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Coordination chemistry of 2,4,6-tri(pyridyl)-1,3,5-triazine ligands

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ABSTRACT

This review covers the rich coordination chemistry of 2,4,6-tri(pyridyl)-1,3,5-triazine ligands. These polypyridyl derivatives have been coupled to transition metals and lanthanides, and the complexes obtained have been used in various fields such as luminescent materials, for the preparation of coordination polymers and networks as well as for the synthesis of discrete metalla-assemblies. The synthetic and structural aspects of the different isomers of 2,4,6-tri(pyridyl)-1,3,5-triazine are presented, and a survey of their coordination chemistry is given.

Keywords
Coordination polymers, Metal–organic frameworks, Multidentate ligands, Polypyridyl ligands, Porphyrin arrays, Supramolecular assemblies

Contents

1. Introduction

Polypyridyl derivatives are widely used as ligands in coordination chemistry and as building blocks for the generation of supramolecular structures [1]. Many polypyridyl derivatives are commercially available and many others are straightforward to synthesise, which undeniably make them very popular in coordination chemistry. Among these polypyridyl ligands, we have been particularly interested in 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives [2].

Although several non threefold symmetrical isomers of 2,4,6-tri (pyridyl)-1,3,5-triazine can be drawn, only one derivative is known, 2,4-di(pyridyn-2-yl)-6-(pyridyn-4-yl)-1,3,5-triazine, and it

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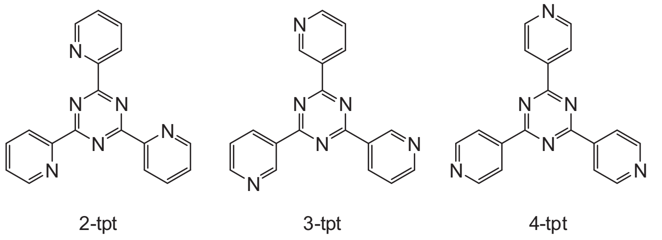


Fig. 1. Threefold symmetrical isomers of 2,4,6-tri(pyridyl)-1,3,5-triazine.

has been only sparingly used in coordination chemistry. On the other hand, all threefold symmetrical isomers of 2,4,6-tri(pyridyl)-1,3,5-triazine, *viz.* 2,4,6-tri(pyridine-2-yl)-1,3,5-triazine (2-tpt), 2,4,6-tri (pyridine-3-yl)-1,3,5-triazine (3-tpt) and 2,4,6-tri(pyridine-4-yl)-1,3,5-triazine (4-tpt), have been extensively engaged in coordination chemistry. These highly symmetrical derivatives are presented in Fig. 1.

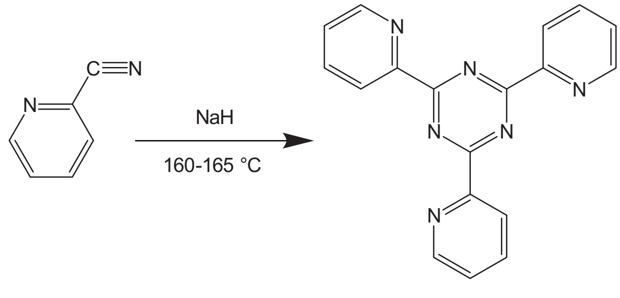
Nevertheless, symmetrical and asymmetrical isomers possess very distinctive coordination properties, and therefore offer diversity and complexity in the structures obtained. This review intends to emphasize these coordination differences and to show the attractiveness of this family of versatile ligands for the construction of complexes, coordination networks, metallo-porphyrin arrays and metalla-assemblies. Moreover, the various synthetic routes to obtain 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives and their stability are discussed.

2. Synthesis of 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives

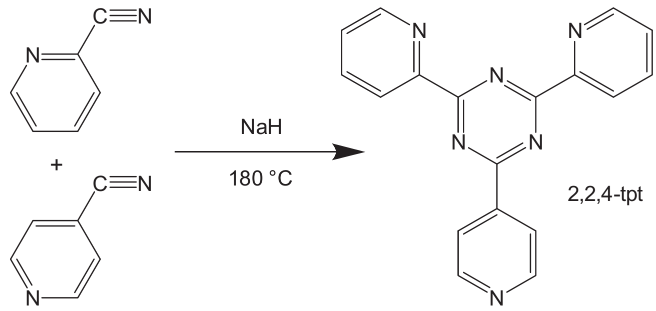
Trimerization of cyanopyridine under basic condition remains the most common route to prepare 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives. 2,4,6-Tri(pyridin-2-yl)-1,3,5-triazine (2-tpt) was the first derivative to be synthesised [3]. Reaction of 2-cyanopyridine in the presence of a catalytic amount of sodium hydride at 160–165 °C for 5 h afforded 2-tpt in reasonable yield (Scheme 1). The synthetic strategy to obtain 2-tpt was based on the synthesis of 2,4,6-triphenyl-1,3,5-triazine, published a few years earlier [4].

The synthesis of 3-tpt and 4-tpt followed a similar strategy using respectively 3-cyanopyridine and 4-cyanopyridine in the presence of potassium hydroxide and 18-crown-6 in decalin at 200 °C [5]. This procedure conveniently replaced the initial method to prepare 4-tpt introduced by Biedermann and Wichmann requiring strong base and high pressure [6].

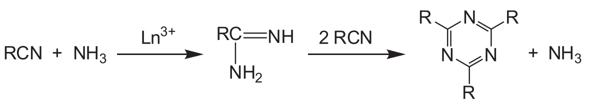
The 2-tpt and 4-tpt can be obtained as well under catalytic conditions using Ln^{3+} derivatives as catalysts [7]. The reaction of cyanopyridine with ammonia (Eq. (1)) or *n*-hexylamine in the presence of catalytic amount of lanthanide(III) ion produced the corresponding 2,4,6-tri(pyridyl)-1,3,5-triazines in excellent yield.



Scheme 1. Synthesis of 2,4,6-tri(pyridin-2-yl)-1,3,5-triazine from 2-cyanopyridine and sodium hydride [3].



Scheme 2. Synthesis of 2,4-di(pyridyn-2-yl)-6-(pyridyn-4-yl)-1,3,5-triazine (2,2,4-tpt) [8].

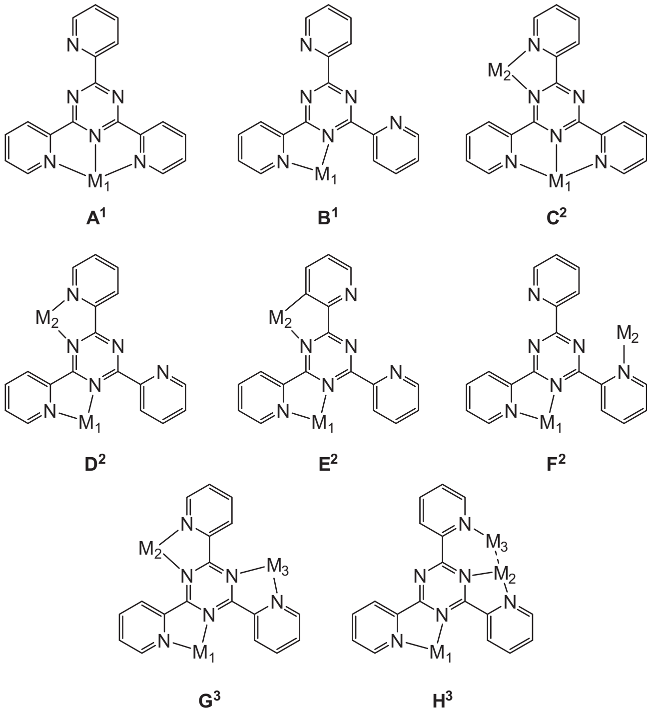


(1)

A few years ago, an asymmetric isomer, 2,4-di(pyridyn-2-yl)-6-(pyridyn-4-yl)-1,3,5-triazine (2,2,4-tpt), has been prepared from the reaction of an equimolar amount of 2-cyanopyridine and 4-cyanopyridine with sodium hydride as catalyst at 180 °C (Scheme 2). The mixture of isomers obtained (2-tpt, 4-tpt, 2,4,4-tpt and 2,2,4-tpt) was separated by complexation with Ni(II) and after decomplexation, the 2,2,4-tpt isomer was isolated by recrystallisation from ethanol [8].

3. Coordination chemistry of 2,4,6-tri(pyridin-2-yl)-1,3,5-triazine (2-tpt)

The 2-tpt ligand, which is commercially available, has been mainly used analytically in the spectroscopic determination of transition metals [9]. Several transition metal and lanthanide ions react with 2-tpt to form metal complexes. The possibility for the polypyridyl ligand to coordinate metals in different modes has been



Scheme 3. Possible coordination modes of 2-tpt to form mononuclear (A^1, B^1), dinuclear (C^2, D^2, E^2, F^2) or trinuclear (G^3, H^3) complexes.

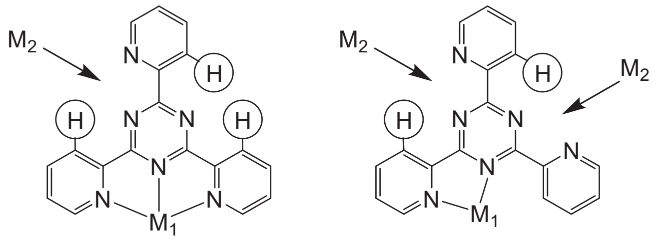


Fig. 2. Steric constraints imposed by the hydrogen atoms on the incoming metal (M_2) after coordination of a first metal centre (M_1) to 2-tpt.

studied for 50 years. The different coordination modes adopted by 2-tpt are presented in Scheme 3. The 2-tpt ligand can form mononuclear complexes through its terpyridine-like tridentate coordination site (form A^1) or a bipyridine-like bidentate coordination site (form B^1). These mononuclear complexes are the most common derivatives involving the 2-tpt ligand and they are presented in Section 3.1.

A wide variety of dinuclear complexes can be obtained using a combination of tridentate, bidentate and monodentate coordination sites provided by the 2-tpt ligand (forms C^2, D^2, E^2 and F^2). These dinuclear complexes built with the 2-tpt ligand are described in Section 3.2. Studies have showed that the coordination of a second metal centre to 2-tpt is difficult due to the deactivation of the triazine ring by the inductive effect of the first coordinated metal centre and by the steric clash between hydrogen atoms and the potential incoming metal ions (Fig. 2) [10]. Consequently, further coordination to 2-tpt to form trinuclear complexes is even more difficult, and as showed in Section 3.3, examples in which 2-tpt coordinates three metal centres (forms G^3 or H^3) are extremely rare.

3.1. Mononuclear derivatives

Mononuclear complexes have been obtained with almost all transition metals. The most common coordination mode adopted by 2-tpt is the terpyridine-like form (A^1 in Scheme 3), in which 2-tpt acts as a tridentate ligand. Complexes of the following metal ions Mn^{2+} [11], Fe^{2+} [12], Fe^{3+} [13], Co^{2+} [14], Ni^{2+} [15], Cu^{2+} [16], Zn^{2+} [17] Ru^{2+} [18], Rh^{3+} [19], Cd^{2+} [20], Os^{2+} [21], Pb^{2+} [22], Bi^{3+} [23] are found in the literature. The molecular structure of a typical mononuclear complex of the form A^1 is showed in Fig. 3.

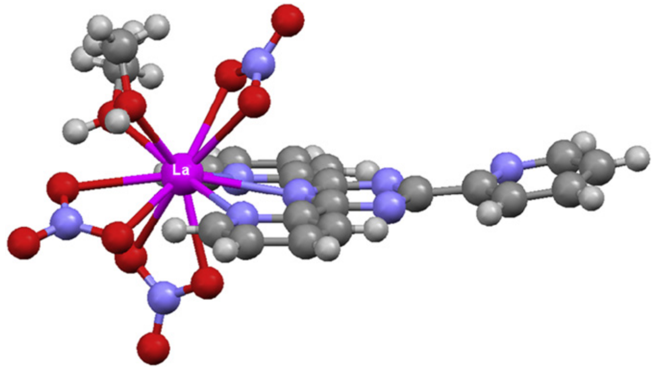


Fig. 4. Molecular structure of $[La(NO_3)_3(CH_3OH)_2(2\text{-tpt})]$ (Form A^1) [24h].

Lanthanides form only A^1 type coordination complexes with 2-tpt [24]. Interestingly, a mixed Tb^{3+}:Gd^{3+} lanthanide complex of 0.1:0.9 stoichiometry, $[Tb_{0.1}Gd_{0.9}(2\text{-tpt})(H_2O)_6]Cl_3 \cdot 3\ H_2O$ has been recently synthesised [25]. However, like the other lanthanide derivatives, it forms a 1:1 ligand lanthanide (2-tpt:Ln^{3+}) complex. The molecular structure of the lanthanum derivative containing three coordinated bidentate nitrate groups and two methanol molecules together with the 2-tpt ligand, $[La(NO_3)_3(CH_3OH)_2(2\text{-tpt})]$, is presented in Fig. 4 [24h].

The second coordination mode adopted by 2-tpt to generate mononuclear complexes involved a bipyridine-like site. Form B^1 is obtained with tetravalent metals such as Pd^{2+} [26], Ag^{1+} [27] and Pt^{2+} [26], but is observed as well with penta- and hexavalent metal centres such as Co^{2+} [28], Ni^{2+} [28,29], Cu^{2+} [28], Zn^{2+} [28,30] Ru^{2+} [31], Rh^{3+} [32], Re^{1+} [31c,33], Os^{2+} [31a] and Ir^{3+} [32,34]. The molecular structure of the neutral $[ReCl(CO)_3(2\text{-tpt})]$ complex showing the B^1 coordination form of the 2-tpt ligand is given in Fig. 5.

