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Coordination Chemistry Reviews
222 (2001) 219–250

COORDINATION CHEMISTRY REVIEWS

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Simple 1:1 and 1:2 complexes of metal ions with heterocycles as building blocks for discrete molecular as well as polymeric assemblies

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Received 22 January 2001; accepted 25 May 2001

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PII: S0010-8545(01)00390-3

Abstract

The use of transition metals with low coordination numbers or blocked bonding positions in combination with nitrogen heterocyclic ligands of different geometries (e.g. pyrazole, imidazole, bipyrazine, pyrimidine or purine) leads to formation of both discrete supramolecular assemblies and 1D polymers. When highly coordinating 'naked' metal ions are applied instead, 2D and 3D frameworks are generated. Some of the assemblies, both molecular and polymeric, possess cavities or channels that can reversibly include guest molecules, including anions. The chemistry reported provides a vast playground for potential applications and future synthetic work.

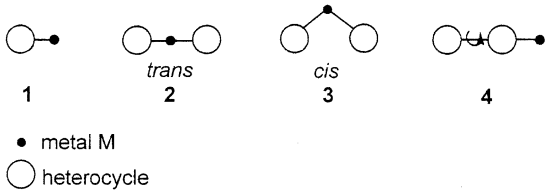
Keywords: Molecular architecture; Metals; Platinum; Metal-rich supramolecules

1. Introduction

Nitrogen-containing heterocycles with their pronounced propensity of acting as ligands for metal ions have played a major role in the development of the field now generally termed supramolecular chemistry [1–7]. Like transition metal ions, heterocycles frequently provide *directionality*, at least if endocyclic donor sites are concerned, thereby facilitating construction of a particular molecular architecture, and providing some degree of predictability concerning the composition of the product. Frequently, the heterocyclic ring systems have in addition functional groups for hydrogen bonding interactions. This feature then permits the unique opportunity to combine hydrogen bonding motifs for the generation of supramolecular architectures [8–10] with the concept of utilizing the coordinative bond [11,12].

We have, in recent years, studied metal complex formation of purine (pu) and pyrimidine (pym) nucleobases as well as of selected other heterocyclic ligands such as pyrazole (Hpz), imidazole (Him) derivatives, pyrazine (pyz), 2-aminopyridine

(Hampy), 2-hydroxopyrimidine (Hpymo), 4,4′-bipyridine (4,4′-bpy), and 2,2′-bipyrazine (2,2′-bpz), among others, with particular attention to the programmed construction of larger aggregates. Virtually in all cases we started out from very simple compounds (**1**–**4**) which contained a metal entity fixed to one (**1** and **4**) or two (**2** and **3**) heterocyclic ligands via an endocyclic N atom. In all cases the heterocycle contained additional metal binding sites, either in the ring (N atom) or in an exocyclic position (NH_2 group or O atom). With **4**, e.g. with 2,2′-bipyrazine, the flexibility of the molecule, viz. the possibility of rotation of the two halves about the central C–C bond, is to be noted.



In the following, selected examples originating from this work will be presented and discussed. Special emphasis will be on systems containing pyrimidine bases, including models of the naturally occurring pyrimidine bases cytosine, uracil and thymine. As will be pointed out, the high affinity of some of these ligands for more than just one metal ion [13] frequently leads to supramolecular entities that are rich in metal ions and consequently highly charged, thereby constrasting the situation seen in supramolecular chemistry without metals and with metals occurring at most in a 1:1 ratio with the heterocyclic ligand, respectively.

supramolecular chemistry without metal ions	supramolecular chemistry with low metal ions content	supramolecular chemistry with excess metal ions

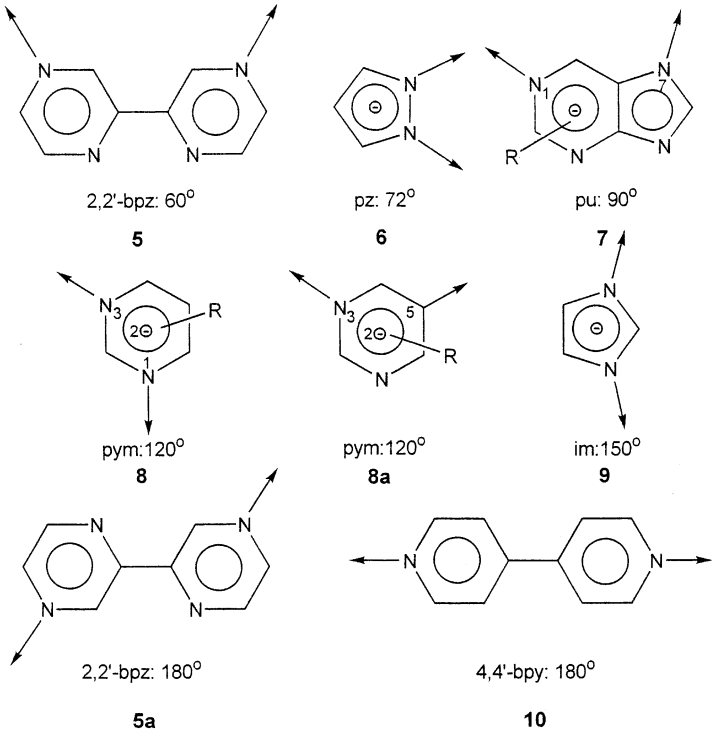
For example, the molecular polygons prepared by Stang and Olenyuk [14] usually contain the metal ion and the organic linker entity in a 1:1 ratio. On the other hand, in Fujitas coordination nanotubes bases on oligo(3,5-pyridine) ligands the ratio of metal ions to ligands is considerably higher, e.g. 2.5 with the pentamer ligand [15]. What is unique about some of the pyrimidine-based compounds discussed hereafter is the small size of the heterocyclic ring as opposed to the oligo(3,5-pyridine)-based systems.

2. General aspects

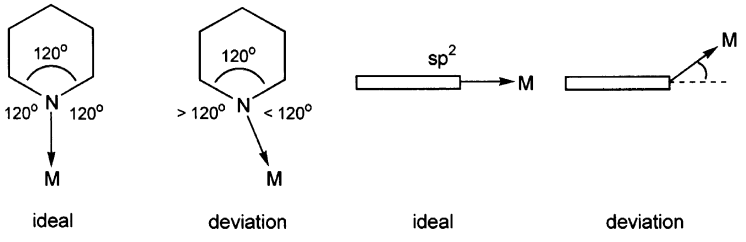
2.1. Angles provided by heterocyclic ligands

Following up on work by Fujita et al. [16], the group of Stang has systematized the formation of cyclic polygonal and polyhedral motifs from angular (A) and

linear units (L) in a so called 'molecular library' approach [4,14]. In the following we shall examine briefly this approach by restricting ourselves primarily to heterocyclic ligands we have applied. Heterocyclic ligands provide a variety of 'ideal' angles to be used in molecular architecture. These range from 60 to 180° if metal binding to endocyclic donor atoms is considered only.



Experience shows that metal binding to ring atoms of nucleobases frequently leads to rather 'soft' structures and that marked deviations from expectations can be anticipated for a number of reasons: (i) External ring angles (Scheme 1). They may strongly deviate from the ideal case, e.g. from 120° in six-membered ring systems. Even H bond formation between substituents of the heterocyclic ring and

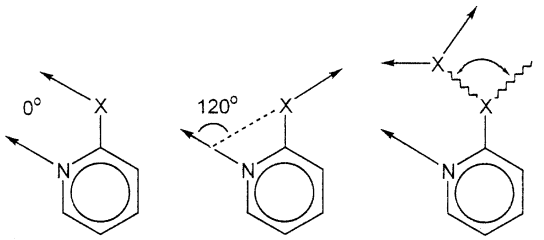


Scheme 1.

other ligands at the metal may be sufficient to cause marked deviations [17]. (ii) Metal out-of-plane. In heteroaromatic systems the metal may be substantially out-of-plane, hence deviation from the 'ideal' sp^2 hybridazation may be large. (iii) Torsional angles within C–C coupled heterocycles. With flexible heterocycles such as 2,2′-bipyrazine (**5a**) or 4,4′-bipyridine (**10**), any torsion between the two halves of the molecule may have a strong influence on the resulting architecture. (iv) Metal geometry. Deviations of 'ideal' angular values of square-planar, tetrahedral or octahedral metal ions can be substantial (see also Section 2.2).

Taken together, all these effects can add up to situation in which combinations of A and L building blocks do not lead to the expected architecture yet to a priori unexpected ones, sometimes in equilibrium. Thus combinations of 90 and 180° building blocks can also lead to molecular triangles [18,19] rather than to the expected square, and imidazole moieties and square-planar metal units may produce either triangles or tetracyclic systems (cf. Section 3.2).

Things become even more complex when exocyclic substituents of heterocyclic rings are involved in metal coordination. In the simplest case, with exocyclic donor groups consisting of a single atom or group X (e.g. X = O or NH_2 or NH^-), two extreme situations can be envisaged, viz. an approximately parallel orientation of the metal–X and metal–N vectors (**11**) or an orientation, in which the two vectors are at an ideal 120° angle (**12**). If the exocyclic substituents become large, hence a linker, 'anything' becomes possible (**13**), as it depends on the mutual orientation of N and X donor atoms as well the metal geometry what type of polygon or polyhedron is formed [4,5].



