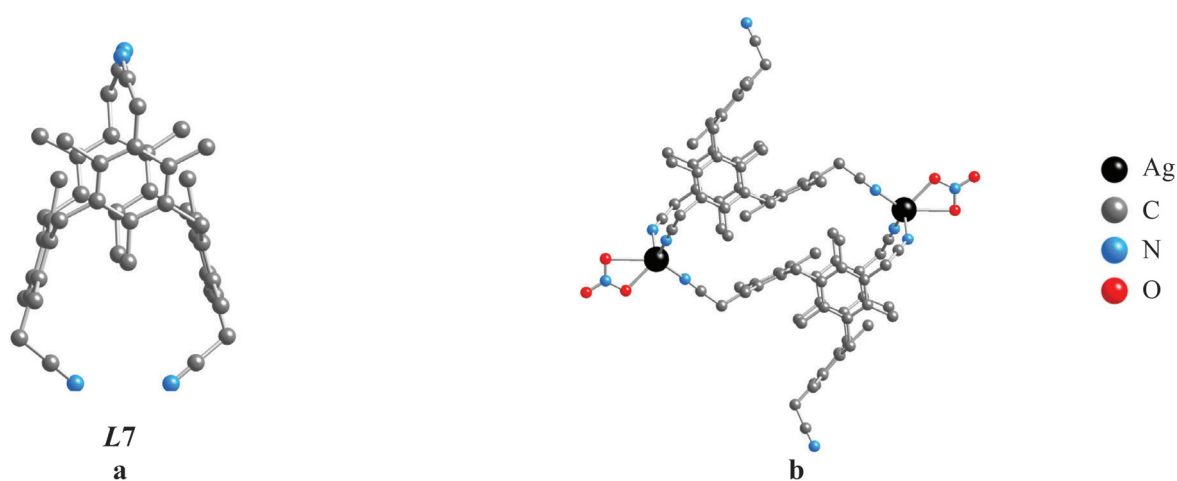
Figure 9. A portion of the X-ray structure showing a) the methylcyanotetrasusbtituted **L**7 ligand, and b) the resulting metallamacrocycle of formula [**L**7(AgNO$_3$)$_3$]$_2$·6CHCl$_3$. H atoms and solvent molecules are not presented for sake of clarity. Adapted from Ref.[31]
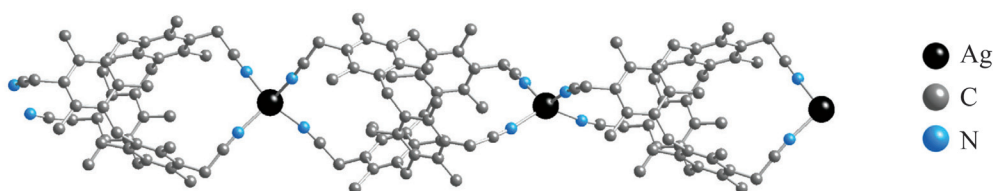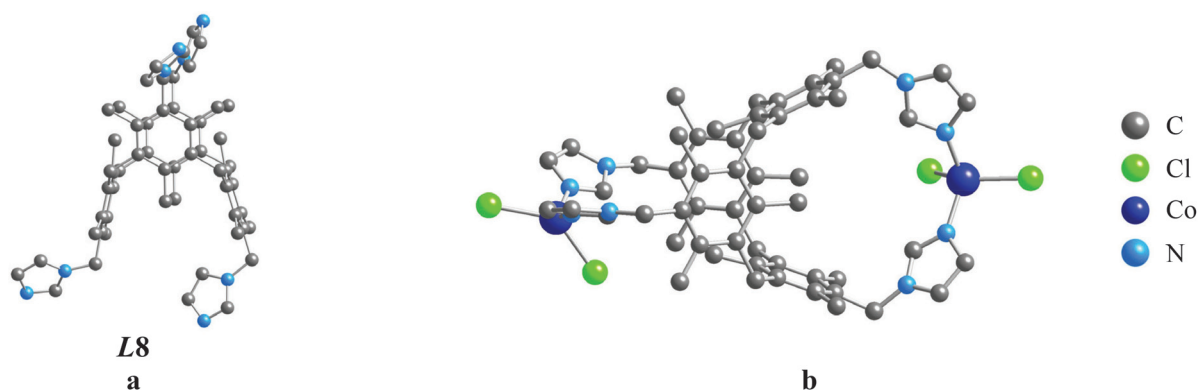