The 2-tpt is generally stable towards hydrolysis [35], however, it was found that in aqueous media, Cu^{2+} ions promote the hydrolysis of 2-tpt to form bis(2-pyridylcarbonyl) amide anion. Firstly reported by Lerner and Lippard [36], the hydrolysis of 2-tpt by Cu^{2+} ion involves the generation of several intermediates (Scheme 4). The first intermediate contains two imino groups, while the second intermediate possesses one imino and one carbonyl group, and the

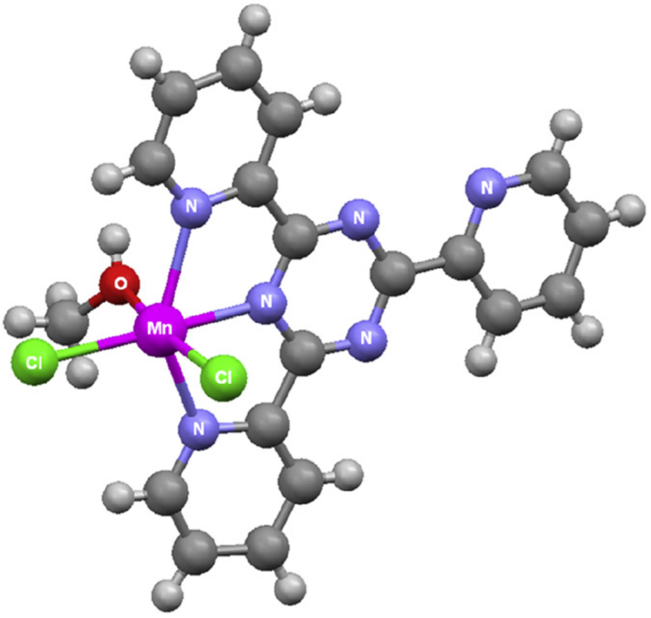


Fig. 3. Molecular structure of $[MnCl_2(CH_3OH)(2\text{-tpt})]$ (Form A^1) [11d].

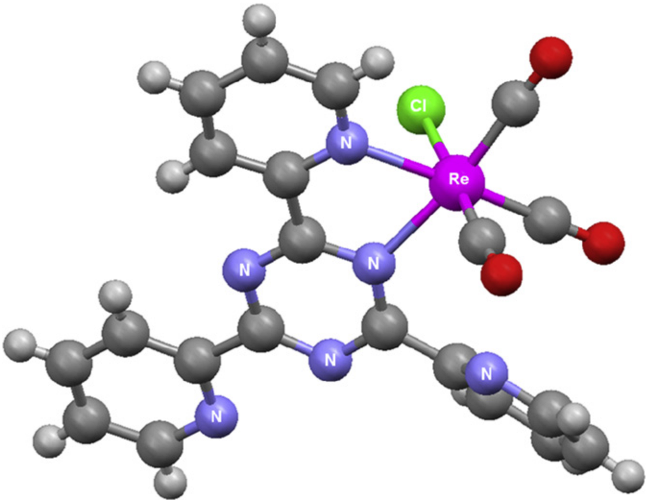
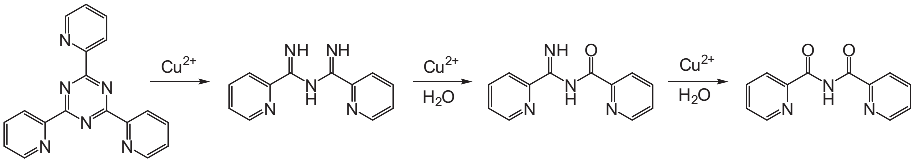
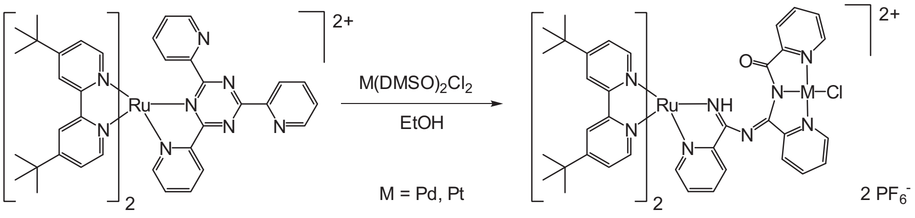


Fig. 5. Molecular structure of $[ReCl(CO)_3(2\text{-tpt})]$ (Form B^1) [33b].



Scheme 4. Hydrolysis of 2-tpt with Cu^{2+} ions.



Scheme 5. Partial hydrolysis of 2-tpt [31a].

last step yields the fully hydrolysed product, bis(2-pyridylcarbonyl) amine. The Cu^{2+} supported hydrolysis of 2-tpt has been observed by many groups [37] and even with Rh^{3+} ions [18f,38].

Partial hydrolysis of 2-tpt has been occasionally observed where a ring opening reaction of the triazine core occurs [31a]. The reaction between $[Ru(tbbpy)_2(2\text{-tpt})]^{2+}$ (tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and $M(DMSO)_2Cl_2$ (M = Pd, Pt) gave the dinuclear complex $[(tbbpy)_2Ru(tptO)MCl]^{2+}$ [tptO = (picolinamido(pyridin-2-yl)methylene)picolinamide], see Scheme 5. Steric hindrance and electronic considerations have been discussed, but no conclusive explanation for this partial hydrolysis of 2-tpt has been given.

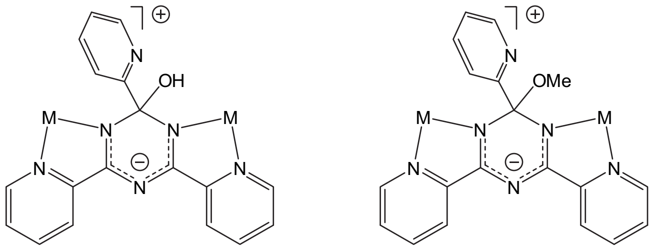
Both hydroxylation [21b] and methoxylation [33b,39] at the carbon atom of the triazine ring have been observed for some dinuclear complexes of 2-tpt, see Scheme 6. The coordination of two metal centres to 2-tpt leads to a destabilisation of the triazine ring by enhancing electron deficiency, thus allowing nucleophilic attack at the carbon atom on the triazine ring adjacent to the uncoordinated pyridyl ring.

3.2. Dinuclear derivatives

The synthesis of dinuclear complexes with 2-tpt ligand can be achieved in one or two steps. Homo-dinuclear complexes are in general prepared in one step, while hetero-dinuclear complexes are only obtained in two steps from a mononuclear 2-tpt derivative to which a second metal centre is added subsequently. Homo-dinuclear complexes of Co^{2+} [14d,40], Ni^{2+} [14d,15a,40,41] and Cu^{2+} [14d,16c,40,42] have been found in both coordination forms, C^2 and D^2 (see Scheme 3). Similarly, two Ru^{2+} ions coordinate 2-tpt in both forms [18d,21b,31b,43], while only the D^2 coordination form has been observed for the isoelectronic Os^{2+} ion [21b]. An Ir^{3+} hydrido dinuclear complex, $[\{Ir(H)_2(PPh_3)_2\}_2(2\text{-tpt})](PF_6)_2\cdot 2H_2O$ [34], and a dinuclear Re^{1+} carbonyl complex, $[\{Re(CO)_3Br\}_2(2\text{-tpt})]$ [33b], have been characterised by single-crystal structure analysis, both showing the D^2 coordination form. The molecular structure of $[\{Re(CO)_3Br\}_2(2\text{-tpt})]$ is presented in Fig. 6.

A coordination dimer of the general formula $\{[Ag_2(2\text{-tpt})(CF_3COO)_2(H_2O)][Ag_2(2\text{-tpt})(CF_3COO)_2]\}\cdot 0.5H_2O$ involving Ag^{1+} ions, 2-tpt, H_2O, CF_3COO^- bridging and terminal anions has been synthesised and characterised [44]. In this dimer, one silver atom is coordinated through a terpyridine-like site, while the other uses a bipyridine-like site, thus giving rise to two dinuclear 2-tpt moieties of the coordination form C^2 linked by a CF_3COO^- bridge. One half of the dimeric species is presented in Fig. 7 showing the typical C^2 coordination form in the solid state. Likewise, the dinuclear Hg^{2+} complex, $[Hg_2(CF_3COO)_4(2\text{-tpt})]$, has been found by X-ray structure analysis to adopt the C^2 coordination form as well [45].

Interestingly, complexes including Pt^{2+} ions have been found not only in the relatively common D^2 coordination form [46], but as well in the unique F^2 coordination mode [47] which involved a



Scheme 6. Hydroxylation and methoxylation of 2-tpt in dinuclear complexes.

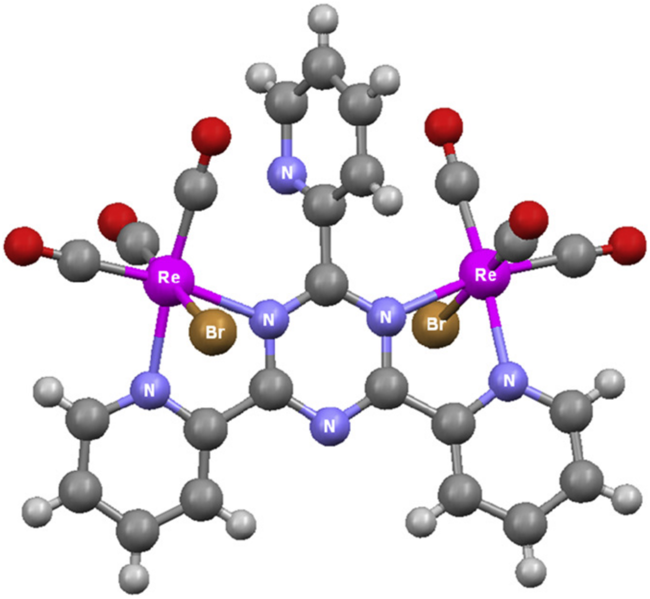


Fig. 6. Molecular structure of the dinuclear complex $[\{Re(CO)_3Br\}_2(2\text{-tpt})]$ (Form D^2) [33b].

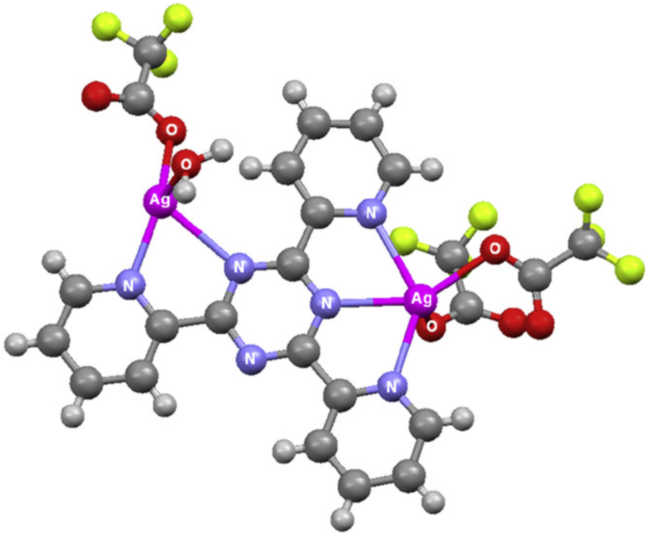


Fig. 7. Coordination environment of silver atoms (Form C^2) in the dimer {[Ag_2(2-tpt)(CF_3COO)$_2$(H_2O)][Ag_2(2-tpt)(CF_3COO)$_2$]}·0.5H_2O [44].

bipyridine-like bidentate coordination site together with a monodentate pyridyl group. The reaction of the salt K_2PtCl_4 with 2-tpt in a water/ethanol mixture give rises to the trinuclear complex [{($PtCl_2$)(2-tpt)}$_2$(μ-$PtCl_2$)] in which the 2-tpt ligands are coordinated by two platinum atoms, see Scheme 7.

A series of mixed-valent Ru^{2+}:Ru^{3+} dinuclear complexes have been described by Lahiri [18a]. In these dinuclear complexes, the 2-tpt ligand binds the Ru^{2+} ion through a standard terpyridine-like coordination site, while the Ru^{3+} ion coordinates a remaining nitrogen atom of the triazine ring and the adjacent carbon atom of the uncoordinated pyridyl group (Fig. 8). The formation of a Ru—C^- bond from a pendant pyridyl group has been previously observed in related complexes [48], but it was the first time within the 2-tpt ligand.

Hetero-dinuclear complexes of Ru^{2+}:Ag^{1+} [18c], Ru^{2+}:Pd^{2+} [31a] and Ru^{2+}:Rh^{3+} [18b] have been obtained in two steps from a mononuclear [$RuCl_2$(PPh_3)(2-tpt)] precursor. Interestingly, the ruthenium silver mixed metal complex consists of a trinuclear system in which the Ag^{1+} ion coordinates two [Ru(tpy)(2-tpt)]$^{2+}$ (tpy = 2,2′:6′,2′′-terpyridine) units through the remaining bipyridine-like coordination site of the 2-tpt ligands. The molecular structure of the cationic Ru:Rh mixed metal complex [18b], [{$RuCl_2$(PPh_3)}{RhCl(Cp*)}(2-tpt)]$^+$ (Cp* = pentamethylcyclopentadienyl), obtained from the precursor [$RuCl_2$(PPh_3)(2-tpt)] is presented in Fig. 9.