11 **12** **13**

2.2. Metal entity

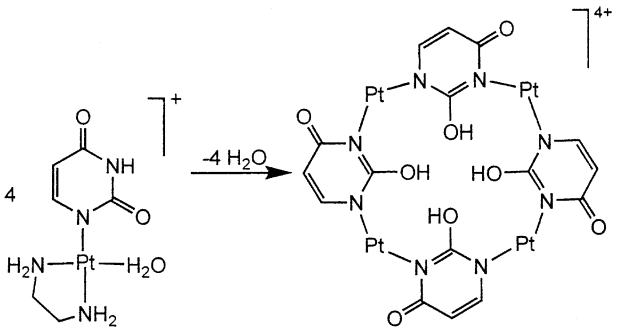
The fast reaction kinetics of Pd^{II} and Ag^{I} has made these metal ions preferred constituents of supramolecular systems containing metal ions. Self-assembly processes are usually particularly efficient if these metal ions are employed. In favorable cases self-assembly is also observed with slower reacting Pt^{II} species. Alternatively, Pt^{II} can be used to prepare supramolecules in a sequential process. The disadvantages of the latter strategy are long reaction times and frequently low yields. The advantage on the other hand is that intermediates may be isolated and characterized, thus shedding light on the reaction pathway leading to the supramolecule.

As a rule, angles about metal ions, whether in square-planar, tetrahedral or octahedral coordination environments, may substantially deviate from the ideal case. While this is common knowledge, it again has to be emphasized that these deviations may add up and favor polygons or polyhedra other than those anticipated from a strict application of the rules provided in the 'molecular library' approach.

3. *cis* Geometry of metal

3.1. Metallacalixarenes with pyrimidine ligands

We have previously shown that $Pt(en)Cl_2$ reacts with unsubstituted uracil (UH_2) to give, among others, the N1 linkage isomer *cis*-[(en)PtCl(UH–*N*1)] (**14**) (UH = uracil monoanion) [20]. Upon hydrolysis of the Cl ligand, the monomeric complex spontaneously tetramerizes to the cyclic complex $\{[(en)Pt(UH–N1,N3)]_4\}^{4+}$ (**15**). Compound **15** crystallizes as its NO_3^- salt in a 1,3-alternate arrangement, meaning that opposite positioned uracil bases adopt pair-wise identical orientations, viz. have their O4 groups up and down, respectively. The overall appearance of **15** is that of an open box. The resemblance with purely organic calix[4]arenes is obvious and consequently the compound has been termed a metallacalix[4]arene. Like the calix[4]arenes, **15** undergoes in solution conformational changes with rotation of the pyrimidine nucleobases. In the case of **15** this equilibrium is pH dependent and influenced by the presence of additional metal ions (vide infra). It is also feasible, although not yet explicitly proven, that anions likewise have an effect on this equilibrium. In any case, cation **15** proved to be unique in the sense that it can act both as a cation binder (due to the availability of exocyclic oxygen donors in 2- and 4-positions, cf. Section 3.1.1) *and* as an anion receptor (cf. Section 3.1.3).



14 **15**

Structurally similar metallacalix[4]arenes are formed from deprotonated 2-hydroxopyrimidine and either $enPd^{II}$ (**16**) or $enPt^{II}$ (**17**) (Fig. 1) [21]. Dimensions of these open boxes are expectedly similar to those of **15**, with M···M separations of

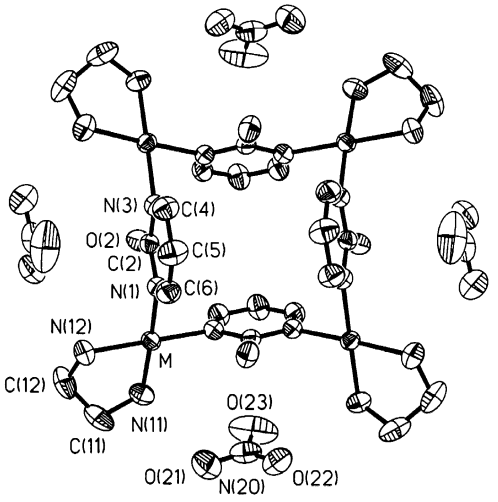


Fig. 1. Molecular structure of isomorphous pymo complexes **16** ($M = Pd^{II}$) and **17** ($M = Pt^{II}$) (nitrate salts) [21].

ca. 5.9 Å for the sides and ca. 8.3 Å for the diagonal. A major difference between **15** on one hand and **16** and **17** on the other, relevant to their metal binding properties (cf. Section 3.1.1 and Section 3.1.2), is the lower basicity of the exocyclic oxygen atoms in 2-positions of **16** and **17**.

3.1.1. Cation binding via exocyclic O donor sites

Despite the positive charge of +4 of cation **15**, it has a pronounced affinity for additional metal ions. This feature, demonstrated many times for platinated anions of 1-substituted uracil and thymine ligands [13,22] and interpreted in terms of a marked delocalization of negative charge onto the exocyclic oxygen atoms, also holds up for unsubstituted uracil bases as present in **15**. Thus, reaction of $[Pt(en)(UH–N1,N3)]_4^{4+}$ with *cis*-$(NH_3)_2Pt^{II}$ yields the octanuclear complex $[\{Pt(en)\}_4(U–N1,N3,O2,O4)_4\{Pt(NH_3)_2\}_4]^{8+}$ (**18**) (Fig. 2) containing four bridging uracil dianions (U) [23]. Similar octanuclear complexes can be prepared with metal entities other than *cis*-$(NH_3)_2Pt^{II}$ [23,24]. In few cases, such heteronuclear complexes have also been structurally characterized, e.g. $[\{(en)Pt(U–N1,N3,O2,O4)\text{-}CuCl(H_2O)_2\}_4]^{4+}$ or $[\{(en)Pt(U–N1,N3,O2,O4)M(H_2O)_3\}_4]^{8+}$ ($M = Cu^{II}$, Zn^{II}) [24]. In all these cases the 1,3-alternate arrangement of the uracil bases is maintained. Pt–M distances in these compounds range from 2.74 to 2.80 Å.

As pointed out, the presence of metal ions capable of binding to the exocyclic oxygen atoms in **15** can influence the conformational equilibrium. Thus we had observed that in the presence of an excess of Ag^+ ions an octanuclear derivative $[\{(en)Pt(UH–N1,N3,O2)Ag\}_4]^{8+}$ forms which has the four bases oriented in a cone conformation [23]. Similarly, it has been found [24], that a single Zn^{II} ion, bridging

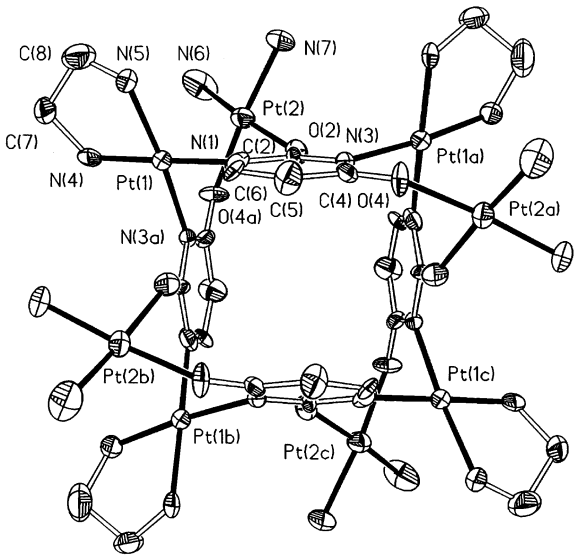


Fig. 2. Octanuclear cation $[\{Pt(en)\}_4(U)_4\{Pt(NH_3)_2\}_4]^{8+}$ (**18**) derived from **15** upon addition of *cis*-$(NH_3)_2Pt^{II}$ [23].

two exocyclic oxygen atoms of two bases and H bonding to the two other oxygens via a coordinated water molecule, can stabilize to cone conformation of **15**. Unfortunately in both cases a complete X-ray structure determination was not achieved, despite a satisfactory characterization of the cations. However, applying 4,6-dimethyl-2-hydroxopyrimidine and $(en)Pd^{II}$ and cocrystallizing the resulting metallacalix[4]arene with Gd^{3+} resulted in formation of the pentanuclear complex $[\{(en)Pd(dmpymo–N1,N3,O2)\}_4Gd(NO_3)_2(H_2O)]^{5+}$ (**19**) which could be fully characterized (Fig. 3) [25].

3.1.2. $[Cu(H_2O)_6]^{2+}$ binding via H bond formation

The reduced basicity of the exocyclic oxygen atoms in **16** and **17**, compared to **15**, apparently prevents direct coordination of other metal ions to the oxo surface [21]. However, there is evidence for weak binding of metal aqua complexes in a few cases, with one example X-ray structurally characterized. Thus two $[\{(en)Pt(pymo–N1,N3)\}_4]^{4+}$ (**17**) can sandwich a $[Cu(H_2O)_6]^{2+}$ between their oxo-surfaces, adopting cone conformations, to give complex **20** (Fig. 4) [21]. Another proof of low basicity at the oxo-surface is that titration of **17** with $HClO_4$ does not lead to calix protonation but to isolation of a protonated $[H_{20}O_8]^{4+}$ water cluster encapsulated by two **17** cations.

3.1.3. Anion binding

Inspection of models of 1,3-alternate and cone conformers of **15**–**17** reveals that anion inclusion, expected to be favorable due to the positive charge of the host, is

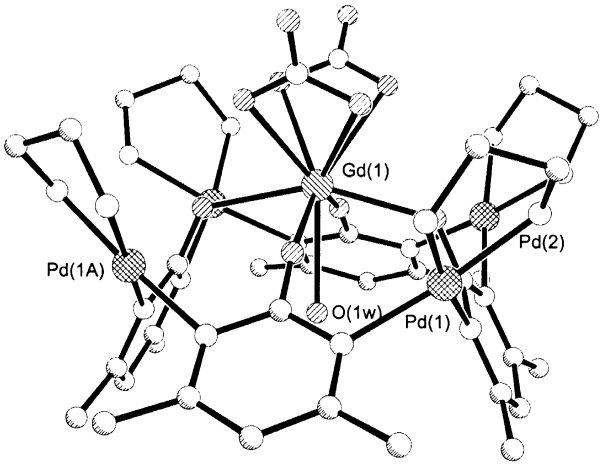


Fig. 3. Cation $[\{Pd(en)(dmpymo–N1,N3,O2)\}_4Gd(NO_3)_2(H_2O)]^{5+}$ (**19**) [25].