Figure 10. A portion of the X-ray structure the resulting monodimensional coordination compounds of formula [**L**7(AgX)]$_3$ (X= BF$_4$ or NO$_3$). H atoms and anions are not presented for sake of clarity. Adapted from Ref.[31]

fold excess, leads in the solid-state to the formation of iso-structural non-tubular 1D coordination polymers of formula [**L**7(AgX)]$_3$ (Figure 10).[31] Although the M/L ratio remains the same (1/1) in the crystal of [**L**7(AgX)]$_3$ (X=BF$_4$ or NO$_3$), all appended coordinating sites of **L**7 are involved in coordination bonds with tetrahedral silver atoms. The recognition pattern between ligands and metals results from the connection between two units acting as tetrahedral building blocks using coordination bonds.

Imidazolyl tetrasubstituted compounds

When the tetrachloromethylene derivative[24] (Figure 1c, R1=R2=R3=R4=CH$_2$Cl) was treated with sodium imidazolate, **L**8 has been successfully obtained (Figure 11a).[32] Its combination with MX$_2$ species (M=Co, Cu and Zn and Hg; X=Cl or Br) affords the formation of a series of analogous neutral metallamacrotricycles of formula [**L**8(MX$_2$)$_2$]S (M=Co, Cu and Zn and Hg; X=Cl or Br), S=CHCl$_3$, C$_2$H$_4$Cl$_2$,

Figure 11. A portion of the X-ray structure showing a) the imidazolyl tetrasusbtituted ligand **L8**, and b) the resulting metallamacrocycle of general formula [**L8**(MX$_2$)$_2$]S (M=Co, Cu and Zn and Hg; X=Cl or Br), S=CHCl$_3$, C$_2$H$_4$Cl$_2$, H$_2$O or CH$_3$OH (here M=Co and X=Cl). H atoms and solvent molecules are not presented for sake of clarity. Adapted from Ref.[32]

H$_2$O or CH$_3$OH (Figure 11b).[32] No solvent molecules were found to be accommodated inside the formed cavities of the metallamacrocycles.

Pyrazolyl tetrasubstituted compounds

Following the synthetic procedure described earlier for **L8**, when sodium pyrazolate was used instead of sodium imidazolate, the tetrasubstituted compound **L9** has been obtained in a high yield (Figure 12a).[33] Unlike the previous case, this compound, while being combined with CuBr$_2$, leads to formation of a 1D tubular-like coordination polymer of formula [**L9**(CuBr$_2$)$_2$], that presents a M/L ratio of 2/1 (Figure 12b).[33] Its structure results from the connection between pseudo-linear shaped CuBr$_2$ nodes and two monodentate coordinating N pyrazolyl atoms, located at the vertices of a tetrahedrons formed by the adjacent metacyclophane molecules.

At the same time, when MX$_2$ (M=Co, Zn and X=Cl or Br) was used in combination with **L9**, the formation of a series of isostructural 2D coordination networks was observed, presenting a M/L ratio of 2/1, with the formula [**L9**(MX$_2$)$_2$] (M=Co, Zn and X=Cl or Br) (Figure 13a).[33] The connectivity pattern of the obtained 2D grids results from the interconnection between the neutral metallic nodes acting as pseudo linear connectors, and the macrocycle molecules, acting as tetramonodentate ligands adopting deformed rectangular

shape. The crystal packing of the 2D arrays is presented on the Figure 13b, showing the antiparallel arrangement.

Dipyridyl and dipyrazolyl tetrasubstituted compounds

Compared to the previously described highly symmetrical compounds **L6**-**L9**, tetrasubstitued ligand **L10** presents two different monodentate moieties: pyridyl and imidazolyl, located both in alternate fashion on the macrocyclic unit. The synthesis of **L10** was achieved by Suzuki cross-coupling using **L4** and 4-pyridylboronic acid ester under microwave heating conditions (Figure 14a).[29]

The combination of the acentric ligand **L9** with ZnCl$_2$ afforded a directional grid-like 2D network of formula [**L10**(ZnCl$_2$)$_2$]$_4$·2(CH$_3$OH), 2(H$_2$O), with a M/L ratio of 2/1 (Figure 14b).[29] The tetrahedral metallic centres act as linear connectors between the rectangle building blocks formed by **L10**. The packing of the two-dimensional layers leads to a non-polar 3D organisation in the crystal.