Using the same strategy, a series of mixed Re^{1+}:M^{2+} systems (M = Mn^{2+}, Co^{2+}, Cu^{2+}) were synthesised [33a]. The mononuclear complex [ReCl(CO)$_3$(2-tpt)] reacts with various [M(hfac)$_2$] (hfac = hexafluoroacetylacetonato) complexes to afford the corresponding hetero-dinuclear systems [{ReCl(CO)$_3$}{M(hfac)$_2$}(2-tpt)], which dissociate in polar solvents such as acetone and acetonitrile to simply yield the starting materials.

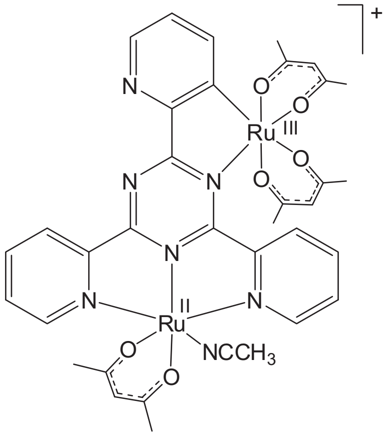


Fig. 8. Molecular structure of [{Ru(acac)$_2$}{Ru(acac)(CH_3CN)}(2-tpt)]$^+$ (Form E^2) [48].

3.3. Trinuclear derivatives

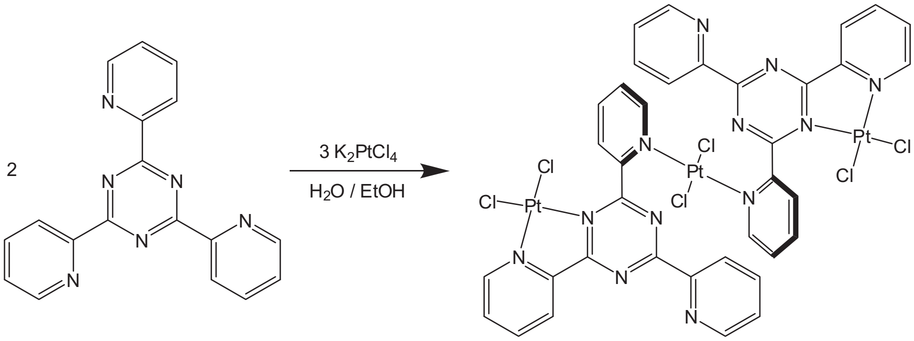
Trinuclear complexes of 2-tpt are extremely rare and to the best of our knowledge only two publications deal with these derivatives. However, on Scifinder the structure of a third complex, a bicyclo [2.2.1]hepta-2,5-dienyl Rh^{3+} trinuclear complex of the coordination form G^3 can be found, but without any reference (registry number 113006-61-4).

The trinuclear Cu^{1+} coordinated network [Cu_3I_3(2-tpt)]$_n$ was obtained by mixing CuI, 2-tpt, 1,2-bis(diphenylphosphino)ethane and acetonitrile in a sealed reactor heated at 180 °C for 60 h [49]. The molecular structure of this unique trinuclear 2-tpt system (Form H^3 in Scheme 3) is presented in Fig. 10.

The symmetrical trinuclear derivative of the formula [{Co(bfac)$_2$}$_3$(2-tpt)] (bfac = (benzothiophen-3-yl)-trifluoro-acetylacetonato) in which the 2-tpt ligand is surrounded by three cobalt atoms coordinated through the three equivalent bipyridine-like sites (form G^3 in Scheme 3), has been proposed based on elemental analysis and spectroscopic measurements [50]. The molecular structure of the trinuclear complex is presented in Fig. 11.

4. Coordination chemistry of 2,4,6-tri(pyridin-3-yl)-1,3,5-triazine

The extended and potentially planar tri-aryl ring system in 3-tpt with multiple coordinating groups at the periphery has been barely



Scheme 7. Synthesis of the trinuclear complex [{($PtCl_2$)(2-tpt)}$_2$(μ-$PtCl_2$)] [47].

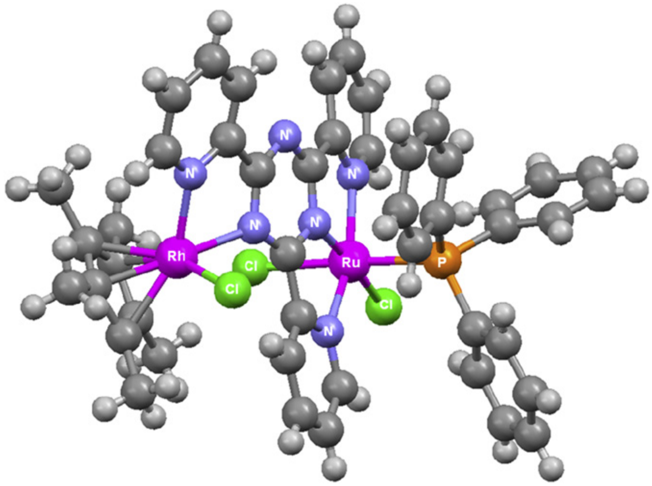


Fig. 9. Molecular structure of the cationic mixed metal complex $[\{RuCl_2(PPh_3)\}\{RhCl(Cp^*)\}(2\text{-tpt})]^+$ [18b].

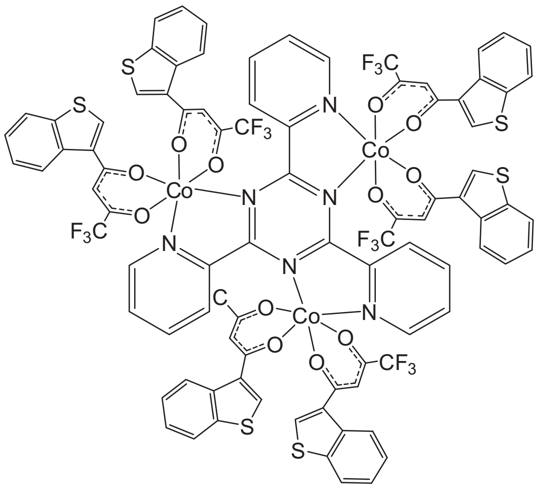


Fig. 11. Proposed molecular structure of $[\{Co(bfac)_2\}_3(2\text{-tpt})]$ (Form G^3) [50].

used in coordination chemistry. As opposed to the 4-tpt isomer (Section 5), in 3-tpt a rotation by 180° of one of the three C—C triazine-pyridyl bonds reduces the threefold symmetry, thus generating atropoisomerism before coordination (Scheme 8). Consequently, the synthesis and characterisation of well-defined complexes, metalla-assemblies or coordination networks with the tridentate 3-tpt ligand remain difficult and hazardous.

4.1. Coordination networks

The construction of coordination networks and coordination polymers has received a great deal of attention in recent years [51]. These large structures offer interesting opportunities for applications as receptors, devices and catalysts. Incorporation of metal ions in the synthesis of polymers and networks allows the introduction of new chemical functions in these supramolecular devices. Therefore, it is not surprising that 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives have been employed in the preparation of coordination networks.

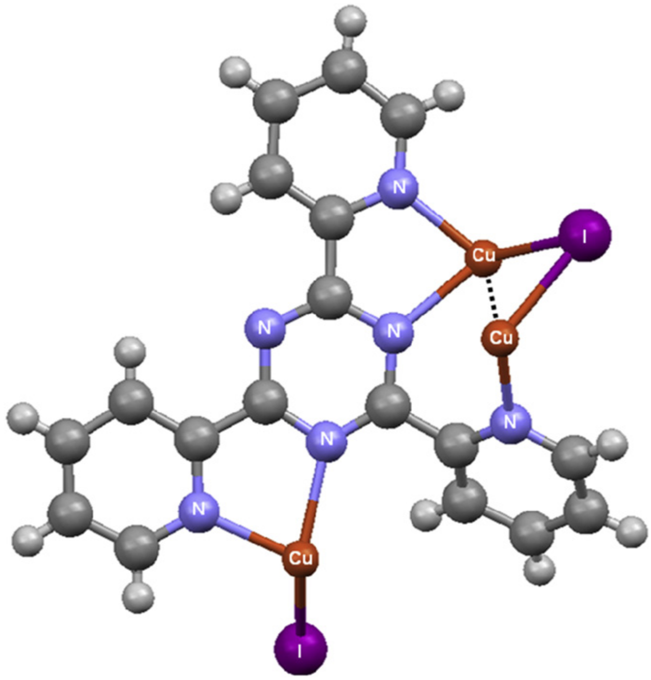


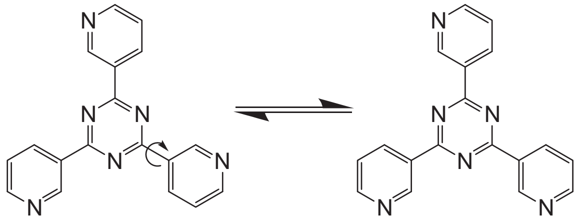
Fig. 10. The 2-tpt environment (Form H^3) in the $[Cu_3I_3(2\text{-tpt})]_n$ coordination network [49].

Indeed, 3-tpt and dinuclear Cu^{2+} units have been connected together to generate infinite one-dimensional zig-zag chains [52]. These polymeric systems were obtained by carefully layering over a buffer of benzene, a benzyl alcohol solution of 3-tpt and a methanol solution of $[Cu_2(O_2CCH_3)_4]$ or $[Cu_2(O_2CPh)_4]$. After slow diffusion over several days, crystals of the coordination networks were harvested and characterised by single-crystal X-ray structure analysis. In the infinite complex $\{[Cu_2(O_2CCH_3)_4](3\text{-tpt})(CH_3OH)_2\}_n$, methanol molecules were found between the one-dimensional chains, while in the second infinite complex $\{[Cu_2(O_2CPh)_4](3\text{-tpt})(C_6H_6)_{1.5}\}_n$, benzene molecules were encapsulated.

Using a different synthetic strategy, but similar building blocks, three-dimensional networks incorporating 3-tpt and Cu^{2+} ions have been prepared [53]. The hydrothermal reaction of $CuSO_4 \cdot 5H_2O$, 3-tpt and 1,2,4,5-benzenetetracarboxylic acid (H_4btec) affords depending on conditions and solvents, three distinct coordination polymers, $[Cu_4(3\text{-tpt})_2(btec)_2(H_2O)_4]_n \cdot 6nH_2O$, $[Cu(3\text{-tpt})_2(H_2btec)]_n$ and $[Cu_3(3\text{-Htpt})_2(H_2btec)_2(btec)]_n \cdot 4nH_2O$, respectively. Interestingly, the 3-tpt ligand coordinates one metal ion in $[Cu(3\text{-tpt})_2(H_2btec)]_n$, two metal ions in $[Cu_4(3\text{-tpt})_2(btec)_2(H_2O)_4]_n$ and three metal centres in the last isolated coordination polymer $[Cu_3(3\text{-Htpt})_2(H_2btec)_2(btec)]_n$. The various coordination behaviours adopted by 3-tpt in these Cu^{2+} coordination networks are presented in Fig. 12.

4.2. Discrete supramolecular assemblies

The synthesis of discrete, well-defined, supramolecular metalla-assemblies using 3-tpt ligands is quite uncommon. The difficulty of forming discrete metalla-assemblies with 3-tpt ligands resides in



Scheme 8. Atropoisomerism of 3-tpt before coordination.

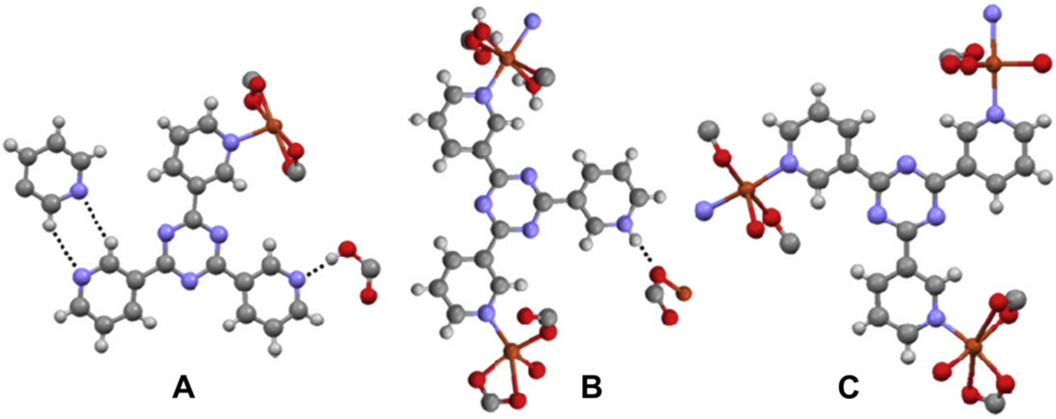


Fig. 12. Coordination environment of the 3-tpt ligands in $[Cu_4(3\text{-tpt})_2(btec)_2(H_2O)_4]_n \cdot 6nH_2O$ (**A**), $[Cu(3\text{-tpt})_2(H_2btec)]_n$ (**B**) and $[Cu_3(3\text{-Htpt})_2(H_2btec)_2(btec)]_n \cdot 4nH_2O$ (**C**) [53].

controlling the orientation of the pyridyl groups prior to the coordination of the metal centres (Scheme 8). Nevertheless, a few examples can be found in the literature. Bowl-shaped hexanuclear Pd and Pt coordination cages of the general formula $[M_6(en)_6(3\text{-tpt})_4]^{12+}$ (en = ethylenediamine), able to encapsulate guest molecules, have been described by Fujita [54]. The molecular structure of the palladium cage, which is identical to the platinum analogue, is presented in Fig. 13. The hydrophobic cavity of these cationic hexanuclear assemblies has been used to act as a microreactor for catalytic reactions [55], to control [2 + 2] photodimerisation reactions [56], as well as to encapsulate guest molecules [57].