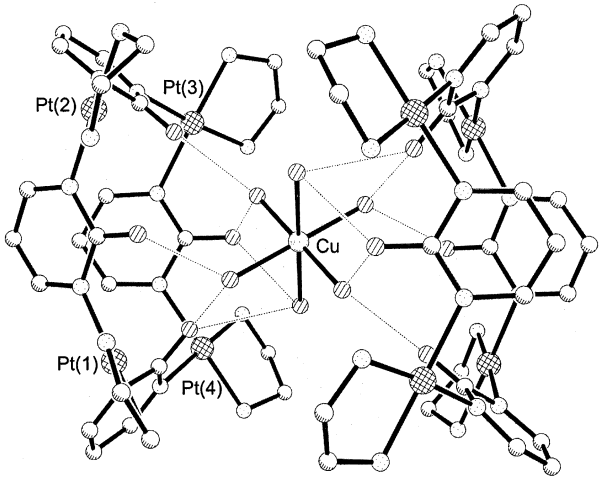


Fig. 4. View of cation of complex $[\{Pt(en)(pymo–N1,N3)\}_4\}_2 \cdot Cu(H_2O)_6]^{10+}$ (**20**) with $[Cu(H_2O)_6]^{2+}$ sandwiched between the oxo surfaces of two metallacalix[4]arenes **17** [21]. H bonds are indicated.

possible only for the cone conformer. In the 1,3-alternate arrangement the effective inner cavity of the host is clearly too narrow to permit inclusion of even the smallest anions. We had come across the phenomenon of anion inclusion during our ^{1}H-NMR spectroscopic studies with **15** when we noticed that 3-(trismethylsilyl)-1-propanesulfonate (TSP) was no longer a reliable standard in a pH range where a dramatic NMR spectroscopic change took place [20b]. Subsequent work [26] has shown that the cone conformation of **15** in its protonated form as well as its Zn^{2+} and Be^{2+} complexes possess a hydrophobic cavity capable of encapsulating either

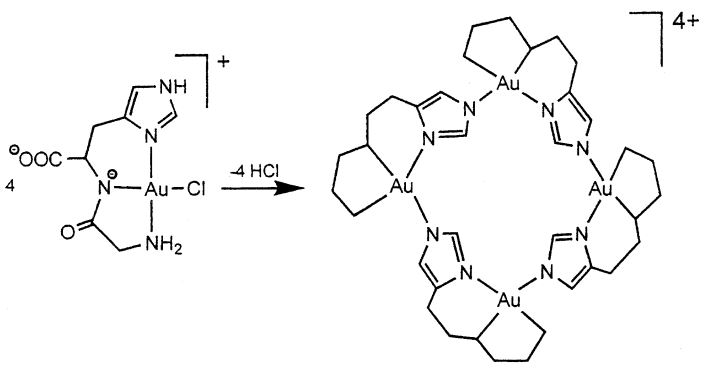
aliphatic or aromatic residues of sulfonate anions. Association constants for such interactions have been measured with the observation that guest incorporation is highly dependent on hydrophobic interactions with the cavity of **15** rather than on electrostatics.

3.1.4. Structural alternatives to calix[4]arene motif

Without exception, the combination of pyrimidine ligands with their 120° angle and *cis*-a_2M building blocks with their 90° angles has yielded metallacalix[4]arene compounds, hence open molecular boxes. From model building, however, and taking into consideration the caution expressed in Section 2.1 and Section 2.2, it is conceivable that alternative structures exists (cf. also discussion in Section 3.2). Thus, cyclic tri- and hexanuclear structures seem possible based on steric grounds. Indeed, we have very recently succeeded in isolating a cyclic hexamer which has been fully characterized by X-ray crystallography [27]. As with the tetracyclic systems, different rotational arrangements of the pyrimidine ligands are possible.

3.2. Versatility of motifs with imidazolate ligands

In metal complexes containing bridging imidazolate ligands, the two M–N vectors form roughly a 150° angle. When combined with metal entities providing 90° angles (*cis*-square-planar; *cis*-square-pyramidal; *cis*-octahedral) a unique polygon is not formed. Rather, depending on the substituents of the imidazole ring (e.g. benzimidazole, purine–*N*7,*N*9, histidine, imidazoles as part of Schiff base ligands, imidazole linked to each other, etc.) and the softness of the metal coordination geometry, different architectures are realized. For example, triangles [28–30], cyclic tetra- [31–37] and hexamers [32,35], as well as 1D chains [33] have been verified. Substituents of the imidazole ring apparently have a marked effect on the size of the cycle and, especially in cases of metal chelating abilities, also decide on the degree of puckering of the tetracyclic compound, for example. As an extreme in tetracyclic systems the four metals can be positioned at the vertices of a tetrahedron. The latter case is observed, for example, in [Au(gly-L-his)]$_4$ (**22**)



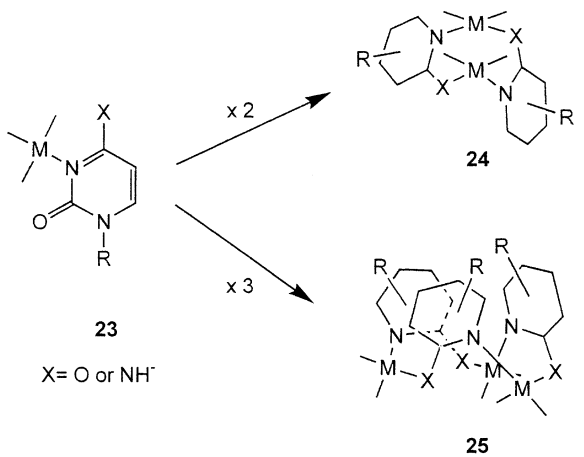
21 **22**

(gly-L-his = glycyl-L-histidine trianion) [31]. It is formed from monomeric **21** upon treatment with base. In purine nucleobases (adenine, guanine, theophylline) additional donor atoms are available in the pyrimidine ring condensed to the imidazole ring, which frequently get involved in metal binding as well. With adenine, for example, N6, N7, N9 metal binding can produce a tetranuclear cation [38], and O6, N7, N9 metal binding with theophylline generates a cyclic hexamer [39].

3.3. Other cyclic purine complexes

In addition to the cyclic structure of purine containing metal complexes that utilize the imidazole ring N atoms (see above), there are also numerous examples where only one of these sites (N7) is involved and in addition other sites in the pyrimidine ring. This situation is realized in complexes derived from N9 blocked bases. N1, N7 metal bridging has been proposed for tetracyclic guanosine and GMP species of $enPd^{II}$ [40], and a cyclic hexamer displaying this binding motif has been X-ray structurally characterized for a 9-methylguanine complex of *cis*-$(PMe_3)_2Pt^{II}$ [41]. Again, we note that the combination of two identical building blocks (90° metal fragment; 90° entity of N1, N7 bridge) yields two different motifs, the square and the hexagon. Numerous molecular triangles have been constructed with N9 blocked adenine via N1, N6, N7 metal binding sites [38,42] and N9 blocked hypoxanthine (N1, O6, N7) [43] and studied with regard to host–guest chemistry [44].

Fascinating structural motifs are generated if groups capable of metal ion binding are tethered to the N9 position of purine bases. Depending on the other site(s) of metal attachment (N7 or N7, N3) 1D polymers [45] of different habit or tetracyclic species [46] are formed.



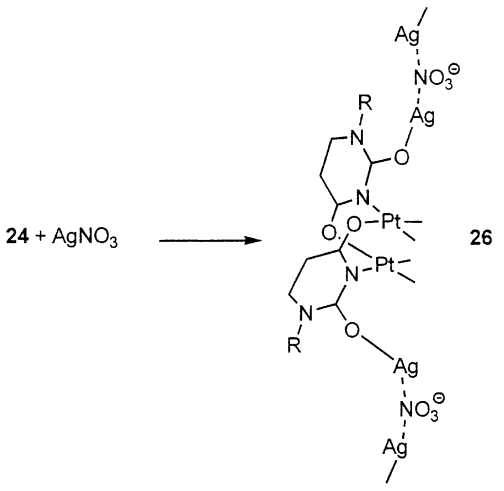
The smallest self-assembled entity obtained from a mononuclear precursor, and consequently in the structural sense a (admittedly small) supramolecule, *head–tail* dimers [47] derived from 1:1 complexes of purines and metals, shall not be explicitly discussed here (see also next paragraph).

3.4. Combining endo- and exocyclic donor sites in pyrimidines

In Section 3.1.1 it has been pointed out that following construction of a framework based on metal cross-linking endocyclic *N* atoms of the pyrimidine bases, additional metal ions can be attached to exocyclic groups in favorable cases, viz. when these sites are sufficiently basic. The consequent combination of endo- and exocyclic donor atoms of heterocyclic ligands may, however, also become the principle of constructing supramolecular assemblies.

In the simplest case, a 1:1 complex **23** of a metal with a heterocyclic ligand containing both functions, e.g. a pyrimidine nucleobase, can dimerize in *head–tail* fashion to give **24** [48–50]. Alternatively, a cyclic trimer (**25**) may form [51]. A major difference between dimer and trimer refers to the relative orientation of the metal at the exocyclic group X with respect to the metal at N3: it is *syn* in **24** and *anti* in **25**. From a comparison of the reaction conditions applied for di- and trinuclear 1-methylcytosinato complexes of *cis*-$(PMe_3)_2Pt^{II}$ [48b,51] it appears that the *head-tail* dimer is the kinetic product, while the cyclic trimer is the thermodynamic product. It remains to be seen if other factors contribute to this difference.

Dinuclear complexes **24** can further aggregate, either via intermolecular H bond formation [49b] or through heterometal ion binding [52], provided the heterocyclic ligand has additional functional groups capable of acting as donors for the heterometal or donors/acceptors in H bonds. Uracil and thymine nucleobases have proven particularly useful in this context **26** [52].