Pyridyl tetrasubstituted compounds

To the best our knowledge, only two examples of [1.1.1.1]metacyclophane derivatives bearing four pyridyl coordinating sites **L11** and **L12**, different by the junc-
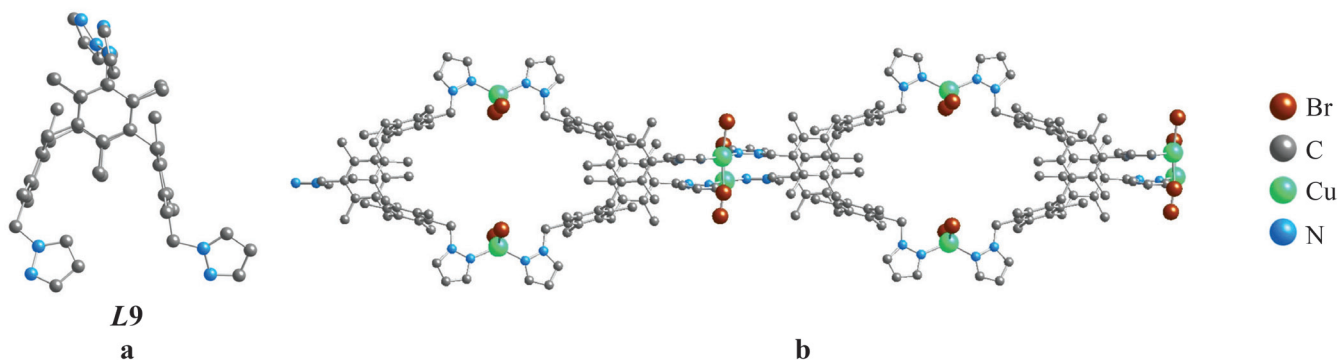
Figure 12. A portion of the X-ray structure showing a) the pyrazolyl tetrasusbtituted **L9** ligand, and b) the resulting monodimensional tubular-like 1D coordination polymer of formula [**L9**(CuBr$_2$)$_2$], H atoms are not presented for sake of clarity Adapted from Ref.[33]
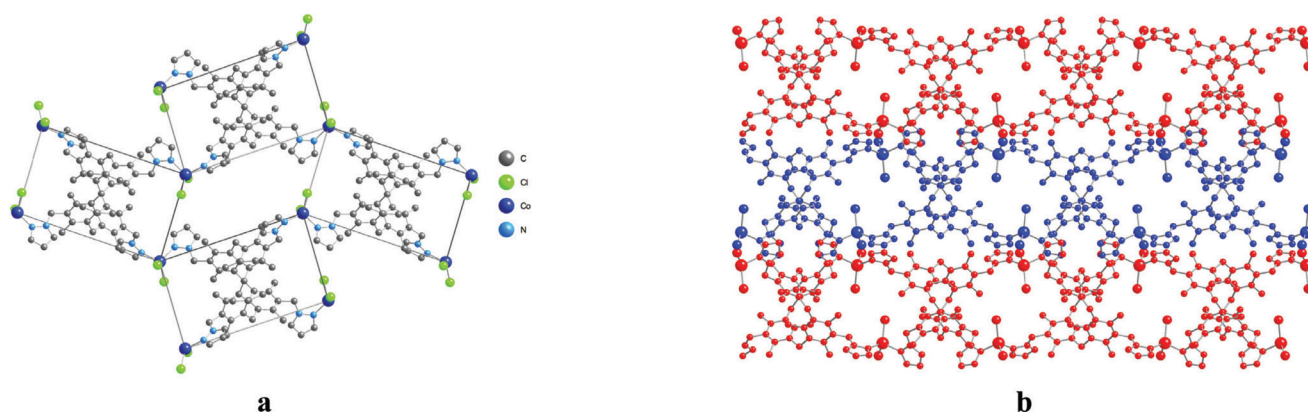
Figure 13. A portion of the X-ray structure showing a) the resulting two-dimensional coordination compound of general formula [**L**9(MX$_2$)$_2$] (M=Co, Zn and X=Cl or Br) (here M=Co and X=Cl) and b) packing of the grids. H atoms are not presented for sake of clarity. Adapted from Ref.[33]
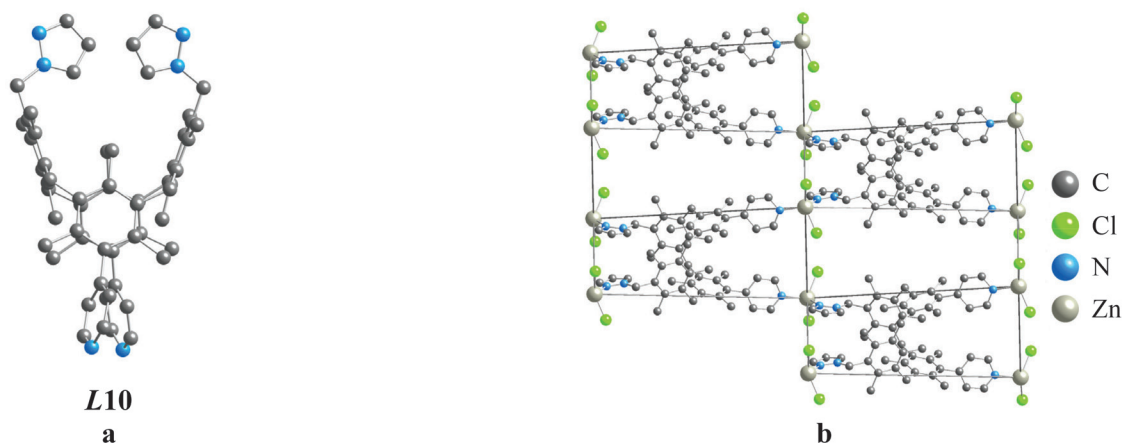
Figure 14. A portion of the X-ray structure showing a) the imidazolyl tetrasubstituted **L**10 ligand, and b) the resulting two-dimensional directional coordination compound of formula [**L**10(ZnCl$_2$)$_2$]$_4$·2(CH$_3$OH), 2(H$_2$O). H atoms and solvent molecules are not presented for sake of clarity. Adapted from Ref.[29]