The trinuclear rhenium tricarbonyl diimine complex, $[\{Re(CO)_3(dmbpy)\}_3(3\text{-tpt})]^{3+}$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) (Fig. 14), obtained by refluxing 3-tpt and $[Re(CO)_3(dmbpy)(CH_3CN)]PF_6$ in THF, possesses a π-acidic cavity that showed good sensing affinity for F over PF_6 anions [58].

Hexanuclear arene ruthenium prisms, $[Ru_6(arene)_6Cl_6(3\text{-tpt})_2]^{6+}$ (arene = *p*-cymene, hexamethylbenzene), in which the two arene ruthenium 3-tpt panels are linked together in a face-to-face arrangement by chloro bridges have been recently described [59].

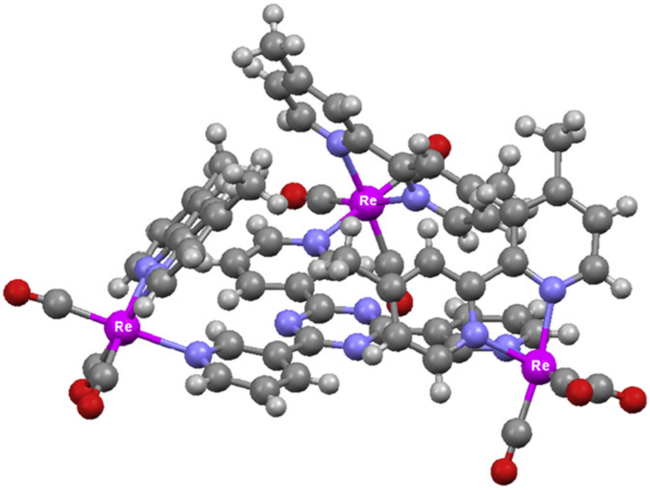


Fig. 14. Molecular structure of $[\{Re(CO)_3(dmbpy)\}_3(3\text{-tpt})]^{3+}$ [58].

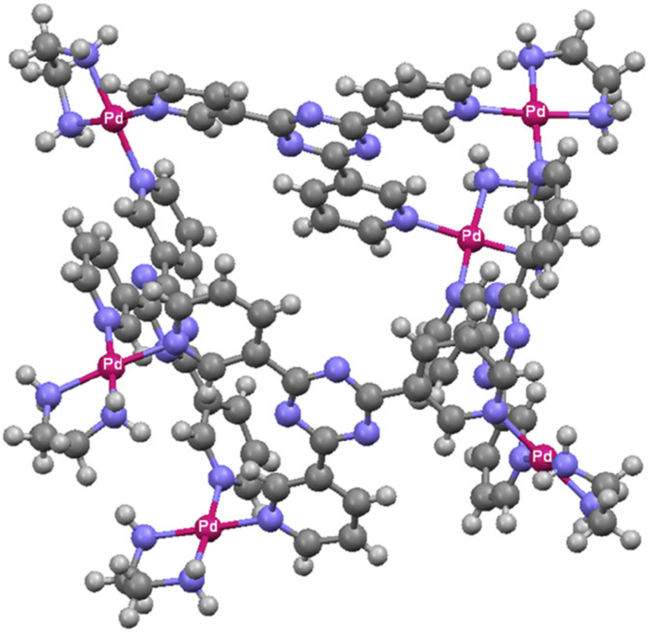


Fig. 13. Bowl-shaped hexanuclear cage, $[Pd_6(en)_6(3\text{-tpt})_4]^{12+}$ [54a].

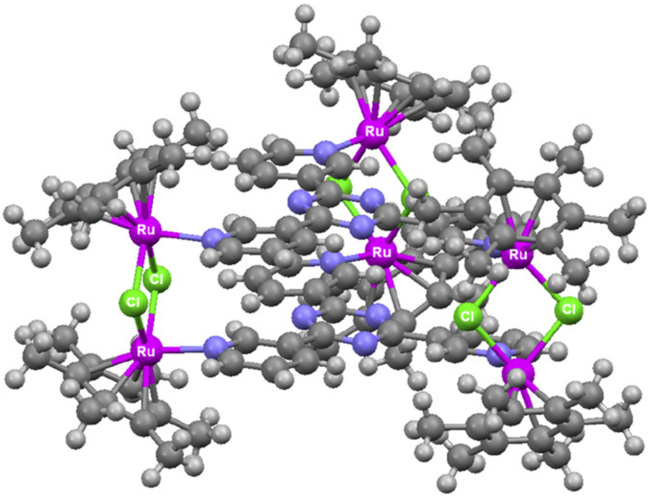


Fig. 15. Hexanuclear arene ruthenium prism, $[Ru_6(C_6Me_6)_6Cl_6(3\text{-tpt})_2]^{6+}$ [59].

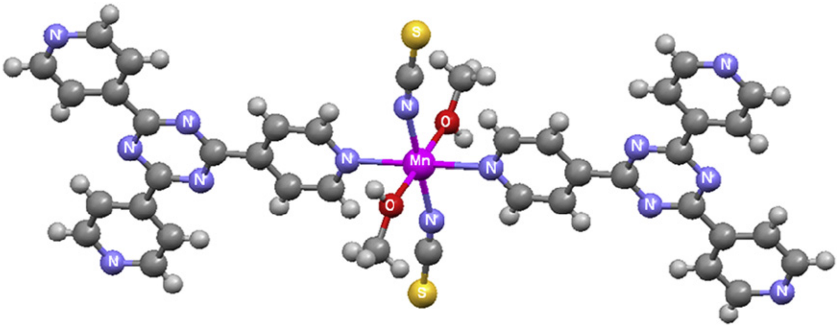


Fig. 16. Molecular structure of $[Mn(NCS)_2(CH_3OH)_2(4\text{-tpt})_2]$ [61].

Interestingly, two isomers were found for the *p*-cymene derivative, while only the threefold symmetrical isomer was obtained for the sterically more demanding hexamethylbenzene analogue (Fig. 15).

5. Coordination chemistry of 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine

Among all known 2,4,6-tri(pyridyl)-1,3,5-triazine isomers, 4-tpt is undeniably the most versatile. The tridentate ligand possesses D_{3h} symmetry, which cannot be lost easily upon coordination of three metal centres. The ligand can remain perfectly planar if necessary and the three pyridyl groups are equally accessible for complexation. Therefore, 4-tpt has been not only exploited in coordination chemistry, supramolecular chemistry and in preparing coordination networks, but has also been used as template for the controlled formation of multimetallo-porphyrin arrays.

A few examples in which 4-tpt is used as a monodentate ligand can be found in the literature. Two complexes of Fe^{2+} in which the two 4-tpt ligands are coordinated *trans* with respect to each other have been described [60]. A similar orientation of the 4-tpt ligands has been observed in the Mn^{2+} complex, $[Mn(NCS)_2(CH_3OH)_2(4\text{-tpt})_2]$ [61]. The molecular structure of this mononuclear manganese complex is presented in Fig. 16.

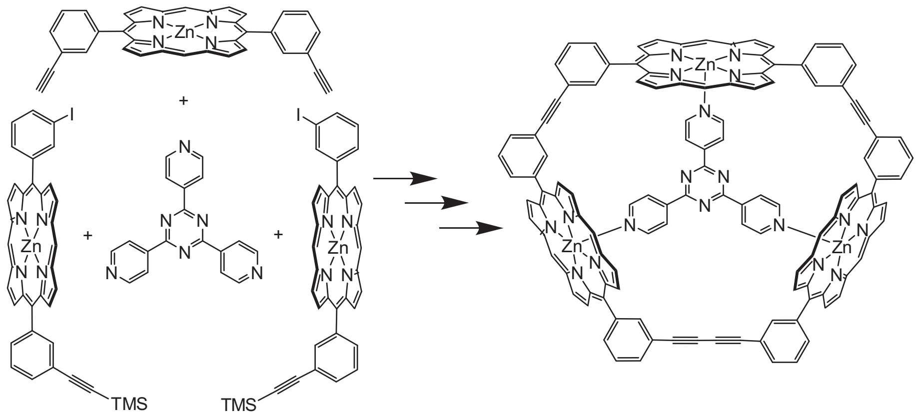
5.1. Metallo-porphyrin arrays

Pioneered by Sanders about 15 years ago [62], the construction of metallo-porphyrin arrays using 4-tpt as template has been extensively studied. These systems have potential interest as models to mimic natural light-harvesting complexes, and also materials in the preparation of extended π-systems for organic semiconductors, molecular sensing, and molecular-sized boxes or networks with large channels/cavities for selective molecular recognition and catalysts.

The first strategy developed by Sanders to afford well-defined metallo-porphyrin arrays is illustrated in Scheme 9. This strategy is based on the combination of two unsymmetrical metallo-porphyrins and one symmetrical di-alkyne metallo-porphyrin coupled under Pd-catalytic conditions and, after deprotection of the terminal alkyne groups, a final cyclization by Glaser–Hay coupling [62]. The presence of 4-tpt is not essential to form the trinuclear system, however the yield is greatly improved by addition of 4-tpt during the cyclization process, due to the templating effect of the tridentate ligand. Accordingly, a wide range of trinuclear metallo-porphyrin arrays involving 4-tpt has been obtained following similar synthetic routes using multiple coupling reactions between pre-oriented functionalised metallo-porphyrins [5,63].

By replacing the zinc porphyrin by ruthenium porphyrin units such as carbonyl[5,15-bis(3,5-di-^{t}butylbenzene)-2,8,12,18-tetra^n-hexyl-3,7,13,17-tetramethylporphyrinato]ruthenium, three Ru(CO) porphyrin monomers have been coordinated around 4-tpt, thus providing a highly stable trinuclear metallo-porphyrin array [64]. The molecular structure shows a closed pack arrangement of the three metallo-porphyrin moieties with the 4-tpt ligand being situated in the core of the triangular assembly and the carbonyl ligands pointing outwards (see Fig. 17).

The cavity of a supramolecular metalla-square built from $[ReCl(CO)_3]$ corners and {5,15-di(4-pyridyl)-2,8,12,18-tetra^{n}butyl-3,7,13,17-tetramethylporphyrinato}zinc connectors has showed good affinity for 4-tpt [65], while the orientation of multilayers assembly deposited on surfaces, constituted of (tetra-pyridyl-porphyrinato)zinc porphyrins and 4-tpt building blocks, was found to be influenced by the presence of the tridentate 4-tpt ligand during the deposition process [66].



Scheme 9. Controlled synthesis of Zn_3 metallo-porphyrin arrays using 4-tpt as a template [62].

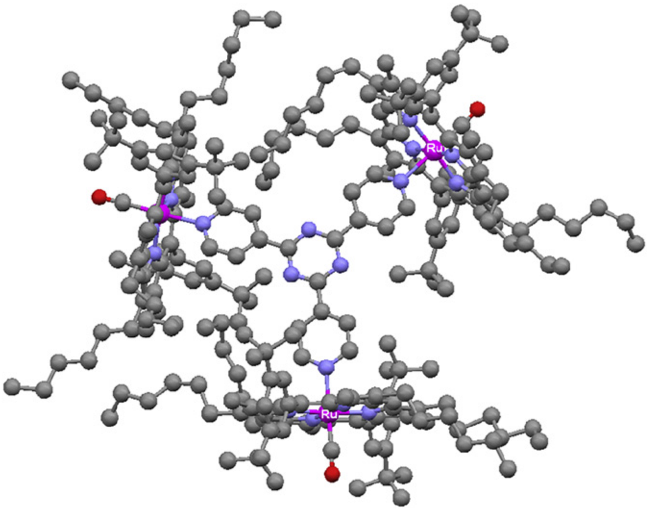


Fig. 17. Molecular structure of a trinuclear [{Ru(CO)porphyrin}$_3$(4-tpt)] array [64].

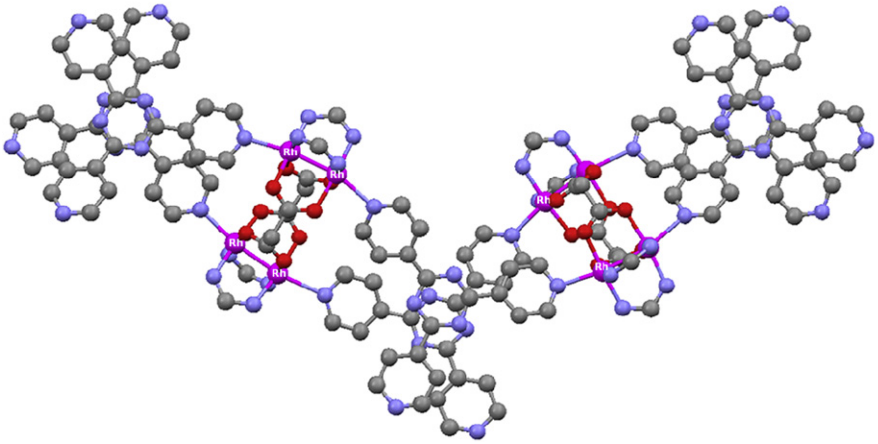


Fig. 18. 2D network observed in [{Rh_2(DAniF)$_2$}($O_2CCH_2CO_2$)$_2$(4-tpt)$_2$]$_n$ [71].