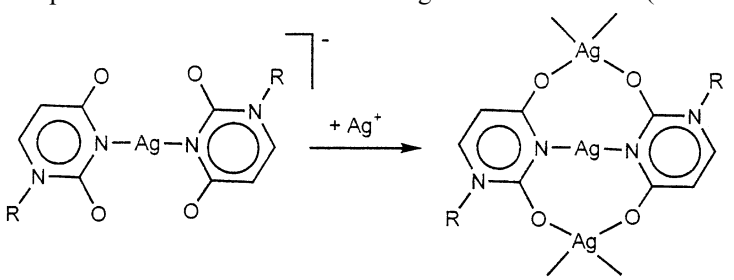
4. *trans* Geometry of metal

4.1. Endocyclic donor sites of pyrimidines

The 120° angle provided by the two ring nitrogen atoms of pyrimidines is, in combination with a linear metal fragment, ideal for the generation of molecular hexagons. Formation of the latter is entropically favored over polymeric products [4c], but the complexity of the assembly process increases with the number of ring members, implying a considerable degree of rotational freedom in the intermediate structures. There are relatively few examples of metal-containing molecular hexagons known as compared to hexagons based on labile H bonds. Very recently, it has been found that reaction between $[Cu(MeCN)_4]BF_4$ and 2-hydroxopyrimidine (Hpymo) leads to a polycrystalline solid in which molecular hexagons $[Cu(pymo–N1,N3)]_6$ coexist with polymeric helicates $[Cu(pymo–N1,N3)]_\infty$ [53], which should be taken as a proof of the low energy barrier between these two different products. In this context, it has been proven that polymeric [Ag(pymo–*N*1,*N*3)] [54] converts upon heating to the thermodynamically more stable hexagon $[Ag(pymo–N1,N3)]_6$ [55]. In the case of Cu^{II} salts with Hdmpymo in aquous amine solutions we have only observed formation of infinite 1D polymers *trans*-$[\{(amine)_2Cu(dmpymo–N1,N3)\}_n]^{n+}$ [56]. Aoyama et al. observe a high versatility for the M/substituted pyrimidine system ($M = Co^{II}$, Cu^{II}, Cd^{II}) as a consequence of metal plasticity. 1D zig-zag chains and helicates are observed [57]. Surprisingly, and again corroborating the caution expressed, the parent ligand pyrimidine and Ag^+ ions does neither yield cyclic hexamers nor 1D polymers but rather squares [58]. This is the consequence of a marked deviation of the coordination geometry of the silver ion from linear towards tetrahedral.

4.2. Combining endo- and exocyclic donor sites in pyrimidine

Polymeric complexes of 1:1 stoichiometry have been obtained upon reaction of Ag^+ salts with the pyrimidine nucleobases 1-methylthymine [59] and 1-methyluracil [60]. Metal binding in these compounds involves the endocyclic N3 position and the exocyclic O2 and O4 positions. Only the central N3–Ag–N3 bond is linear, whereas the Ag^+ ions cross-linking the exocyclic oxygen atoms are distorted tetrahedral. Formally, the building blocks **27b** can be considered as being derived from the linear 1:2 complex **27a** to which additional Ag^+ ions are added (cf. Section 6.1).



27a **27b**

Also a polymeric structure is realized in [Ag(1-methylcytosine)]NO_3, but there a dimeric unit with two tetrahedral Ag^+ ions represents the repeating unit [61].

5. 2D and 3D open-frameworks

When highly coordinating 'naked' metal ions are applied in combination with *N*,*N*′-bidentate spacers construction of 2D and 3D frameworks is possible. Open-framework coordination polymers are especially interesting due to the novel properties and applications derived from their porous nature. This is actually a fast growing subject of research as a result of the high potential of such materials in absorption, molecular sieving, ion exchange, chemical sensing and catalysis [62–66]. Crystal engineering of such materials is possible if appropriate spacers and metal ions are used.

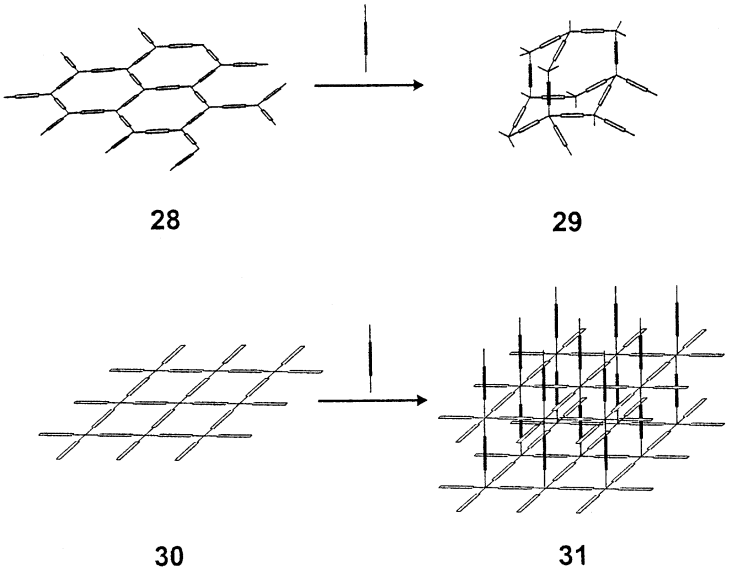
5.1. Materials containing linear spacers

Combination of a trigonal metal ion with a linear spacer can lead to formation of a 2D honeycomb framework **28** in $[\{Cu_2(pyrazine)_3\}SiF_6]_\infty$ [67]. Such a system can be extended to the third dimension by formal addition of an additional spacer to the 2D framework which leads to 3D diamond framework **29**. This structure type has been found for the $[\{Cu(4,4'\text{-bpy})_2\}PF_6]_\infty$ system [68] which possesses a fourfold interpenetrated diamond framework with the anions located in ~ 6 Å channels. Other types of geometrical combinations are also possible, i.e. a square-planar metal entity in combination with a linear *N*,*N*′-spacer leads to formation of 2D square grids **30**. An illustrative example is provided by $[Co(pyrazine)_2(SCN)_2]_\infty$ [69] and $[\{Cd(4,4'\text{-bpy})_2(NO_3)_2\} \cdot 2C_6H_4Br_2]_\infty$ [70]. Mixed pyrazine/4,4′-bipyridine systems have also been described which generate rectangular grids instead, i.e. $[\{Cu(4,4'\text{-bpy})(pyrazine)(H_2O)\}PF_6]_\infty$ [71] with channels of 6.8×11.2 Å. If an additional spacer perpendicular to the 2D grid is introduced a square 3D network **31** is built. An illustrative example of this structural type is the $[Cu(4,4'\text{-bpy})_2(SiF_6)]_\infty$ system with the 2D to 3D interaction being transmitted through the SiF_6^{2-} anions [72].

5.2. Materials containing nonlinear spacers

One might assume that the use of nonlinear *N*,*N*′-spacers will result in a more complex assembly process that leads to new structure types, since both metal ion and ligand bond angles are bent. Surprisingly, in spite of geometrical differences, it has been found that applying trigonal $[Cu(ClO_4)]^+$ metal entities in combination with benzothiadiazole (btd), formation of a 2D honeycomb framework similar to **28** is possible in $[\{Cu(btd)(ClO_4)\}ClO_4]_\infty$ [73]. Analogously, square-planar metal entities in combination with unsubstituted pyrimidine rings forms 2D square grids similar to **30** in $[Co(pym)_2(SCN)_2]_\infty$ [69]. It seems that distortion introduced by the nonlinear spacer can be overcome by an appropriate disposition of coordination

polyhedra of metal ions and ligands disposition in an alternate fashion. Examples of three-dimensional structures containing simple pyrimidine derivatives are, however, more scarce. One of the rare examples is generated by combination of tetrahedral Cu^{I} with unsubstituted pyrimidine generating the acentric $[\{Cu(pym)_2\}BF_4]_\infty$ framework [74] analogous to feldspar aluminosilicate minerals which possess large voids filled with BF_4^- anions. Likewise, we have very recently observed that the combination of square planar Cu^{II} with 2-hydroxopyrimidine (Hpymo) leads to noncharged $[Cu(pymo)_2]_\infty$, which displays a three-dimensional diamondoid framework with pores of ~ 8 Å [75].



28 29

30 31

5.3. Host–guest chemistry

Most of the open-frameworks are positively charged with channels being filled by anions and in some cases solvent or organic molecules of compatible size. In some cases, exchange of guest molecules is possible. Applications derived from their host–guest chemistry range from gas storage [76] to anion exchange [77]. In this context, we note that host–guest chemistry of $[Cu(pymo)_2]_\infty$ framework is particularly rich, with gases and Group 1 metal perchlorates salts being selectively adsorbed [75]. Another example of versatility of these systems is $[\{Cd(4,4'\text{-bpy})_2(NO_3)_2\} \cdot 2C_6H_4Br_2]_\infty$ [70] which has been found to possess shape specific catalytic properties for cyanosilylation of aldehydes.

6. Molecular architecture based on $M(Ligand)_2$ building blocks

Just like 1:1 complexes of metal ions and heterocycles can lead to supramolecular motifs, compounds of 1:2 stoichiometry can also be the source of supramolecular

structures. The intermolecular forces may again be the coordinative bond, π–π stacking, as well as hydrogen bonding, and the supramolecular entity may exist in the solid state only or be a discrete molecular entity present also in solution.

6.1. Derivatives of *trans*-$X_2M(Ligand)_2$

We have lately prepared a large series of compounds of general composition *trans*-$X_2M(Ligand)_2$ ($X = NH_3$ or $MeNH_2$ or halogen; charge of complex omitted) with ligands being heterocycles having additional donor/acceptor functionalities. In the large majority of cases these ligands were nucleobases such as 1-methylcytosine (major [78] or minor tautomer [79]), 1-methyluracil [80], 9-alkyladenine [81], 2-aminopyrimidine [23], 2-hydroxopyrimidine [82], and 2-hydroxopyridine [83].