tion between the macrocyclic platform and the appended substituents, have been reported. **L**11 was obtained using the Suzuki cross-coupling of the tetrabromo derivative[24] (Figure 1b, R1=R2=R3=R4=Br) and 4-pyridineboronic acid ester (Figure 15a).[34] The self-assembly of **L**10 with AgPF$_6$ afforded the formation of a fourfold interpenetrated 3D coordination network (Figure 15b) in the solid-state, presenting the following formula [**L**11(AgPF$_6$)$_2$]2C$_6$H$_4$Cl$_2$10H$_2$O.[34] The pseudo diamondoid 3D network, with a M/L ratio of 2/1, is formed due to the bridging of linearly coordinated silver cations with consecutive ligands acting as pseudo-tetrahedral molecular building block soffering four coordinating sites for binding metallic cations.[35] Although such type of coordination pattern leads to the formation of very large pores, the fourfold interpenetration of networks within the crystal reduces the porosity of obtained coordination compound (Figure 15c).

It is worth to note that, unlike the previous case, the more flexible **L**12,[36] obtained upon condensation reaction between the tetrahydroxy[12] derivative (**2**, Figure 1b, R1=R2=R3=R4=OH) and nicotinoyl chloride (Figure 16a), leads to the formation of a tubular 1D coordination polymer

of formula [**L**12(AgC$_7$H$_7$SO$_3$)$_2$]·6(CHCl$_3$), (C$_2$H$_6$OH), when combined with silver tosylate. The compound presents a with a M/L ratio of 2/1. In the crystal, the consecutive macrocycles are double bridged by metal centres (Figure 16b), adopting a *T*-shape geometry of coordination sphere where two sites are occupied by N atoms belonging to adjacent macrocycle molecules and the third one is coordinated a tosylate anion through the oxygen atom.

At the same time, it was shown, that the coordination of **L**12 with HgCl$_2$ leads to the formation of a doubly interpenetrated structure of 2D coordination networks[36] with the formula [**L**12(HgCl$_2$)$_2$]·2(C$_2$H$_6$OH)·0.5(C$_6$H$_5$Cl) (H$_2$O) (Figure 17b). Displaying a M/L ratio equal to 2/1, this coordination compound is formed by the interconnection between the neutral metallic nodes acting as linear connectors, and ligands **L**12 are adopting a deformed rectangular shape in the tetrakismonodentate mode.