5.2. Coordination networks

As previously mentioned in Section 4.1 the preparation of supramolecular networks can be accomplished by a judicious combination of organic ligands and metal ions, thus giving rise to 1D, 2D or 3D metal–organic frameworks [51,67]. Accordingly, as for the 3-tpt ligand, metal–organic frameworks involving 4-tpt and metal centres have been prepared by several groups.

Inspired by the work of A.F. Wells [68], Robson and his co-workers have generated over the last 15 years several coordination networks by combining 4-tpt and metal ions [69]. They have not only worked with single metal centres linked together by bridging ligands to afford coordination networks, but also with bimetallic copper acetate building blocks. Indeed, by mixing a benzyl alcohol solution of 4-tpt and $Cu_2(O_2CCH_3)_4(H_2O)_2$ in methanol, they obtained a two-dimensional coordination network of the general formula $[\{Cu_2(O_2CCH_3)_4\}_3(\text{4-tpt})_2]_n\cdot 2n\text{MeOH}$ [70]. Similarly, a coordination network with interlocking lattices and double helices involving bimetallic Rh_2(DAniF)$_2$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate) building blocks and 4-tpt has been described by Cotton and Murillo [71]. In the solid state strong π-stacking interactions were observed between parallel 4-tpt connectors of the 2D network $[\{Rh_2(\text{DAniF})_2\}(O_2CCH_2CO_2)_2(\text{4-tpt})_2]_n\cdot 3n\text{CHCl}_3\cdot n\text{CH}_2\text{Cl}_2$, see Fig. 18.

A three-dimensional coordination network containing copper cyanide and 4-tpt ligands has been prepared by Li and co-workers [72]. The structure shows the Cu^{1+} ion to adopt a trigonal geometry with two cyanides and the nitrogen atom of a pyridyl group being coordinated, thus forming a $[Cu_3(CN)_3(\text{4-tpt})]_n$ coordination network, as presented in Fig. 19. Other interesting coordination

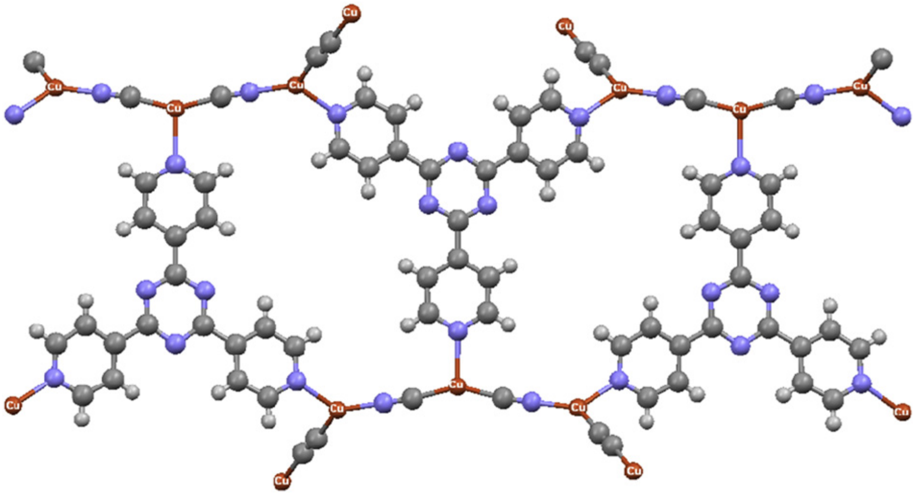
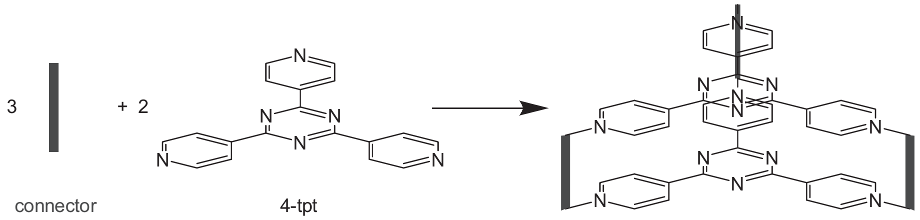


Fig. 19. The 4-tpt environment in the [Cu$_3$(CN)$_3$(4-tpt)]$_n$ network [73].



Scheme 10. Preparation of triangular prism incorporating 4-tpt panels.

networks built around Cu^{1+} and Cu^{2+} ions have been described [53,73]. They all show great potential as metal–organic frameworks.

A combination of hydrogen bonding and coordination chemistry has allowed the construction of a coordination network consisting of two interpenetrating chains. The platinum complex, [PtBrMe$_2$(Bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)] (Bu$_2$bipy = 4,4′-di-^{t}butyl-2,2′-bipyridine), which possesses a carboxylic acid function and a labile bromo ligand, was used with 4-tpt to generate the trinuclear salt, [{(HO$_2$CC$_6$H$_4$CH$_2$)(Bu$_2$bipy)Me$_2$Pt}$_3$(4-tpt)]$^{3+}$ isolated with hexafluorophosphate anions [74]. Upon crystallisation, hydrogen bonds between adjacent carboxylic acid groups generate the intriguing 3D-coordination network.

Encapsulation of various solvent molecules (THF, Et$_2$O, DMF) was performed using Co^{2+} one-dimensional coordination networks of the general formula, [Co(dmb)$_4$(4-tpt)]$_n \cdot n$ solvent molecules (dmb = dibenzoylmethane) [75]. The nature of the solvent significantly changes the supramolecular organisation, thus modifying the antiferromagnetic properties of these Co^{2+} coordination networks.

With the view of generating porous materials with new properties, different shapes and new chemical functionalities, the linkage of metal containing layers with 4-tpt has been explored [76]. The insertion of 4-tpt instead of the traditional bi-pyridyl linkers has yielded interesting materials. Among these interesting materials involving 4-tpt, coordination nanotubes have been described [77]. The nanotubes are assembled at the interface of an aqueous solution of HgCl$_2$, and a chloroform solution of 5,10,15,20-tetrapyridylporphyrin and 4-tpt.

5.3. *Discrete supramolecular assemblies*

The coordination of polynuclear clusters around the 4-tpt ligand has been studied with the view to generate systems with enhanced electronic properties. Indeed, [Re$_6$Se$_8$]$^{2+}$ [78] and [Ru$_3$O(OOCCH$_3$)$_6$(CO)(py)] [79] clusters coordinated to a 4-tpt core have been synthesised. In all cases, the 4-tpt ligand is surrounded by three cluster units, thus keeping its threefold symmetry even after complexation. The rich electrochemistry of these multicluster systems was studied and it showed interesting electronic properties.

Trinuclear systems coordinated to the pyridyl groups of a central 4-tpt ligand, incorporating pentamethylcyclopentadienyl cobalt, rhodium and iridium units containing an ancillary *ortho*-carborane-1-2-dithiolato or *ortho*-carborane-1-2-diselenolato ligands, have

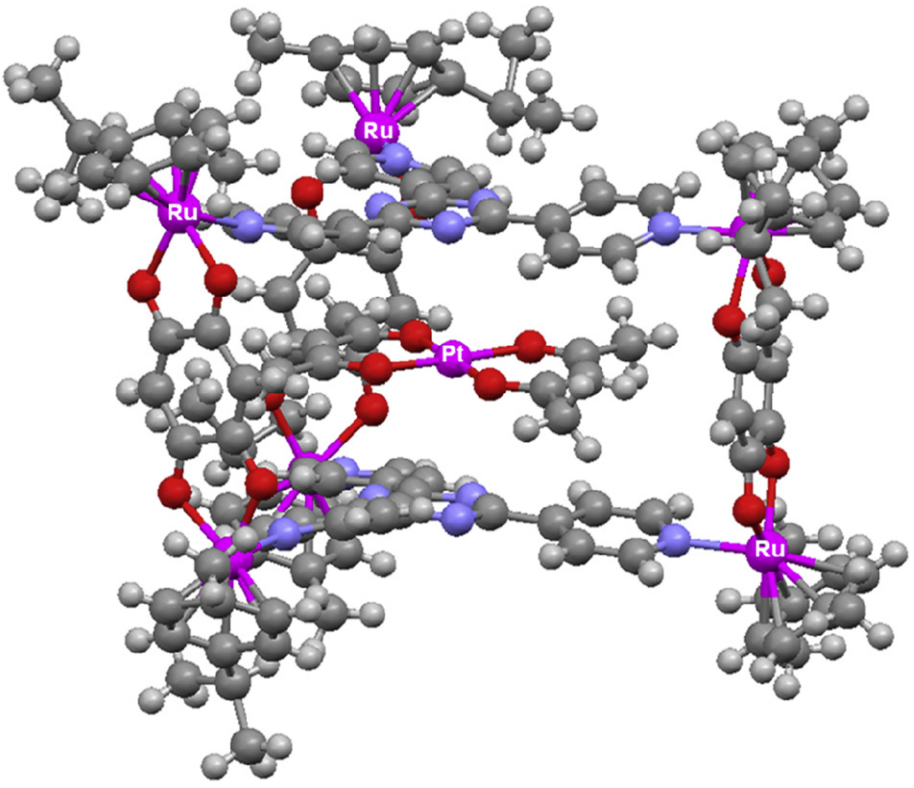
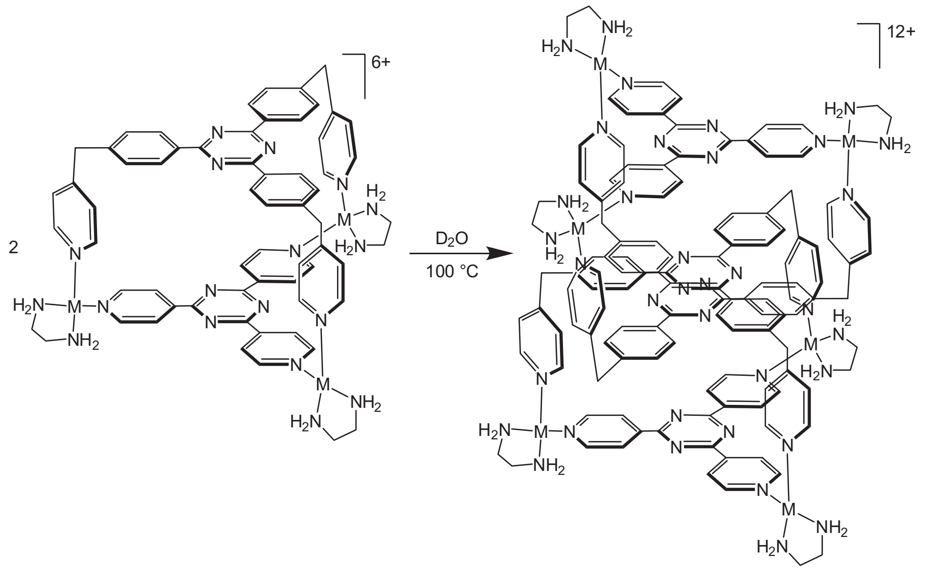


Fig. 20. Molecular structure of $[\{Pt(acac)_2\}\subset\{Ru_6(p\text{-}^{i}PrC_6H_4Me)_6(dobq)_3(4\text{-}tpt)_2\}]^{6+}$ [84c].



Scheme 11. Preparation of the interlocked $[\{M(en)\}_3(tpmt)(4\text{-tpt})]^{6+}$ (M = Pd, Pt) system [88].

been recently prepared by the group of Jin [80]. These multinuclear complexes with ancillary carboranyl groups offer new structural perspective and the introduction of original functions [81].

The simplest three-dimensional assembly is the triangular prism which requires only five components, two triangular panels (4-tpt for example) and three linear connectors (Scheme 10). Therefore, it is not surprising to find in the literature numerous examples of triangular prisms built with 4-tpt ligands and metal ions. Indeed, triangular prisms with 4-tpt ligands connected by square-planar Pd^{2+} [82] and Pt^{2+} [83] corners as well as by octahedral metal centres Ru^{2+} [59,84], Rh^{3+} [85], Re^{1+} [86] and Ir^{3+} [85] have been assembled with various connectors. Interestingly, a slight deviation from an eclipsed conformation of the two 4-tpt units introduces chirality in these systems [87].