6.1.1. Heterometal derivatives of *trans*-$X_2Pt(Ligand)_2$

Additional metal binding to the ligands in *trans*-$X_2Pt(Ligand)_2$ is a common phenomenon, in particular if the ligand is already anionic or if the heterometal can still substitute protons at the heterocyclic ligand. We do not wish to term discrete di- or trinuclear complexes [84,85], derived from *trans*-$X_2Pt(Ligand)_2$ by addition of one or two metal ions 'supramolecular', in particular if the overall appearance of

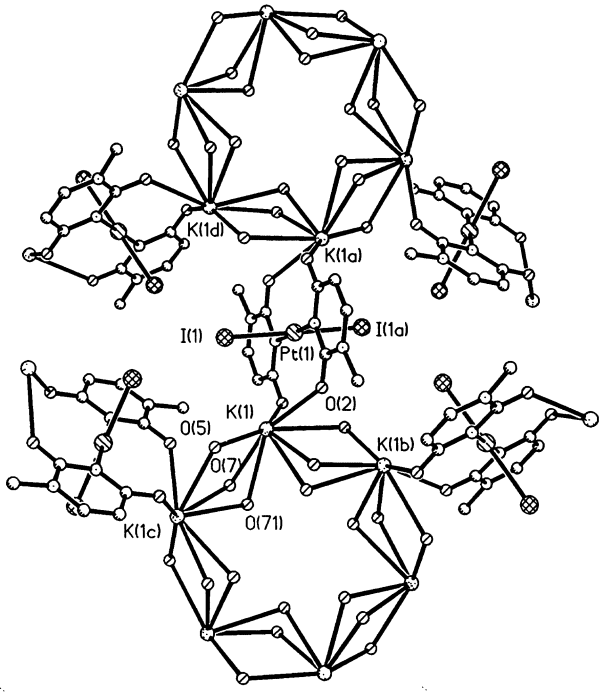
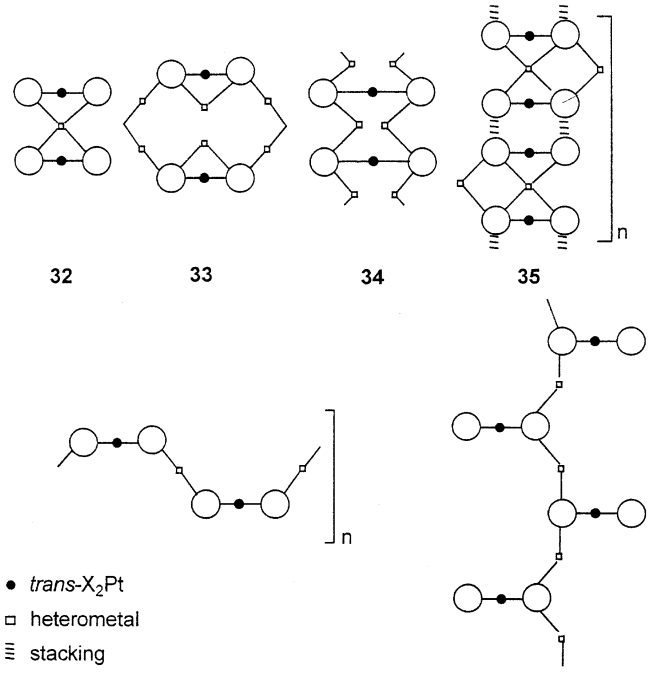


Fig. 5. Cyclic arrangement of *trans*-$K_2[PtI_2(1\text{-MeU})_2]4H_2O$ (**37**) (1-MeU = 1-methyluracilate) [87]. Water molecules O(7) and O(71) with occupancy factors of 0.5; two additional H_2O molecules omitted.

the molecular ion is not dramatically altered. However, there are cases where heterometal ions explicitly cross-link *trans*-$X_2Pt(Ligand)_2$ building blocks to larger aggregates, be it discrete (**32** [83], **33** [23]) or polymeric (**34** [86], **35** [80], **36** [82], **37** [87] (Fig. 5)), including helical structures (**38** [88]).

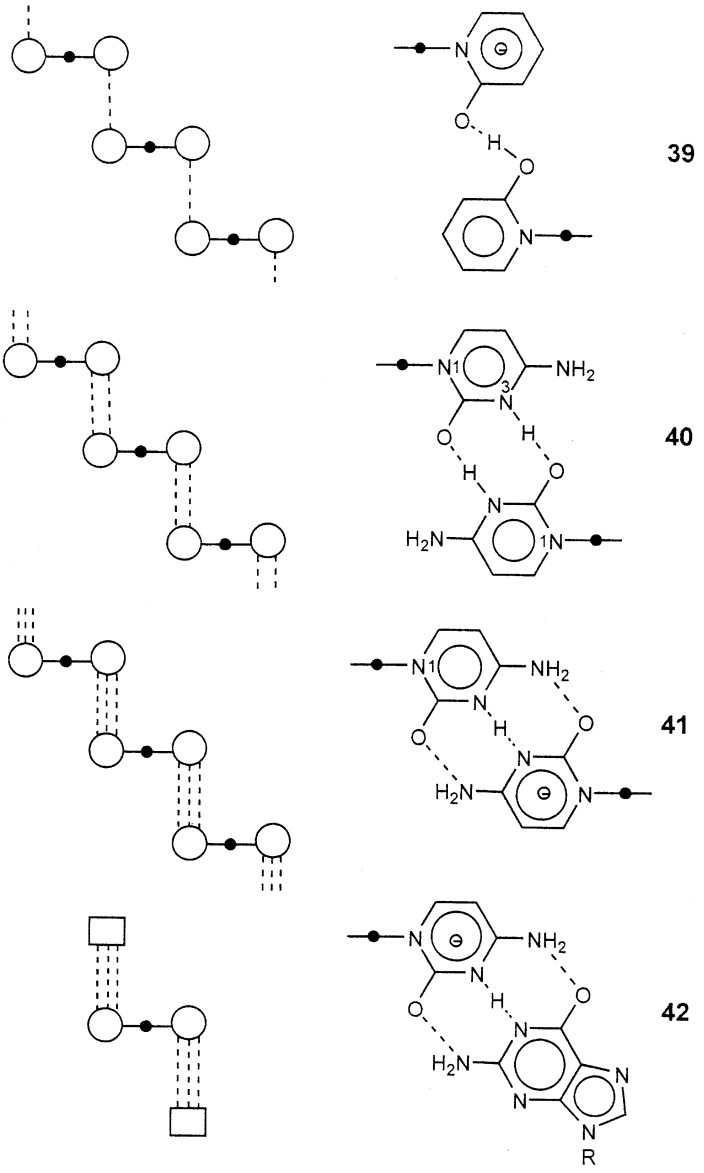


32 **33** **34** **35** **36** **38**

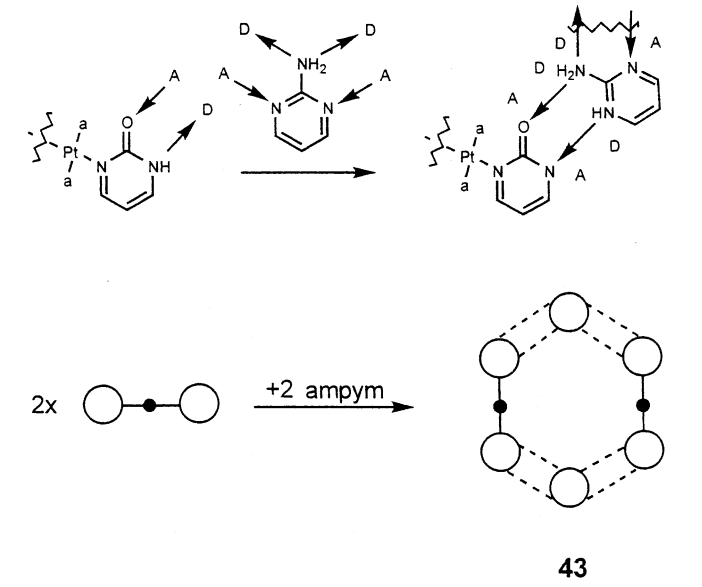
6.1.2. trans-$X_2Pt(Ligand)_2$ and hydrogen bonding

Even a single available functional entity in the ligands of *trans*-$X_2Pt(Ligand)_2$ permits association of the building blocks, but this association becomes stronger as the number of possible H bonds increases. Thus a single, albeit very short H bond of 2.443(9) Å forms between neutral and anionic 2-hydroxopyridine (Hpyo) ligands in *trans*-$[Pt(CH_3NH_2)_2(Hpyo)(pyo)]^+$ (**39**) [83], two H bonds are formed in the complex with two rare cytosine tautomers bound to Pt (**40** [53]), and three H bonds form if hemideprotonation makes the two cytosine ligands self-complementary (**41** [89]).

Hydrogen bonding of the ligands in *trans*-$X_2Pt(Ligand)_2$ with other complementary ligands is likewise possible. With Ligand = cytosine-*N*1, Watson–Crick pairing with guanine has been established both in solution and in the solid state (**42** [89]). A major difference with the conventional Watson–Crick pair is the pH range in which it exists in aqueous soltuion. It is shifted from the weakly acidic to neutral pH range into the neutral to weakly basic one as a consequence of the differences in pK_a values of the N(3)H in free cytosine (ca. 4–4.5) and N1 platinated cytosine (ca. 7).



Another case of molecular recognition has been observed in an adduct between *trans*-$[Pt(MeNH_2)_2(Hpymo)_2]^{2+}$ and 2-aminopyrimidine (ampym) (**43**) [82] (Fig. 6). The resulting molecular hexagon reveals that its formation is associated with a proton transfer from one of the Hpymo residues to ampym against a pK_a gradient with consequent loss of the original symmetry of both ampym and the two Hpymo residues. Proton transfer is apparently favored by a more even distribution of positive charge along the molecular assembly and a more efficient H bonding pattern, i.e. instead of two pairs of DA:AD hydrogen bonds a pair of the more favorable DD:AA scheme is generated [90,91].