As it has been expected, the combinations of tetrasubstituted **L**6-**L**12 with different metal salts generally leads to formation of coordination compounds of various dimensionalities (metallamacrocycles, 1D, 2D and 3D).
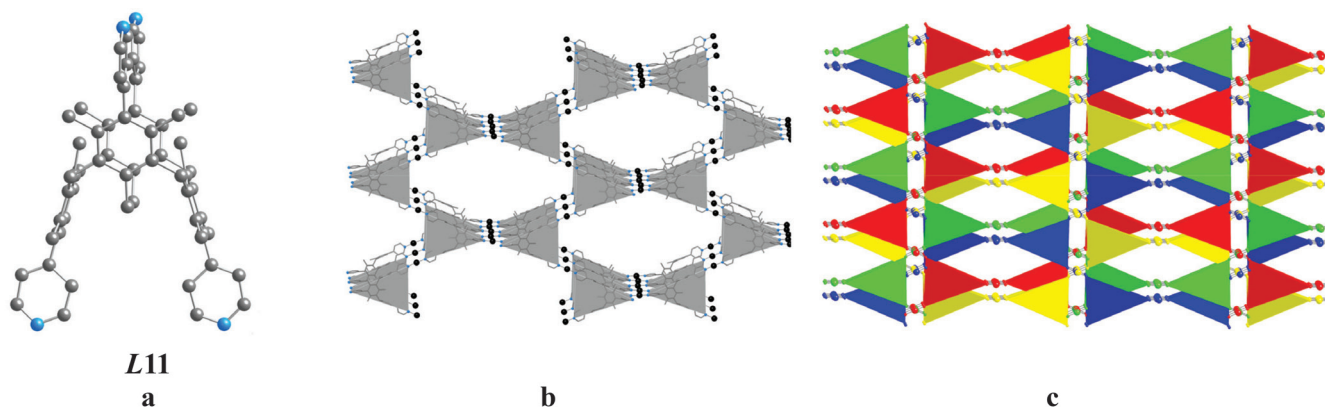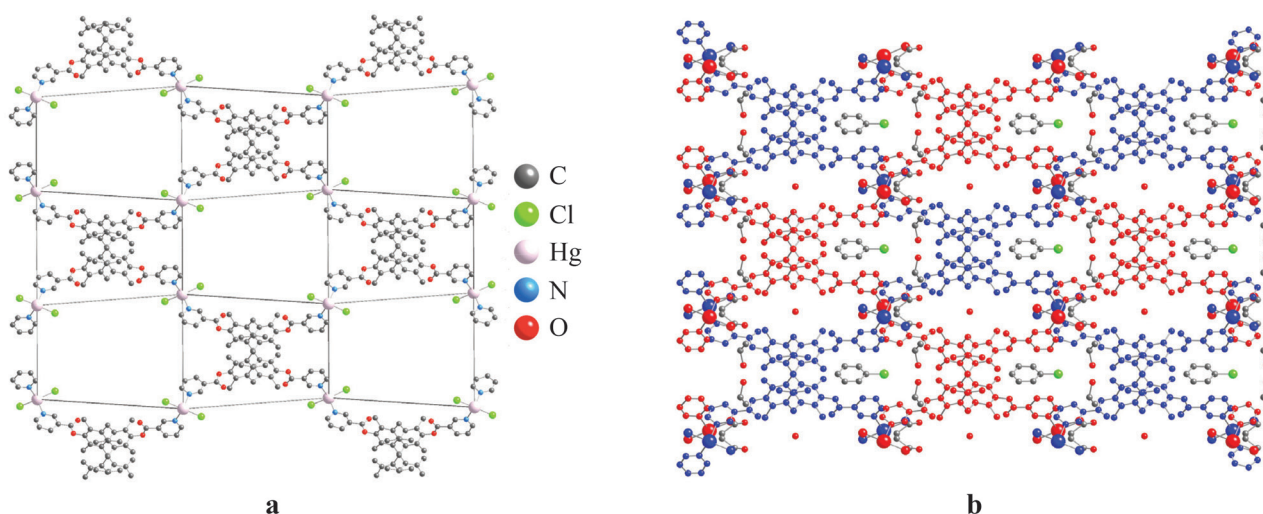
Figure 15. A portion of the X-ray structure showing a) the pyridyl tetrasusbtituted *L*11 ligand, b) the resulting pseudo diamondoid 3D coordination network of formula [*L*11(AgPF$_6$)$_2$]·2C$_6$H$_4$Cl$_2$·10H$_2$O in polyhedral representation, and c) the fourfold interpenetrated networks. H atoms, solvent molecules and anions are not presented for sake of clarity. Adapted from Ref.[34]
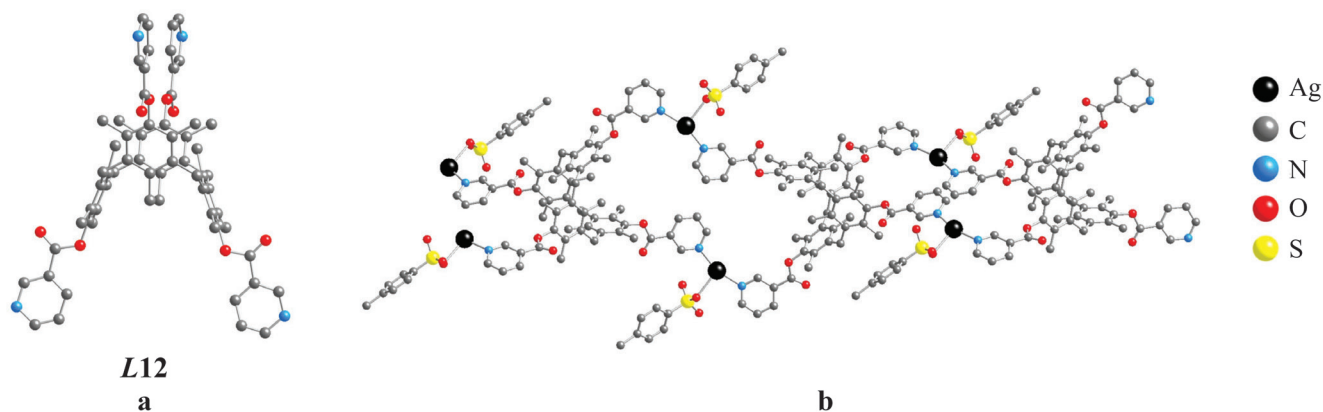
Figure 16. A portion of the X-ray structure showing a) the pyridyl tetrasusbtituted *L*12 ligand, and b) the resulting mono-dimensional tubular-like coordination compound of formula [*L*12(AgC$_7$H$_7$SO$_3$)$_2$]·6(CHCl$_3$), (C$_2$H$_6$OH). H atoms, anions and uncoordinated solvents are not presented for sake of clarity. Adapted from Ref.[36]