Triangular prisms built with longer connectors have allowed the inclusion of molecules within the cavity of the prism, thus giving rise

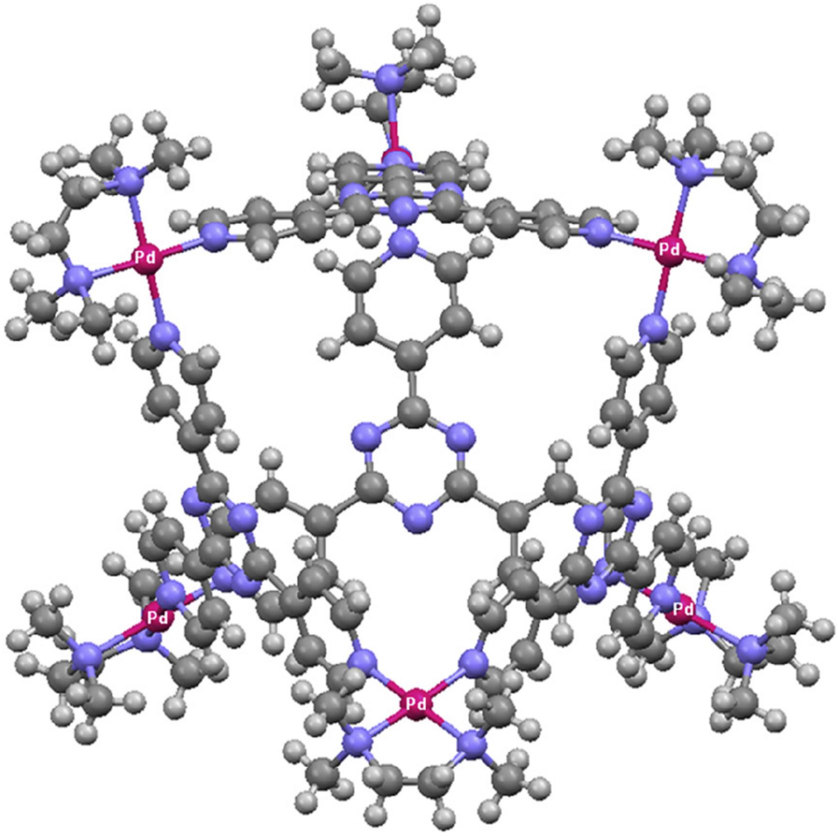


Fig. 21. $[\{Pd(en)\}_6(4\text{-tpt})_4]^{12+}$ coordination cage introduced by Fujita [91].

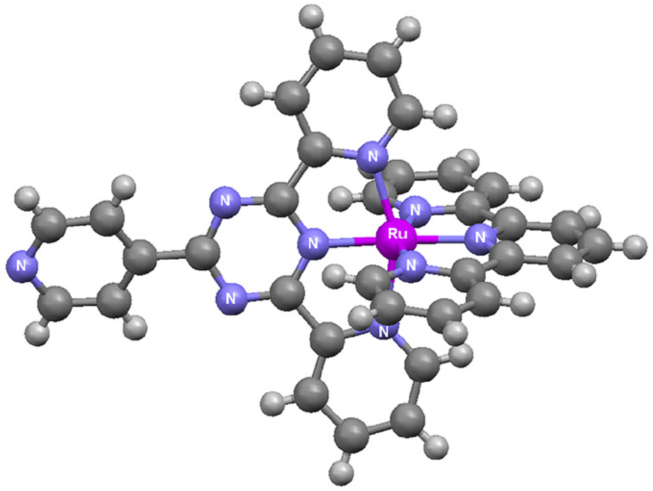


Fig. 22. Molecular structure of $[Ru(tpy)_2(2,2,4\text{-}tpt)]^{2+}$ [95].

to either carceplexes or host–guest systems. Carceplexes as opposed to host–guest systems imply a permanent encapsulation of the molecule trapped in the cavity, while in a host–guest system the molecule can be released without damaging the structure of the triangular prism. Therefore, these carceplexes and host–guest systems have found applications in chemistry (recognition and selective transformations), biology (translocation of drugs across membranes, sensors, biomimetics), and material science (construction of macroscopic architectures for storage and devices at the molecular level).

Recently, the hexacationic prism $[Ru_6(p\text{-}{}^{i}PrC_6H_4Me)_6(dobq)_3(4\text{-}tpt)_2]^{6+}$ (dobq = 2,5-dioxydo-1,4-benzoquinonato) has been synthesised [84c]. The cage compound is capable of encapsulating planar Pt and Pd acetylacetonate complexes (Fig. 20), as well as planar aromatic compounds of various sizes. In these systems the encapsulated guest is stable, with the physical properties of the prism being retained following encapsulation. The biological activity of some of these carceplexes has been evaluated and encouraging results obtained. The metalla-prism itself exhibits some activity which increases with the encapsulation of a guest, suggesting transport and leaching of the guest once inside the cell. The ability of the cationic cage to deliver guest molecules to cells was further confirmed by encapsulation of a fluorescent labelled pyrene-R derivative (1-(4,6-dichloro-1,3,5-triazin-2-yl)pyrene), and fluorescence spectroscopy was used to monitor uptake and release of the pyrene-R molecule in cancer cells [84g].

A ten component system, in which two triangular prisms of the general formula $[\{Pd(en)\}_3(tpmt)(4\text{-}tpt)]^{6+}$ (tpmt = 2,4,6-tris(4-pyridinylmethylphenyl)-1,3,5-triazine) are interlocked, has been described by Fujita [88]. The thermodynamically driven interlocked system is obtained after 3 days in D_2O at 100 °C (Scheme 11). Similar strategy was used to generate an even larger interlocked system in which four pyrene molecules were encapsulated in the multistacked aromatic assembly [89]. Likewise, stack of porphyrin molecules was obtained in the more spacious hexanuclear prism, $[\{Pd(en)\}_6(L_{bpy})_3(4\text{-}tpt)_2]^{12+}$ (L_{bpy} = 2,2′-6,6′-tetramethyl-4,4′-bipyridine or 1,4-bis(2,6-dimethylpyridin-4-yl)benzene) [90]. These two multistacked porphyrin systems exhibit unique UV/vis and ESR properties.

The most studied coordination cages are those generated with 4-tpt panels and $M(en)^{2+}$ corners (en = ethylenediamine; M = Pt, Pd), $[\{M(en)\}_6(4\text{-}tpt)_4]^{12+}$ (Fig. 21). Introduced by Fujita in 1995 [91], the three-dimensional M_6L_4 cage compound possesses T_d symmetry and diagonal M–M distances of 22 Å, thus providing a large hydrophobic cavity [92]. These coordination cages have been extensively used as molecular flasks to study reactivity and properties of molecules within a confined well-defined environment [93].

A similar cationic coordination cage of the formula $[\{Ru(aneS_4)\}_6(4\text{-}tpt)_4]^{12+}$ ($aneS_4$ = 1,4,7,11-tetrathiacyclododecane), in which four 4-tpt panels are connected by six $Ru(aneS_4)^{2+}$ instead of the $Pd(en)^{2+}$ or $Pt(en)^{2+}$ corners, has shown a bathochromic shift of the MLCT band upon encapsulation in its cavity of 1-adamantanol guest molecule [94].

6. Other 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives

Although the symmetrical 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives, 2-tpt, 3-tpt and 4-tpt, are quite easy to prepare, only one asymmetric isomer, 2,4-di(pyridyn-2-yl)-6-(pyridyn-4-yl)-1,3,5-triazine (2,2,4-tpt), has been isolated, characterised and used in coordination chemistry [8]. This asymmetric ligand was coordinated to ruthenium in view to prepare luminescent complexes of the type $[Ru(tpy)_2(2,2,4\text{-}tpt)]^{2+}$ [95]. The molecular structure of this cationic complex is presented in Fig. 22.

7. Outlook

The coordination adaptability of 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives has been emphasised in this review, and in view of the number of recent publications dealing with this family of polypyridyl ligands, the era of 2,4,6-tri(pyridyl)-1,3,5-triazine derivatives is not over yet and these versatile ligands will surely find in the future new applications in coordination chemistry.

Acknowledgements

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References

[1] (a) A.G. Blackman, Eur. J. Inorg. Chem. (2008) 2633–2647;
(b) C.R.K. Glasson, L.F. Lindoy, G.V. Meehan, Coord. Chem. Rev. 252 (2008) 940–963;
(c) M.D. Ward, Chem. Commun. (2009) 4487–4499.
[2] B. Therrien, Eur. J. Inorg. Chem. (2009) 2445–2453.
[3] F.H. Case, E. Koft, J. Am. Chem. Soc. 81 (1959) 905–906.
[4] F.W. Swamer, G.A. Reynolds, C.R. Hauser, J. Org. Chem. 16 (1951) 43–46.
[5] H.L. Anderson, S. Anderson, J.K.M. Sanders, J. Chem. Soc. Perkin Trans. 1 (1995) 2231–2245.
[6] H. Biedermann, K. Wichmann, Z. Naturforsch. Teil B 29 (1974) 360–362.
[7] (a) J.H. Forsberg, V.T. Spaziano, S.P. Klump, K.M. Sanders, J. Heterocyclic Chem. 25 (1988) 767–770;
(b) F. Xu, X.-H. Zhu, Q. Shen, J. Lu, J.-Q. Li, Chin. J. Chem. 20 (2002) 1334–1339;
(c) J. Wang, F. Xu, T. Cai, Q. Shen, Org. Lett. 10 (2008) 445–448.
[8] M.I.J. Polson, N.J. Taylor, G.S. Hanan, Chem. Commun. (2002) 1356–1357.
[9] (a) B.G. Stephens, H.L. Felkel Jr., W.M. Spinelli, Anal. Chem. 46 (1974) 692–696;
(b) M.J. Janmohamed, G.H. Ayres, Anal. Chem. 44 (1972) 2263–2268;
(c) Y. Sasaki, Anal. Chim. Acta 98 (1978) 335–342;
(d) J. Wei, N. Teshima, T. Sakai, Anal. Sci. 24 (2008) 371–376;
(e) G.S.R. Krishnamurti, P.M. Huang, Talanta 37 (1990) 745–748.
[10] D.A. Durharm, G.H. Frost, F.A. Hart, J. Inorg. Nucl. Chem. 31 (1969) 571–574.
[11] (a) A. Das, G. Pilet, S. Mitra, Ind. J. Chem. 45A (2006) 1988–1993;
(b) X.-P. Sun, W. Gu, X. Liu, Acta Cryst. E63 (2007) m1027–m1028;
(c) A. Majumder, G. Pilet, M.T. Garland Rodriguez, S. Mitra, Polyhedron 25 (2006) 2550–2558;
(d) H. Zhao, M. Shatruk, A.V. Prosvirin, K.R. Dunbar, Chem. Eur. J. 13 (2007) 6573–6589;
(e) G.-Y. Hsu, P. Misra, S.-C. Cheng, H.-H. Wei, S. Mohanta, Polyhedron 25 (2006) 3393–3398;
(f) A. Das, G.M. Rosair, M.S. El Fallah, J. Ribas, S. Mitra, Inorg. Chem. 45 (2006) 3301–3306;
(g) P. Tyagi, U.P. Singh, J. Coord. Chem. 62 (2009) 1613–1622;
(h) M. Zhang, R. Fang, Q. Zhao, J. Chem. Cryst. 38 (2008) 601–604;

(i) A. Majumder, C.R. Choudhury, S. Mitra, C. Marschner, J. Baumgartner, Z. Naturforsch. 60b (2005) 99–105.

[12] (a) G.K. Pagenkopf, D.W. Margerum, Inorg. Chem. 7 (1968) 2514–2519;
(b) P.G. Hela, R.N. Reddy, N.R. Anipindi, K.I. Priyadarsini, T. Mukherji, React. Kinet. Catal. Lett. 85 (2005) 79–87.

[13] (a) A. Majumder, G. Pilet, M.S. El Fallah, J. Ribas, S. Mitra, Inorg. Chim. Acta 360 (2007) 2307–2312;
(b) S.A. Cotton, V. Franckevicius, J. Fawcett, Polyhedron 21 (2002) 2055–2061;
(c) R. Zibaseresht, W.T. Robinson, R.M. Hartshorn, Acta Cryst. E62 (2006) m1150–m1153.

[14] (a) J.D. Holbrey, K.B. Vigour, W.M. Reichert, R.D. Rogers, J. Chem. Cryst. 36 (2006) 799–804;
(b) A. Das, C. Marschner, J. Cano, J. Baumgartner, J. Ribas, M.S. El Fallah, S. Mitra, Polyhedron 28 (2009) 2436–2442;
(c) A. Majumder, V. Gramlich, G.M. Rosair, S.R. Batten, J.D. Masuda, M.S. El Fallah, J. Ribas, J.-P. Sutter, C. Desplanches, S. Mitra, Cryst. Growth Des. 6 (2006) 2355–2368;
(d) S.A. Ibrahim, A.M. Hammam, M.A. El-Gahami, D.M. Fouad, Bull. Pol. Acad. Sci. Chem. 51 (2003) 93–103.

[15] (a) R. Zibaseresht, R.M. Hartshorn, Aust. J. Chem. 58 (2005) 345–353;
(b) M. Carla Aragoni, M. Arca, F.A. Devillanova, M.B. Hursthouse, S.L. Huth, F. Isaia, V. Lippolis, A. Mancini, S. Soddu, G. Verani, Dalton Trans. (2007) 2127–2134;
(c) M. Carla Aragoni, M. Arca, M. Crespo, F.A. Devillanova, M.B. Hursthouse, S.L. Huth, F. Isaia, V. Lippolis, G. Verani, Dalton Trans. (2009) 2510–2520;
(d) P. Byers, G.Y.S. Chan, M.G.B. Drew, M.J. Hudson, C. Madic, Polyhedron 17 (1996) 2845–2849;
(e) R.N. Patel, N. Singh, V.L.N. Gundla, Polyhedron 26 (2007) 757–762;
(f) A. Burkhardt, W. Plass, Inorg. Chem. Commun. 11 (2008) 303–306;
(g) M.E. Díaz de Vivar, S. Baggio, R. Baggio, Acta Cryst. E62 (2006) m986–m988.

[16] (a) R.N. Patel, N. Singh, K.K. Shukla, V.L.N. Gundla, U.K. Chauhan, Spect. Chim. Acta A 63 (2006) 21–26;
(b) Y.-Q. Zheng, W. Xu, F. Lin, G.-S. Fang, J. Coord. Chem. 59 (2006) 1825–1834;
(c) T. Glaser, T. Lügger, R. Fröhlich, Eur. J. Inorg. Chem. (2004) 394–400.