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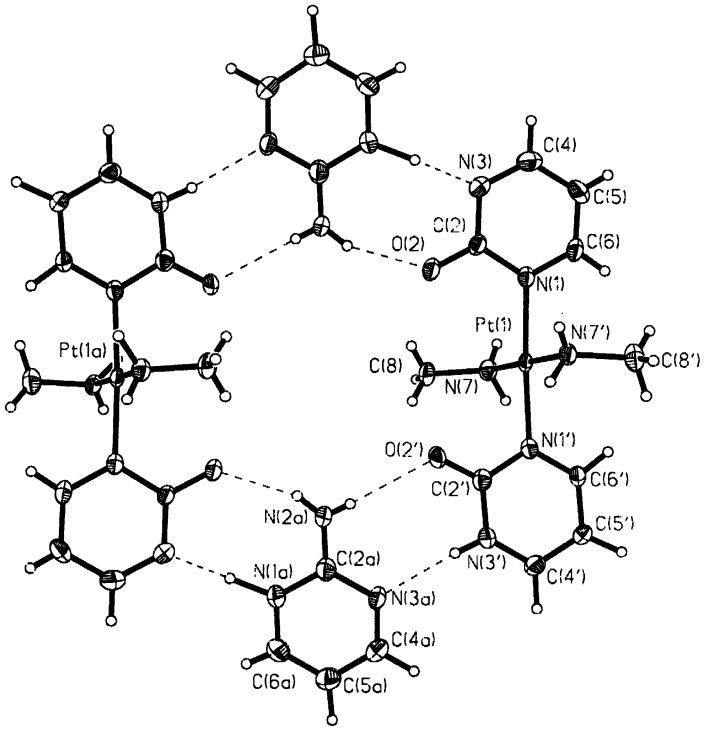
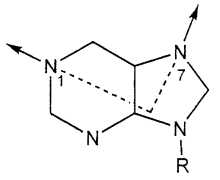


Fig. 6. Supramolecular assembly **43** of *trans*-$[Pt(MeNH_2)_2(Hpymo)(pymo)]^+$ and $Hampym^+$ [82].

6.1.3. Building upon trans-$X_2Pt(Ligand)_2$ entities

As we have demonstrated in a number of cases now, purine nucleobases carrying metal entities at both the N1 and N7 positions represents angular building blocks for 90° angles (**44**). We have previously elaborated on the consequence of this feature for the construction of 'letters of the alphabet', viz. of L, O, S, U and Z shaped aggregates [6]. More recent additions to this class of compounds are meander-like structures [17,88] and nucleobase quartets consisting of four different nucleobases [92,93].



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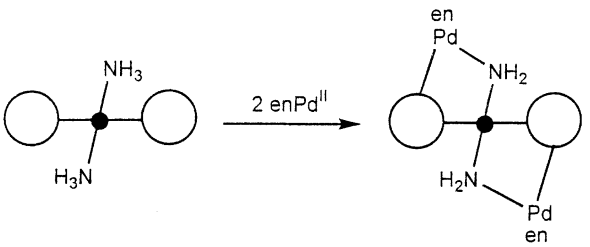
6.1.4. Special case: combining trans-$X_2Pt(Ligand)_2$ with $enPd^{II}$

In the cases discussed in Section 6.1.1 the role of the heterometal ions was simply to cross-link heterocyclic ligands of individual *trans*-$X_2Pt(Ligand)_2$ in an intermolecular fashion. Depending on the specific heterocycle, deprotonation of the ligand or even C–H activation was sometimes necessary to accomplish heterometal ion binding. In principle, $enPd^{II}$ can behave in a similar way [94]. However, in two cases we observed unexpectedly a different reaction pattern, viz. intramolecular cross-linking of the heterocyclic ligands and the ammonia ligands at the Pt [95]. Thus reactions of *trans*-$[Pt(NH_3)_2(pz)_2]$ and of *trans*-$[Pt(NH_3)_2(Hampy–N1)_2]^{2+}$ with $[enPt(H_2O)_2]^{2+}$ result in formation of compounds in which a second donor site of the heterocycle (N2 in case of pz (**45**), N(2)H in case of ampy) and an amide group at the Pt are cross-linked via $enPd^{II}$. In addition, in the ampy complex a Pd^{II} inserts between the two exocyclic N(2)H groups.



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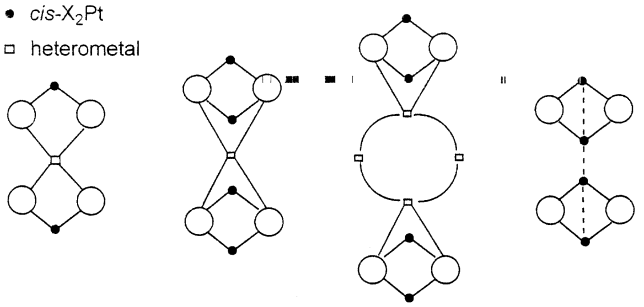
6.2. Derivatives of cis-$X_2M(Ligand)_2$

Although not explicity studied with respect to supramolecular chemistry but rather emerging from the interest in the basic chemistry of the antitumor agent *cis*platin with nucleobases [96–98], some features of this work relate to aspects of molecular architecture. Similar to the strategy for building arrays of *trans*-$X_2M(Ligand)_2$ entities with the help of hetermetal ions (cf. Section 6.1.1), *cis*-

$X_2M(Ligand)_2$ species can be compiled to larger aggregates by using metal ions as the 'glue' between individual units. Again, we do not wish to consider binding of one or two metal ions to the basic unit *cis*-$X_2M(Ligand)_2$, but rather those cases where individual units (or derivatives, e.g. dinuclear ones) are linked together (**46**–**48**). In particular, compounds containing pyrimidine nucleobases (uracil, thymine, cytosine) as well as structurally related molecules (e.g. 2-hydroxopyridine) as ligands were studied, as they were of interest with regard to a class of potential antitumor agents obtained by reaction of solvolysis products of *cis*platin with these ligands ('platinum pyrimidine blues') [99]. Numerous examples for trinuclear species of type **46** exist (e.g. with heterometal ions $M = Pd^{II}$, Cu^{II}, Mn^{II}, Ag^{I}, Tl^{I}) which display a remarkable variability as far as Pt–M–Pt interactions are concerned [100]. Diplatinum(II) building blocks (with *head–head* oriented heterocyclic ligands) may either associate via one (**47**) or more (**48**) heterometal ions [101] or alternatively through direct Pt–Pt bonding as realized in mixed-valence state compounds (**49**) obtained from the former upon partial oxidation [99].



46 **47** **48** **49**

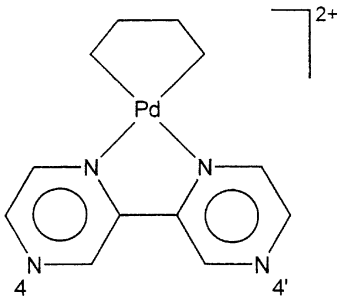
Finally, again as outlined in Section 6.1.2, *cis*-$X_2M(Ligand)_2$ entities are capable of engaging in intermolecular hydrogen bonding. With *cis*-[a_2Pt(9-ethylguanine–*N7*)$_2$]$^{2+}$ complexes H bond formation with cytosine according to Watson–Crick is possible [102]. Another pattern commonly seen in guanine–*N*7 containing compounds is guanine–guanine self-pairing as a consequence of guanine hemideprotonation. This may occur between two *N*7 platinated guanine ligands [103] or a platinated and a free guanine [104].

7. Molecular architecture derived from 2,2′-bipyrazine

The availability of four unprotonated ring nitrogen atoms and the flexibility about the central C2–C2′ bond (**5** and **5a**) makes 2,2′-bipyrazine (2,2′-bpz) a unique ligand for the construction of metal-containing supramolecular assemblies. The obvious metal binding modes are chelation, bridging, and a combination of both, with variants originating from the way in which metal bridging is realized, e.g. N4, N4′ [105,106] or N1, N4 [107–110].

7.1. 2,2′-bpz as chelating ligand

In its *cis* arrangement, 2,2′-bipyrazine can act as a chelating ligand through the N1, N1′ positions. With $enPd^{II}$, for example, the mononuclear chelate $[enPd(2,2'\text{-bpz}–N1,N1')]^{2+}$ (**50**) is formed [105]. The analogous $enPt^{II}$ can likewise be prepared, yet only by the detour via a molecular triangle, which is the kinetically preferred product of this reaction (c. f. Section 7.3) [106]. In *cis*-$PdCl_2$(2,2′-bpz) the 2,2′-bipyrazine is likewise present as a chelating ligand. Subsequent substitution of the chloro ligands by 4,4′-bipyridine leads to formation of a molecular square (or open box) **51** of the Fujita and Stang type compounds [16,111] as shown in Fig. 7.