Figure 17. A portion of the X-ray structure showing a) the resulting two-dimensional coordination compound of formula [*L*12(HgCl$_2$)$_2$]·2(C$_2$H$_6$OH)·0.5(C$_6$H$_5$Cl)(H$_2$O), and b) the interpenetration of two different grids. H atoms are not presented for sake of clarity. Adapted from Ref.[36]

Table 1. Dimensionalities of coordination compounds resulting from interactions between **L**1-**L**12 with MX$_2$ complexes (M=Cu, Co, Zn, Hg and X=Cl, Br or I) or silver salts (*- based on mixed dipyridyl dipyrazolyl derivative **L**10).

R	—C≡N	CH$_2$C≡N	4-methylpyridine	pyridyl ester	N-ethylpyrazole	N-ethylimidazole
Disubstituted compounds	1D $[(L1)_2(AgSbF_6)]\cdot 3H_2O$ C_2H_5OH[27]	–	0D $[L2(ZnX_2)]_2S$ (X=Cl or Br)[28] 1D $[L2(HgCl_2)]$ $C_2H_2Cl_4$[27]	–	1D $[L4(MX_2)]$ (M=Co or Zn and X= Cl and Br)[29] 1D $[L5(CoX_2)]$ (X=Cl and Br)[29]	0D $[L3MX_2]S$ (M=Co, Zn, Cu and Hg; X=Cl or Br)[29]
Tetrasubstituted compounds	1D $[L6(AgPF_6)_2]$2MeOH 1.5CH$_2$Cl$_2$[30]	0D $[L7(AgNO_3)_3]_2$ 6CHCl$_3$[31] 1D $[L7(AgX)]_3$ (X= BF$_4$ or NO$_3$)[31]	2D* $[L10(ZnCl_2)_2]_4$ 2(CH$_3$OH), 2(H$_2$O)[29] 3D $[L11(AgPF_6)_2]$ 2C$_6$H$_4$Cl$_2$ 10H$_2$O[34] 1D $[L12(AgC_7H_7SO_3)_2]$ 6(CHCl$_3$), (C$_2$H$_6$OH)[36]	2D $[L12(HgCl_2)_2]$ 2(C$_2$H$_6$OH) 0.5(C$_6$H$_5$Cl)(H$_2$O)[36]	1D $[L9(CuBr_2)_2]$[33] 2D $[L9(MX_2)]$ (M=Co, Zn and X=Cl or Br)[33] 2D* $[L10(ZnCl_2)_2]_4$ 2(CH$_3$OH), 2(H$_2$O)[29]	0D $[L8(MX_2)_2]$ S (M=Co, Cu, Zn and Hg; X=Cl or Br)[32]