[17] (a) H.-Z. Xie, W.-J. Pan, Acta Cryst. E63 (2007) m1231–m1232;
(b) M. Harvey, S. Baggio, S. Russi, R. Baggio, Acta Cryst. C59 (2003) m171–m174.

[18] (a) S. Ghumaan, S. Kar, S.M. Mobin, B. Harish, V.G. Puranik, G.K. Lahiri, Inorg. Chem. 45 (2006) 2413–2423;
(b) S. Sharma, S.K. Singh, D.S. Pandey, Inorg. Chem. 47 (2008) 1179–1189;
(c) N. Gupta, N. Grover, G.A. Neyhart, P. Singh, H. Holden Thorp, Inorg. Chem. 32 (1993) 310–316;
(d) S. Chirayil, V. Hegde, Y. Jahng, R.P. Thummel, Inorg. Chem. 30 (1991) 2821–2823;
(e) S. Sharma, M. Trivedi, M. Chandra, D.S. Pandey, Ind. J. Chem. 43A (2004) 2573–2577;
(f) P. Paul, B. Tyagi, M.M. Bhadbhade, E. Suresh, J. Chem. Soc. Dalton Trans. (1997) 2273–2277;
(g) K.S. Singh, Y.A. Mozharivskyj, M.R. Kollipara, Z. Anorg. Allg. Chem. 632 (2006) 172–179;
(h) S. Sharma, M. Chandra, D.S. Pandey, Eur. J. Inorg. Chem. (2004) 3555–3563.

[19] P. Paul, B. Tyagi, A.K. Bilakhiya, M.M. Bhadbhade, E. Suresh, G. Ramachandraiah, Inorg. Chem. 37 (1998) 5733–5742.

[20] (a) H.-Z. Xie, W.-J. Pan, Acta Cryst. C63 (2007) m204–m206;
(b) M.E. Díaz de Vivar, S. Baggio, M.T. Garland, R. Baggio, Acta Cryst. C62 (2006) m195–m198.

[21] (a) S.K. Singh, S. Sharma, M. Chandra, D.S. Pandey, J. Organomet. Chem. 690 (2005) 3105–3110;
(b) P. Paul, B. Tyagi, A.K. Bilakhiya, P. Dastidar, E. Suresh, Inorg. Chem. 39 (2000) 14–22.

[22] (a) A. Morsali, Z. Naturforsch. 59b (2004) 1039–1044;
(b) J.M. Harrowfield, D.L. Kepert, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1147–1155;
(c) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1157–1164;
(d) F. Marandi, N. Asghari, M. Gorbanloo, A.A. Soudi, P. Mayer, Z. Anorg. Allg. Chem. 633 (2007) 536–538;
(e) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 55 (2002) 661–666.

[23] J.P.H. Charmant, A.H.M. Monowar Jahan, N.C. Norman, A.G. Orpen, T.J. Podesta, CrystEngComm 6 (2004) 29–33.

[24] (a) D.A. Durham, G.H. Frost, F.A. Hart, J. Inorg. Nucl. Chem. 31 (1969) 571–574;
(b) R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pécaut, Inorg. Chem. 38 (1999) 3581–3585;
(c) M.G.B. Drew, M.J. Hudson, P.B. Iveson, C. Madic, Acta Cryst. C56 (2000) 434–435;
(d) G. Ionova, C. Rabbe, R. Guillaumont, S. Ionov, C. Madic, J.-C. Krupa, D. Guillaneux, New J. Chem. 26 (2002) 234–242;
(e) C.R. De Silva, J. Wang, M.D. Carducci, S.A. Rajapakshe, Z. Zheng, Inorg. Chim. Acta 357 (2004) 630–634;
(f) N.A. Budantseva, G.B. Andreev, A.M. Fedosseev, A.A. Bessonov, M.Yu. Antipin, J.-C. Krupa, C.R. Chimie 8 (2005) 91–95;
(g) C.R. De Silva, R. Wang, Z. Zheng, Polyhedron 25 (2006) 3449–3455;
(h) S.A. Cotton, V. Franckevicius, M.F. Mahon, L.L. Ooi, P.R. Raithby, S.J. Teat, Polyhedron 25 (2006) 1057–1068;
(i) M. Miguirditchian, D. Guillaneux, N. François, S. Airvault, S. Ducros, D. Thauvin, C. Madic, M. Illemassène, G. Lagarde, J.-C. Krupa, Nucl. Sci. Eng. 153 (2006) 223–232;
(j) H. Zhao, N. Lopez, A. Prosvirin, H.T. Chifotides, K.R. Dunbar, Dalton Trans. (2007) 878–888.

[25] Y.-F. Zhao, Y.-L. Zhao, F. Bai, Y. Wang, J. Fluoresc. 19 (2009) 179–182.

[26] A. Gelling, M.D. Olsen, K.G. Orrell, A.G. Osborne, V. Šik, Inorg. Chim. Acta 264 (1997) 257–268.

[27] (a) L. Zhang, X.-Q. Lü, Q. Zhang, C.-L. Chen, B.-S. Kang, Trans. Met. Chem. 30 (2005) 76–81;
(b) H.-W. Xu, J.-X. Li, L. Pin, Z.-N. Chen, J.-G. Wu, Trans. Met. Chem. 32 (2007) 839–844.

[28] L.H. Abdel-Rahman, Trans. Met. Chem. 26 (2001) 412–416.

[29] A.E. Ion, E.T. Spielberg, H. Görls, W. Plass, Inorg. Chim. Acta 360 (2007) 3925–3931.

[30] L.H. Abdel-Rahman, J. Coord. Chem. 60 (2007) 865–875.

[31] (a) M. Schwalbe, M. Karnahl, H. Görls, D. Chartrand, F. Laverdiere, G.S. Hanan, S. Tschierlei, B. Dietzek, M. Schmitt, J. Popp, J.G. Vos, S. Rau, Dalton Trans. (2009) 4012–4022;
(b) A. Singh, N. Singh, D.S. Pandey, J. Organomet. Chem. 642 (2002) 48–57;
(c) C. Metcalfe, S. Spey, H. Adams, J.A. Thomas, J. Chem. Soc. Dalton Trans. (2002) 4732–4739;
(d) R. Lalrempuia, P. Govindaswamy, Y.A. Mozharivskyj, M.R. Kollipara, Polyhedron 23 (2004) 1069–1073;
(e) M. Chandra, A.N. Sahay, D.S. Pandey, M.C. Puerta, P. Valerga, J. Organomet. Chem. 648 (2002) 39–48.

[32] (a) P. Govindaswamy, M.R. Kollipara, J. Coord. Chem. 59 (2006) 663–669;
(b) S.K. Singh, M. Chandra, S.K. Dubey, D.S. Pandey, Eur. J. Inorg. Chem. (2006) 3954–3961.

[33] (a) J. Granifo, Polyhedron 18 (1999) 1061–1066;
(b) X. Chen, F.J. Femia, J.W. Babich, J.A. Zubieta, Inorg. Chem. 40 (2001) 2769–2777.

[34] M. Maekawa, T. Minematsu, H. Konaka, K. Sugimoto, T. Kuroda-Sowa, Y. Suenaga, M. Munakata, Inorg. Chim. Acta 357 (2004) 3456–3472.

[35] E.M. Smolin, L. Rapoport, s-Triazine and Derivatives. Interscience, New York, 1959, p. 163.

[36] (a) E.I. Lerner, S.J. Lippard, J. Am. Chem. Soc. 98 (1976) 5397–5398;
(b) E.I. Lerner, S.J. Lippard, Inorg. Chem. 16 (1977) 1546–1551.

[37] (a) J. Borrás, G. Alzuet, M. González-Álvarez, J.L. García-Giménez, B. Macías, M. Liu-González, Eur. J. Inorg. Chem. (2007) 822–834;
(b) Q.-H. Zhao, M.-S. Zhang, R.-B. Fang, J. Struct. Chem. 47 (2006) 764–767;
(c) I. Castro, J. Faus, M. Julve, J.M. Amigó, J. Sletten, T. Debaerdemaeker, J. Chem. Soc., Dalton Trans. (1990) 891–897;
(d) J. Borrás, G. Alzuet, M. González-Álvarez, F. Estevan, B. Macías, M. Liu-González, A. Castiñeiras, Polyhedron 26 (2007) 5009–5015;
(e) S.S. Massoud, E. Druel, M. Dufort, R. Lalancette, J. Kitchen, J. Grebowicz, R. Vicente, U. Mukhopadhyay, I. Bernal, F.A. Mautner, Polyhedron 28 (2009) 3849–3857;
(f) K.N. Lazarou, C.P. Raptopoulou, S.P. Perlepes, V. Psycharis, Polyhedron 28 (2009) 3185–3192.

[38] (a) P. Paul, Proc. Ind. Acad. Sci. 114 (2002) 269–276;
(b) P. Paul, B. Tyagi, A.K. Bilakhiya, M.M. Bhadbhade, E. Suresh, J. Chem. Soc. Dalton Trans. (1999) 2009–2014.

[39] N.C. Thomas, B. Lachele Foley, A.L. Rheingold, Inorg. Chem. 27 (1988) 3426–3429.

[40] S.A. Ibrahim, M.A. El-Gahami, A.M. Hammam, D.M. Fouad, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 1505–1514.

[41] Z. Trávníček, M. Maloň, Z. Šindelář, Trans. Met. Chem. 24 (1999) 38–41.

[42] L.H. Abdel-Rahman, R.M. Ramadan, J. Coord. Chem. 60 (2007) 1891–1901.

[43] R.M. Berger, D.D. Ellis II, Inorg. Chim. Acta 241 (1996) 1–4.

[44] X.-P. Zhou, X. Zhang, S.-H. Lin, D. Li, Cryst. Growth Des. 7 (2007) 485–487.

[45] J. Halfpenny, R.W.H. Small, Acta Cryst. B38 (1982) 939–942.

[46] S. Rubino, P. Portanova, A. Albanese, G. Calvaruso, S. Orecchio, G. Fontana, G.C. Stocco, J. Inorg. Biochem. 101 (2007) 1473–1482.

[47] S. Rubino, P. Portanova, A. Girasolo, G. Calvaruso, S. Orecchio, G.C. Stocco, Eur. J. Med. Chem. 44 (2009) 1041–1048.

[48] S. Ghumaan, B. Sarkar, S. Patra, K. Parimal, J. van Slageren, J. Fiedler, W. Kaim, G.K. Lahiri, Dalton Trans. (2005) 706–712.

[49] X.-P. Zhou, D. Li, S.-L. Zheng, X. Zhang, T. Wu, Inorg. Chem. 45 (2006) 7119–7125.

[50] I. Yenmez, H. Specker, Fresenius Z. Anal. Chem. 296 (1979) 140–145.

[51] (a) D.N. Reinhoudt, M. Crego-Calama, Science 295 (2002) 2403–2407;
(b) R. Dobrawa, F. Würthner, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 4981–4995;
(c) J.R. Long, O.M. Yaghi, Chem. Soc. Rev. 38 (2009) 1213–1214.

[52] H.-B. Liu, S.-Y. Yu, H. Huang, Z.-X. Zhang, Aust. J. Chem. 56 (2003) 671–674.

[53] N. Zhang, M.-X. Li, Z.-X. Wang, M. Shao, S.-R. Zhu, Inorg. Chim. Acta 363 (2010) 8–14.

[54] (a) M. Fujita, S.-Y. Yu, T. Kusukawa, H. Funaki, K. Ogura, K. Yamaguchi, Angew. Chem. Int. Ed. 37 (1998) 2082–2085;
(b) A. Orita, L. Jiang, T. Nakano, N. Ma, J. Otera, Chem. Commun. (2002) 1362–1363.

[55] M. Yoshizawa, M. Tamura, M. Fujita, Science 312 (2006) 251–254.

[56] M. Yoshizawa, Y. Takeyama, T. Kurusawa, M. Fujita, Angew. Chem. Int. Ed. 41 (2002) 1347–1349.

[57] (a) S.-Y. Yu, T. Kusukawa, K. Biradha, M. Fujita, J. Am. Chem. Soc. 122 (2000) 2665–2666;
(b) Y. Kubota, S. Sakamoto, K. Yamaguchi, M. Fujita, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 4854–4856;
(c) S. Tashiro, M. Tominaga, Y. Yamaguchi, K. Kato, M. Fujita, Angew. Chem. Int. Ed. 45 (2006) 241–244;
(d) S. Tashiro, M. Fujita, Bull. Chem. Soc. Jpn. 79 (2006) 833–837.

[58] C.-Y. Hung, A.S. Singh, C.-W. Chen, Y.-S. Wen, S.-S. Sun, Chem. Commun. (2009) 1511–1513.

[59] P. Govindaswamy, G. Süss-Fink, B. Therrien, Organometallics 26 (2007) 915–924.

[60] (a) M. Hanack, M. Fiedler, L.R. Subramanian, Synth. Met. 100 (1999) 123–130;
(b) S. Hayami, K. Kawamura, G. Juhasz, T. Kawahara, K. Uehashi, Y. Maeda, Mol. Cryst. Liq. Cryst. 379 (2002) 371–376.

[61] J. Kim, S. Han, Acta Cryst. C58 (2002) m521–m522.

[62] A. Vidal-Ferran, C.M. Müller, J.K.M. Sanders, J. Chem. Soc. Chem. Commun. (1994) 2657–2658.