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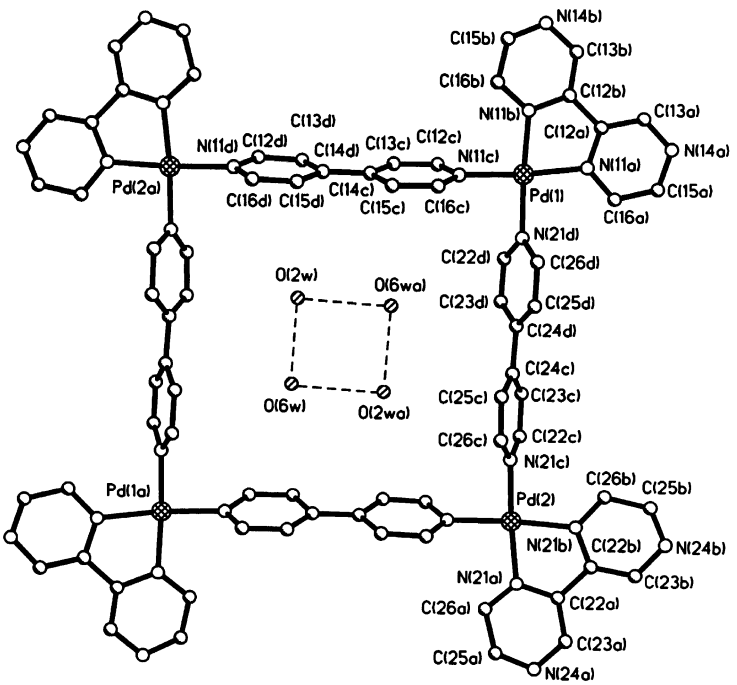


Fig. 7. Tetranuclear cation **51** consisting of Pd^{II}(2,2′-bpz) corner stones and bridging 4,4′-bpy ligands [109]. Water molecules occupy the center of the square.

7.2. enPd(2,2′-bpz) as building block for larger aggregates

Once the N1, N1′ sites are blocked, as is the case with **50**, additional metal ions can be attached via the N4, N4′ sites. Depending on the geometry and type of metal, different aggregates are formed (**52**–**54**). With *trans*-$(NH_3)_2Pt^{II}$, a molecular triangle of charge + 12 forms which has three $enPd^{II}$ units located at the corners of the triangle and three *trans*-$(NH_3)_2Pt^{II}$ units in the centers of the three sides [107]. Except for the NH_3 ligands of the Pt atoms, the triangle is essentially planar. Interestingly, a single ClO_4^- anion is positioned in the center of the triangle, and triangles are packed in such a way as to produce a pipe-like structure with a string of ClO_4^- anions in its center (Fig. 8).

No closed triangle but rather an infinite loop structure **53** forms if $AgClO_4$ is applied instead of *trans*-$(NH_3)_2Pt^{II}$ [109]. Clearly, additional alternative structures such as chain or helix are feasible, but it is unclear as yet under which reaction conditions they may be realized.

Finally, reaction of **50** with $enPd^{II}$ yields a hexanuclear, vase-shaped complex **54** [106]. Its structure is closely similar to related complexes containing three $enPd^{II}$ and three $enPt^{II}$ units or six $enPt^{II}$ units, which will be discussed below (see Section 7.4.1). It is of interest to see that six particles ($3 \times$ **50** + $3 \times enPd^{II}$) aggregate rather than four only, which at least from model building, would have appeared to be possible as well. In the latter case a V-shaped, open structure would have resulted.

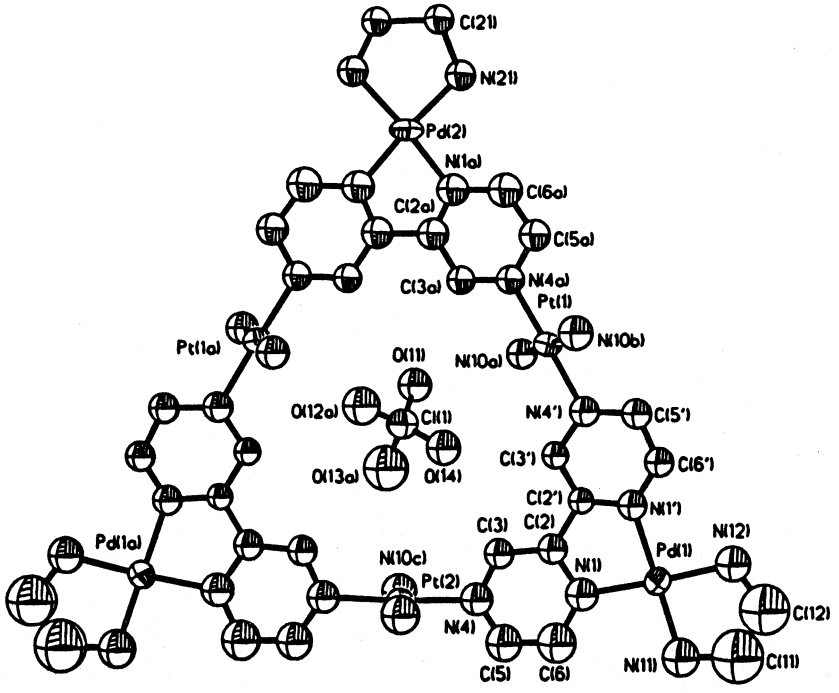
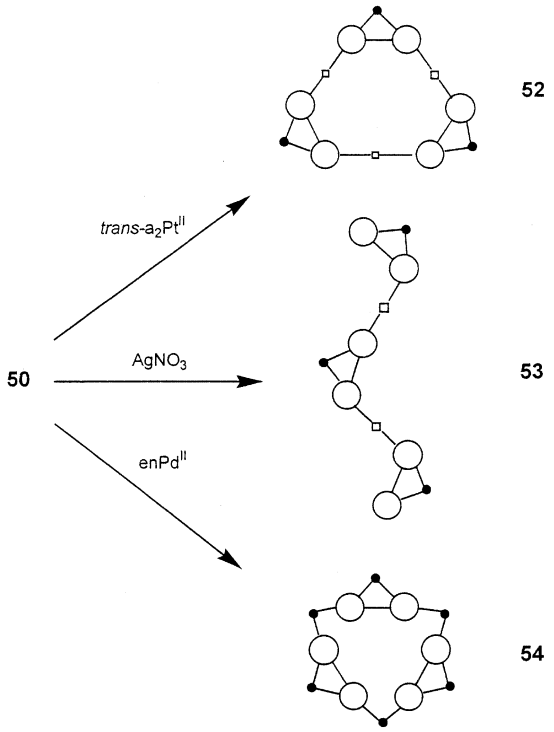


Fig. 8. View of cation **52** with encapsulated perchlorate anion [107].



7.3. Molecular triangle via N4, N4′ bridging

Unlike $enPd^{II}$, which reacts with 2,2′-bpz to a mononuclear chelate compound **50**, $enPt^{II}$ forms a molecular triangle of charge $+6$ with the metal entities coordinated via N4 and N4′ [105,106]. The two halves of the bipyrazine ligand can adopt either a *trans* or a *cis* conformation. Of the ten possible combinations, two types with all-*trans* (**55**) and all-*cis* (**56**) configurations of the bpz ligands have been established by X-ray analysis (Fig. 9). According to ^{1}H-NMR spectroscopy there is rapid interconversion of the various possible conformations in solution at room temperature. Individual species are distinguishable at low temperature (-55 °C) [106]. Compounds **55** and **56** differ markedly in their appearance: While the all-*trans* compound provides the impression of a triangle (Pt–Pt, 9.3–9.5 Å), the all-*cis* compound looks more like a vase or a double cone, with shorter Pt–Pt distances of 7.7–8.0 Å. In virtually all cases the two halves of the bipyrazine ligands are substantially twisted. Results of the X-ray structure determinations strongly suggest that the anions present in solution have an effect on the configuration of the molecular triangle (Fig. 10): thus, the simultaneous presence of NO_3^- *and* ClO_4^- seems to favor the all-*cis* configuration with both anions inserted in the cavity formed by the triangular vase [106]. On the other hand, PF_6^- interacts with both the all-*cis* and the all-*trans* conformers, although to a different extent as far as the

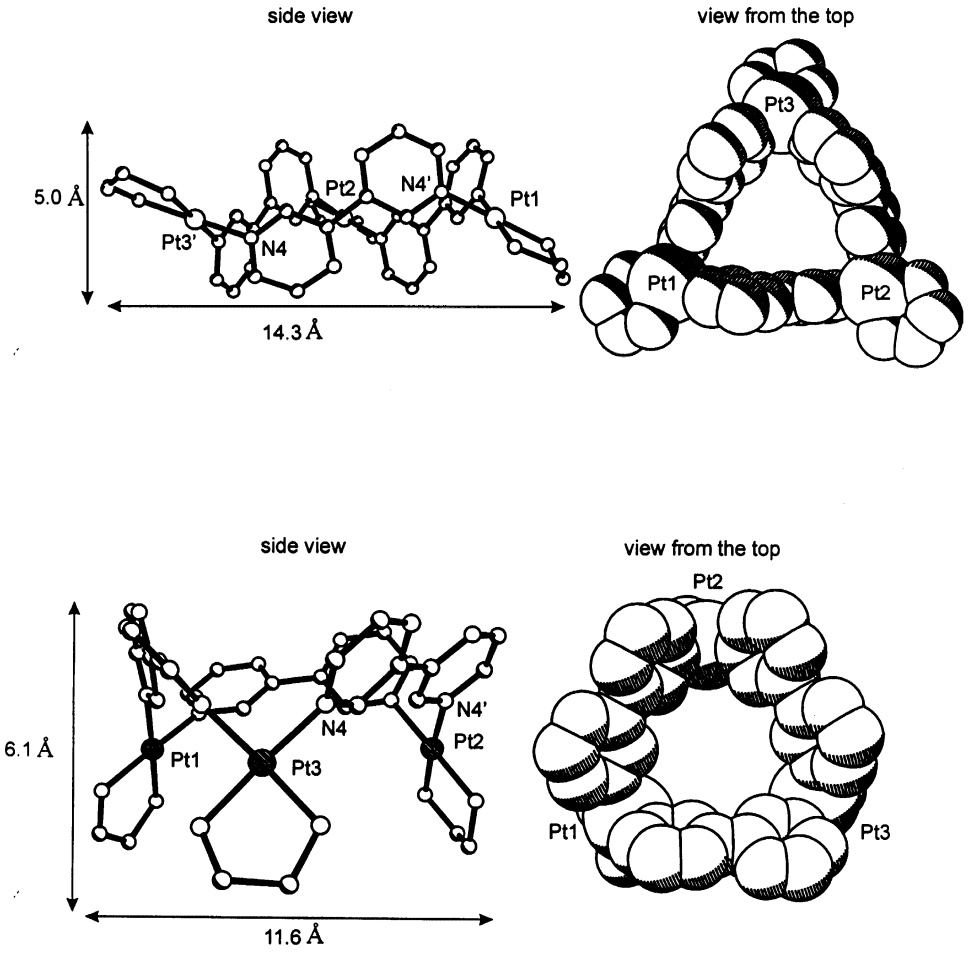


Fig. 9. Views of cations $[\{(en)Pt(2,2'\text{-bpz}\text{–}N4,N4')\}_3]^{6+}$ with all-*trans* (**55**) and all-*cis* (**56**) configurations of the bpz ligands [106].

depth of the insertion is concerned, whereas the NO_3^- salt of the all-*trans* conformer does not display any host–guest interaction [105].