Conclusion

The [1.1.1.1]metacyclophane backbone, due to its rigidity and stability, in *1,3-alternate* conformations has been decorated with coordinating substituents and thus used for the development of new ligands involved in the formation of new coordination compounds. The synthesis of di- and tetrasubstituted derivatives bearing monodentate N donor coordinating sites (cyano, pyridine, imidazole or pyrazole) has been performed leading to a series of 12 ligands **L**1-**L**12. The combinations of **L**1-**L**12 with *V*-shaped metallic neutral MX$_2$ species (M=Cu, Co, Zn, Hg and X=Cl, Br or I) or silver cations, leads in the solid-state, to the formation of a great variety of coordination compounds, from mono and binuclear discrete complexes to 1D systems (with M/L ratio of 2:1 or 1:1), 2D grid-like systems (with M/L ratio of 2:1) or a pseudo diamond-like 3D system, as depicted in Table 1.

As expected, the use of ligands presenting low (disubstituted compounds) and high (tetrasubstituted compounds) number of coordinating sites significantly influences on the dimensionality of the resulting molecular networks in the crystalline phase. It was established, that the combination of disubstituted compounds offering "*V*-shaped" geometry for coordinating sites with linear or *V*-shaped metal linkers (silver(I) cations or metal(II) halides) leads to linear coordination polymers or even to isolated discrete metallomacrocycles. In contrast, the tetrasubstituted [1.1.1.1]metacyclophane derivatives presenting a distorted tetrahedral geometry of coordinating sites form also coordination compounds of higher dimensionalities (2D-3D).

It was found that the nature of the junction between the macrocycle backbone and the coordinating sites tremendously influences on the coordination network formation based on [1.1.1.1]metacyclophane derivatives. The most encountered 1D and 2D architectures have been generated while the appended coordinating sites (cyano, pyridyl or pyrazolyl) were connected to the macrocyclic backbone through rather flexible CH$_2$ or -C(O)O-junctions. However, 1D and 3D structures based on coordination bonds formation between tetracyano (**L**1) or tetrapyridyl compounds (**L**11) with silver cation behaving as linear linkers, has been obtained when a rigid connection with the macrocycle platform has been used. In this case, the formation of a 1D coordination polymers can be explained by the relatively short distances between the opposite N atoms belonging to distal cyano groups (**L**6), compared to those in the case of tetrapyridyl compound (**L**11). It is interesting to note that di- and tetrasubstituted imidazolyl derivatives (**L**3) and (**L**8), respectively, have shown the formation of especially discrete metallomacrocycles, apparently resulting from the spatial orientation of imidazolyl moieties which is favorable to form chelate complexes.

As it was shown, the dimensionality of molecular structure of coordination compounds based on [1.1.1.1] metacyclophane derivatives in the crystalline phase can be controlled also by the type of *V*-shaped metal species. Whereas zinc(II) halides were used in combination with **L**2, only dimeric moieties $[L2(ZnX_2)]_2$S have been obtained. But when zinc(II) cations have been replaced by mercury(II), the 1D zig-zag type coordination polymer was generated.

In summary, this high diversity of observed coordination compounds is due to the nature of the used functional groups, and in some cases to the equilibrium between the thermodynamically and kinetically favourable compounds. This

review has put the first attempts to rationalize the design of [1.1.1.1]metacyclophane macrocyclic backbone to build coordination polymers in the crystalline phase. Further investigations should be continued in this field in order to achieve the potential applications of such coordination compounds as sensors, or porous materials, for example.

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