[63] (a) S. Anderson, H.L. Anderson, J.K.M. Sanders, J. Chem. Soc. Perkin Trans. 1 (1995) 2247–2254;
(b) S. Anderson, H.L. Anderson, J.K.M. Sanders, J. Chem. Soc. Perkin Trans. 1 (1995) 2255–2267;
(c) H.L. Anderson, C.J. Walter, A. Vidal-Ferran, R.A. Hay, P.A. Lowden, J.K.M. Sanders, J. Chem. Soc. Perkin Trans. 1 (1995) 2275–2279;
(d) D.W.J. McCallien, J.K.M. Sanders, J. Am. Chem. Soc. 117 (1995) 6611–6612;
(e) A. Vidal-Ferran, N. Bampos, J.K.M. Sanders, Inorg. Chem. 36 (1997) 6117–6126;
(f) V. Marvaud, A. Vidal-Ferran, S.J. Webb, J.K.M. Sanders, J. Chem. Soc. Dalton Trans. (1997) 985–990;
(g) Z. Clyde-Watson, N. Bampos, J.K.M. Sanders, New J. Chem. 22 (1998) 1135–1138;
(h) S.J. Webb, J.K.M. Sanders, Inorg. Chem. 39 (2000) 5912–5919;
(i) A.L. Kieran, A.D. Bond, A.M. Belenguer, J.K.M. Sanders, Chem. Commun. (2003) 2674–2675;
(j) K.-T. Youm, S.T. Nguyen, J.T. Hupp, Chem. Commun. (2008) 3375–3377.

[64] S.L. Darling, C.C. Mak, N. Bampos, N. Feeder, S.J. Teat, J.K.M. Sanders, New J. Chem. 23 (1999) 359–364.

[65] G.A. Mines, B.-C. Tzeng, K.J. Stevenson, J. Li, J.T. Hupp, Angew. Chem. Int. Ed. 41 (2002) 154–157.

[66] H.-T. Chen, B. Liu, H.-T. Wang, Z.-D. Xiao, M. Chen, D.-J. Qian, Mater. Sci. Eng. C27 (2007) 639–645.

[67] For recent reviews on MOF's (a) D.J. Tranchemontagne, J.L. Mendoza-Cortés, M. O'Keeffe, O.M. Yaghi, Chem. Soc. Rev. 38 (2009) 1257–1283;
(b) J.J. Perry IV, J.A. Perman, M.J. Zaworotko, Chem. Soc. Rev. 38 (2009) 1400–1417;
(c) J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.B.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450–1459;
(d) M.J. Prakash, M.S. Lah, Chem. Commun. (2009) 3326–3341;
(e) B. Chen, S. Xiang, G. Qian, Acc. Chem. Res. (2010). doi:10.1021/ar100023y.

[68] A.F. Wells, Three-Dimensional Nets and Polyhedra. Wiley-Interscience, New York, 1977.

[69] (a) S.R. Batten, B.F. Hoskins, R. Robson, Angew. Chem. Int. Ed. 34 (1995) 820–823;
(b) S.R. Batten, B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 117 (1995) 5385–5386;
(c) B.F. Abrahams, S.R. Batten, H. Hamit, B.F. Hoskins, R. Robson, Angew. Chem. Int. Ed. 35 (1996) 1690–1692;
(d) B.F. Abrahams, S.R. Batten, H. Hamit, B.F. Hoskins, R. Robson, Chem. Commun. (1996) 1313–1314.

[70] S.R. Batten, B.F. Hoskins, B. Moubaraki, K.S. Murray, R. Robson, Chem. Commun. (2000) 1095–1096.

[71] F.A. Cotton, C. Lin, C.A. Murillo, J. Chem. Soc. Dalton Trans. (2001) 499–501.

[72] M.-X. Li, Z.-X. Miao, M. Shao, S.-W. Liang, S.-R. Zhu, Inorg. Chem. 47 (2008) 4481–4489.

[73] (a) D. Hagrman, P. Hagrman, J. Zubieta, Inorg. Chim. Acta 300–302 (2000) 212–224;
(b) D.E. Hagrman, J. Zubieta, J. Solid State Chem. 152 (2000) 141–151;
(c) D.N. Dybtsev, H. Chun, K. Kim, Chem. Commun. (2004) 1594–1595;
(d) G.-F. Liu, W.-H. Zhang, Y. Chen, D. Liu, J.-P. Lang, Inorg. Chem. Commun. 10 (2007) 1049–1053;
(e) W.-H. Zhang, Y.-L. Song, Z.-G. Ren, H.-X. Li, L.-L. Li, Y. Zhang, J.-P. Lang, Inorg. Chem. 46 (2007) 6647–6660;
(f) W. Li, M.-X. Li, M. Shao, S.-R. Zhu, Inorg. Chem. Commun. 10 (2007) 753–756.

[74] C.S.A. Fraser, M.C. Jennings, R.J. Puddephatt, Chem. Commun. (2001) 1310–1311.

[75] L.A. Barrios, J. Ribas, G. Aromi, J. Ribas-Ariño, P. Gamez, O. Roubeau, S.J. Teat, Inorg. Chem. 46 (2007) 7154–7162.

[76] (a) R.S. Rarig Jr., J. Zubieta, J. Chem. Soc. Dalton Trans. (2001) 3446–3452;
(b) R.S. Rarig Jr., J. Zubieta, Dalton Trans. (2003) 1861–1868;
(c) J. Peres Barrio, J.-N. Rebilly, B. Carter, D. Bradshaw, J. Bacsa, A.Y. Ganin, H. Park, A. Trewin, R. Vaidhyanathan, A.I. Cooper, J.E. Warren, M.J. Rosseinsky, Chem. Eur. J. 14 (2008) 4521–4532.

[77] B. Liu, D.-J. Qian, M. Chen, T. Wakayama, C. Nakamura, J. Miyake, Chem. Commun. (2006) 3175–3177.

[78] (a) B.K. Roland, H.D. Selby, M.D. Carducci, Z. Zheng, J. Am. Chem. Soc. 124 (2002) 3222–3223;
(b) Z. Zheng, Polym. Preprints 45 (2004) 458–459.

[79] (a) B.J. Lear, C.P. Kubiak, Inorg. Chem. 45 (2006) 7041–7043;
(b) J.-S. Zhang, S. Liu, G.-L. Wang, Y.-J. Lin, G.-X. Jin, Organometallics 27 (2008) 1112–1118.

[80] (a) J.-Q. Wang, C.-X. Ren, G.-X. Jin, Chem. Commun. (2005) 4738–4740;
(b) S. Liu, G.-L. Wang, G.-X. Jin, Dalton Trans. (2008) 425–432;
(c) Y.-F. Han, W.-G. Jia, W.-B. Yu, G.-X. Jin, Chem. Soc. Rev. 38 (2009) 3419–3434.

[81] (a) G.-X. Jin, Coord. Chem. Rev. 248 (2004) 587–602;
(b) Z. García Hernández, B. Wrackmeyer, R. Kempe, M. Herberhold, ARKIVOC (2008) 65–80.

[82] (a) M. Yoshizawa, M. Nagao, K. Kumazawa, M. Fujita, J. Organomet. Chem. 690 (2005) 5383–5388;
(b) K. Ono, M. Yoshizawa, T. Kato, M. Fujita, Chem. Commun. (2008) 2328–2330;
(c) J.D. Crowley, A.J. Goshe, B. Bosnich, Chem. Commun. (2003) 2824–2825;
(d) J.S. Gardner, R.G. Harrison, J.D. Lamb, D.V. Dearden, New J. Chem. 30 (2006) 1276–1282.

[83] (a) K. Kumasawa, K. Biradha, T. Kusukawa, T. Okano, M. Fujita, Angew. Chem. Int. Ed. 42 (2003) 3909–3913;
(b) M. Yoshizawa, J. Nakagawa, K. Kumazawa, M. Nagao, M. Kawano, T. Ozeki, M. Fujita, Angew. Chem. Int. Ed. 44 (2005) 1810–1813;
(c) K. Kumazawa, M. Yoshizawa, H.-B. Liu, Y. Kamikawa, M. Moriyama, T. Kato, M. Fujita, Chem. Eur. J. 11 (2005) 2519–2524;
(d) M. Yoshizawa, K. Ono, K. Kumazawa, T. Kato, M. Fujita, J. Am. Chem. Soc. 127 (2005) 10800–10801;
(e) M. Yoshizawa, K. Kumazawa, M. Fujita, J. Am. Chem. Soc. 127 (2005) 13456–13457;
(f) K. Ono, M. Yoshizawa, M. Akita, T. Kato, Y. Tsunobuchi, S.-i. Ohkoshi, M. Fujita, J. Am. Chem. Soc. 131 (2009) 2782–2783;
(g) P.J. Lusby, P. Müller, S.J. Pike, A.M.Z. Slawin, J. Am. Chem. Soc. 131 (2009) 16398–16400;
(h) T. Sawada, M. Yoshizawa, S. Sato, M. Fujita, Nature Chem. 1 (2009) 53–56;
(i) Y. Yamauchi, M. Yoshizawa, M. Akita, M. Fujita, Proc. Natl. Acad. Sci. U.S.A. 106 (2009) 10435–10437;
(j) K. Ono, J.K. Klosterman, M. Yoshizawa, K. Sekiguchi, T. Tahara, M. Fujita, J. Am. Chem. Soc. 131 (2009) 12526–12527;
(k) Y. Yamauchi, M. Yoshizawa, M. Akita, M. Fujita, J. Am. Chem. Soc. 132 (2010) 960–966.

[84] (a) P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink, B. Therrien, Chem. Commun. (2006) 4691–4693;
(b) B. Therrien, G. Süss-Fink, P. Govindaswamy, A.K. Renfrew, P.J. Dyson, Angew. Chem. Int. Ed. 47 (2008) 3773–3776;
(c) P. Govindaswamy, J. Furrer, G. Süss-Fink, B. Therrien, Z. Anorg. Allg. Chem. 634 (2008) 1349–1352;
(d) J. Mattsson, P. Govindaswamy, J. Furrer, Y. Sei, K. Yamaguchi, G. Süss-Fink, B. Therrien, Organometallics 27 (2008) 4346–4356;
(e) N.P.E. Barry, B. Therrien, Eur. J. Inorg. Chem. (2009) 4695–4700;
(f) O. Zava, J. Mattsson, B. Therrien, P.J. Dyson, Chem. Eur. J. 16 (2010) 1428–1431;
(g) J. Freudenreich, N.P.E. Barry, G. Süss-Fink, B. Therrien, Eur. J. Inorg. Chem. (2010) 2400–2405;
(h) J. Mattsson, O. Zava, A.K. Renfrew, Y. Sei, K. Yamaguchi, P.J. Dyson, B. Therrien, Dalton Trans. 39 (2010) 8248–8255.

[85] (a) P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink, B. Therrien, Dalton Trans. (2007) 4457–4463;
(b) Y.-F. Han, Y.-J. Lin, W.-G. Jia, L.-H. Weng, G.-X. Jin, Organometallics 26 (2007) 5848–5853;
(c) P. Govindaswamy, G. Süss-Fink, B. Therrien, Inorg. Chem. Commun. 10 (2007) 1489–1492;
(d) Y.-F. Han, W.-G. Jia, Y.-J. Lin, G.-X. Jin, J. Organomet. Chem. 693 (2008) 546–550.

[86] (a) K.D. Benkstein, J.T. Hupp, Mol. Cryst. Liq. Cryst. 342 (2000) 151–158;
(b) S.-S. Sun, A.J. Lees, Chem. Commun. (2001) 103–104;
(c) B. Manimaran, T. Rajendran, Y.-L. Lu, G.-H. Lee, S.-M. Peng, K.-L. Lu, Eur. J. Inorg. Chem. (2001) 633–636;
(d) P.H. Dinolfo, V. Coropceanu, J.-L. Brédas, J.T. Hupp, J. Am. Chem. Soc. 128 (2006) 12592–12593;
(e) M. Casanova, E. Zangrando, F. Munini, E. Iengo, E. Alessio, Dalton Trans. (2006) 5033–5045;
(f) J.-Y. Wu, C.-H. Chang, P. Thanasekaran, C.-C. Tsai, T.-W. Tseng, G.-H. Lee, S.-M. Peng, K.-L. Lu, Dalton Trans. (2008) 6110–6112.

[87] B. Therrien, G. Süss-Fink, Chimia 62 (2008) 514–518.

[88] M. Fujita, N. Fujita, K. Oguras, K. Yamaguchi, Nature 400 (1999) 52–55.

[89] S. Sato, O. Morohara, D. Fujita, Y. Yamaguchi, K. Kato, M. Fujita, J. Am. Chem. Soc. 132 (2010) 3670–3671.

[90] K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita, Angew. Chem. Int. Ed. 46 (2007) 1803–1806.

[91] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, Nature 378 (1995) 469–471.

[92] (a) M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Rev. 38 (2005) 371–380;
(b) J.K. Klosterman, Y. Yamauchi, M. Fujita, Chem. Soc. Rev. 38 (2009) 1714–1725 and references therein.

[93] M. Yoshizawa, J.K. Klosterman, M. Fujita, Angew. Chem. Int. Ed. 48 (2009) 3418–3438 and references therein.

[94] K.-I. Yamashita, M. Kawano, M. Fujita, Chem. Commun. (2007) 4102–4103.

[95] M.I.J. Polson, E.A. Medlycott, G.S. Hanan, L. Mikelsons, N.J. Taylor, M. Watanabe, Y. Tanaka, F. Loiseau, R. Passalacqua, S. Campagna, Chem. Eur. J. 10 (2004) 3640–3648.

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