As mentioned above (Section 7.1), the molecular triangles **55** and **56** are the kinetic products of the reaction of $enPt^{II}$ with 2,2′-bpz. The thermodynamic product is the chelate with N1, N1′ binding of Pt^{II}. It is obtained from the triangles in quantitative yield upon prolonged (14 days) heating (100 °C) in water [106].

7.4. Triangles as building blocks for larger entities

7.4.1. Hexanuclear vases

The all-*cis* conformer **56** has the N1, N1′ donor sites oriented in a way to enable chelation of additional metal ions. Indeed, $enPd^{II}$ is readily bonded to produce the

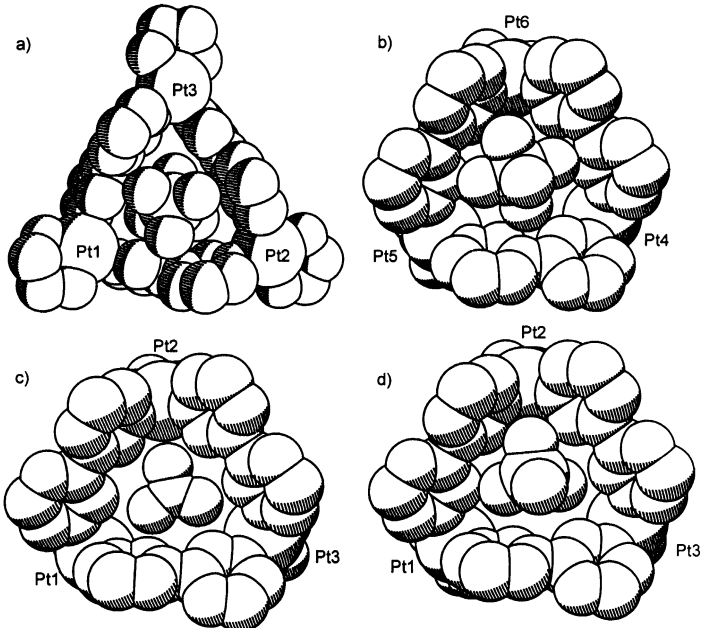


Fig. 10. Cation–anion interactions between all-*trans* conformer **55** and PF_6^- (a) and all-*cis* conformers **56** with PF_6^- (b), NO_3^- (c) and ClO_4^- (d). In (c) and (d) both anions are inserted simultaneously, but for clarity individual presentations are chosen [106].

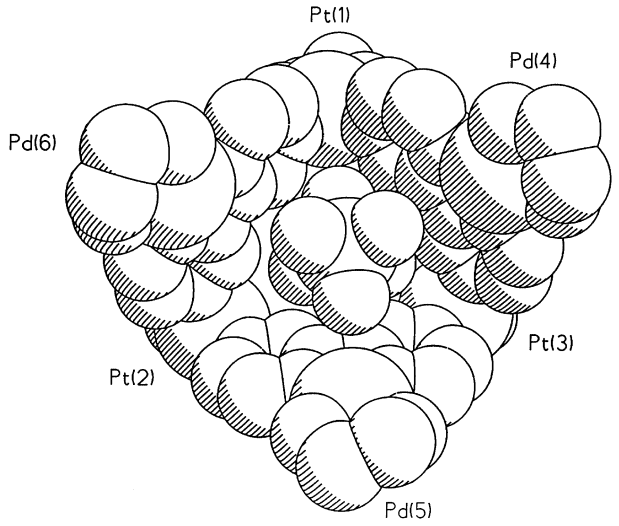


Fig. 11. Space filling model of cation **57** with inserted PF_6^- anion. An additional NO_3^- is located underneath the PF_6^-, in the plane of the Pt triangle and is not visible [108].

hexanuclear, mixed metal compound $[\{(en)Pt(N4,N4'\text{-bpz}\text{–}N1,N1')Pd(en)\}_3]^{12+}$ (**57**). The appearance of **57** is that of a vase, comprised of an equilateral Pt triangle at the bottom (7.9 Å), and a larger, irregular Pd triangle at the rim (8.4–9.7 Å) [108] (Fig. 11). In a similar way the Pt_6 vase has been obtained, while the Pd_6 vase and the Pd_3Pt_3 (with Pds bonded to N4 and N4′sites and Pts bonded to N1 and N1′sites) have been prepared as outlined in Section 7.2. X-ray structures of all four variants have been obtained [106,108] and they are rather similar. A common feature is again the propensity of these hexanuclear cations to insert two different anions, NO_3^- and PF_6^-, in their cavities, which expectedly are deeper than those of their triangular precursors **56**. Anion inclusion has been detected in aqueous solution in a number of cases. K_{ass} values in water are, with the exception of SO_4^{2-} (256 M^{-1}), not particularly high [108] and factors determining these are not well understood at present [108].

7.4.2. Combination of Pt triangles and Ag^+

Cocrystallization of **56** with silver salts leads to products of different stoichiometries and topologies. Two representatives have been characterized structurally to date [106]. They are to be abbreviated as $[(\mathbf{56})_2 \cdot Ag_2]^{14+}$ (**58**) and $[(\mathbf{56})_2 \cdot Ag_3]^{15+} \cdot AgNO_3$ (**59**), respectively, and are formed through bridging of two molecular Pt triangles by two (**58**) and three (**59**) silver ions. The appearance of the two compounds are those of a paddewheel and a container, respectively (Fig. 12). The container compound **59** has in addition a silver ion and three NO_3^- ions in its central cavity. Two other nitrate anions function as lids of the two ends of the barrel. Among the numerous interesting structural features of these two compounds, again insertion of two PF_6^- anions in the two cross-linked Pt_3 vases is to be mentioned.

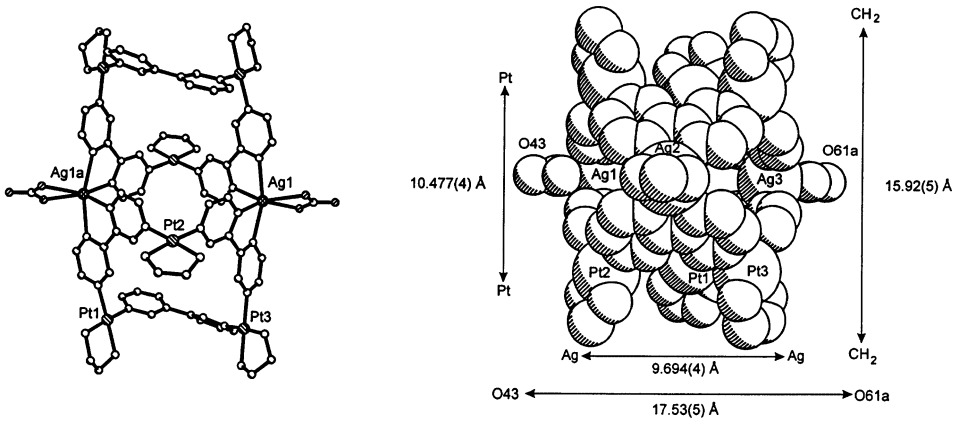


Fig. 12. Views of cations **58** (left) and **59** (right) formed through cross-linking two Pt triangles **56** with two and three Ag^+ ions, respectively [108]. The container compound **59** has an additional Ag^+ and three NO_3^- in its cavity.

8. Summary

In general, the employment of metal ions in supramolecular chemistry is to assist spontaneous self-assembly to larger entities and to reinforce noncovalent interactions between individual, usually organic building blocks. In order to achieve this goal, the metal species applied typically have to form kinetically labile complexes. Our interest in metal–nucleobase chemistry of kinetically inert species such as *cis*- or *trans*-$(NH_3)_2Pt^{II}$ [12,13] and our search for multinuclear species of defined structure [6] has led us to pursue synthetic approaches based essentially on sequential reactions. As we have shown in numerous cases, such kinetically robust species frequently can be self-assembled to larger aggregates by taking advantage of H bond formation or coordination of kinetically labile metal entities, very much as in the 'conventional' way metal ions are used in supramolecular chemistry. Thus, in this report we point out, how simple 1:1 and 1:2 complexes containing one or two *N*-heterocyclic ligands can be utilized to construct entities of higher complexity. Discrete molecular species include, among others, triangles, squares and rectangles, hexagons, open boxes, vases and containers. In a number of cases dimensions of these entities reach the 2 nm scale. Quite a few of these molecular supramolecules are of interest on their own in that they represent rare cases of their existence. To give two examples: the list of structurally characterized molecular triangles containing square-planar metal entities in the corners is very short, and molecular squares having the organic ligand in the corner and the metal fragment on the sides are even rarer. In addition, 1D, 2D, and 3D coordination polymers are produced. Interest in some of these compounds stems for their potential usefulness as receptors, including of anions, and host–guest chemistry in general. The sometimes pronounced affinity of the heterocyclic ligands to bind several metal ions simultaneously in many cases favors formation of metal-rich supramolecular structures.

Acknowledgements

J.A.R.N. thanks the Conserjería de Educación y Ciencia of the Junta de Andalucía (Project FQM-0195) and B.L. the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie (FCI) for financial support.

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