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Molecular architecture with metal ions, nucleobases and other heterocycles

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Contents

Abstract

The combination of transition metal fragments with 90 or 180° angles, viz. *cis*-a_2M^{II} ($a = $ amine or $a_2 = $ diamine; $M = Pt$ or Pd) and *trans*-a_2Pt^{II} or Hg^{II}, respectively, with (heterocyclic ligands providing 90, 120, or 180° angles leads, either in a self-assembly process

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or in a stepwise fashion, to cations of versatile shapes and charges. Examples include open boxes, molecular squares, hexagons, triangles and cups. Intermolecular H bonding can assist association of smaller entities. Synthetic and structural aspects as well as physico–chemical properties of selected examples with be discussed.

Keywords: Molecular architecture; Transplatin; Cisplatin

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1. Introduction

Coordinative bonds between suitable metal ions and organic, frequently heterocyclic ligands have proven extremely useful for the generation of regularly shaped molecules ('molecular architecture'). In fact, the combination of appropriate *angular* and *linear* building blocks in many cases leads to predictable structures [1–3]. Provided that the kinetics of bond formation are favorable, supramolecular self-assembly can take place [4], and if intramolecular forces, such as hydrogen bond formation, are operative, they can either contribute to molecular architecture or may be important for interatomic association and/or recognition.

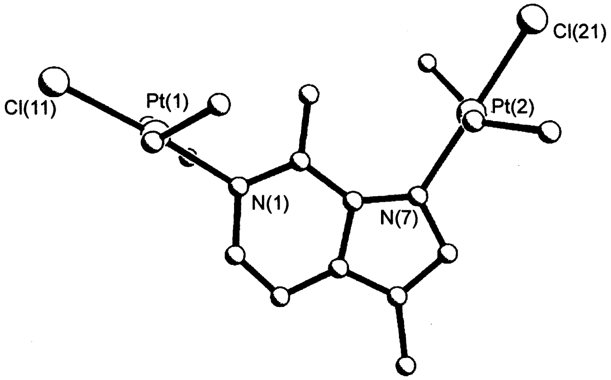
In many instances the metal fragment represents the *angular* component of the supramolecular entity, and the organic ligand is the *linear* component, hence forming the sides of a polygon, a three-dimensional polyhedron or a polymeric sieve. Consequently, the 90° angles of square-planar or octahedral metal entities are ideal for the formation of square planar, rectangular or box-like structures. With increasing size and flexibility of the organic ligand, many more structural motifs are possible, however [5]. Tetrahedrally coordinated d^{10} metal ions such as Cu^{I} are ideally suited to keep two chelating ligands at right angles, hence to generate helices, grids, ladders and even circles [6] and knots [7].

We have been applying model nucleobases and heterocyclic ligands in general and *cis*- as well as *trans*-diamine–platinum(II) entities to generate a number of regularly shaped molecules. This work originated from our interest in metal–nucleic acid interactions, specifically that of the antitumor agent *cis*-$Pt(NH_3)_2Cl_2$ and its respective *trans*-isomer [8].

2. The players: model nucleobases, Pt^{II} entities, H bonds

2.1. Nucleobases as ligands

The results of an X-ray crystal structure analysis of a 9-methyladenine (9-MeA) model nucleobase with two *trans*-$[Pt(CH_3NH_2)_2Cl]^+$ entities bound to the N1 and N7 positions [9], *trans*-$[\{(CH_3NH_2)_2PtCl\}_2(9\text{-MeA-}N7,N1)](ClO_4)_2$ (**1**) which had revealed an almost perpendicular arrangement of the two Pt–N vectors (92.5(6)° in (**1**)).



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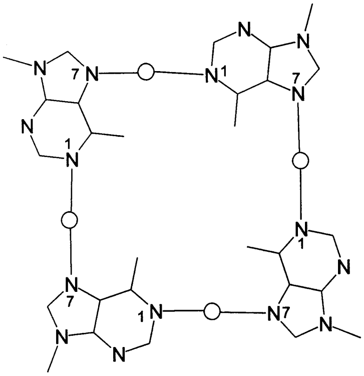
This in turn led us to further pursue the idea of synthesizing purine quartet structures (**2**, **3**) or fragments thereof (**4**).



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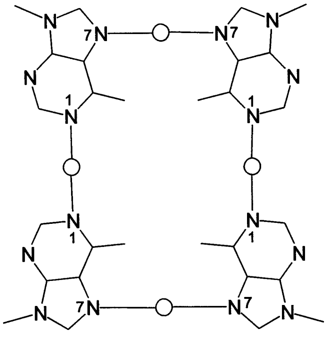

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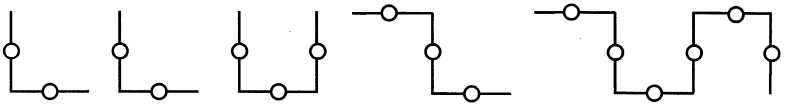

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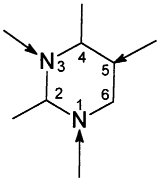
Depending on the combination of binding sites (mixed N1,N7; N1,N1; N7,N7) and on possible H bonds between bases, either closed or open arrangements are possible. There are only two possibilities **2** and **3** that permit generation of closed species, square (**2**) and rectangle (**3**); otherwise open structures (**4**) result, which of course are also formed if less than four purine bases are combined (**4**).

Our earlier observation on right angles between Pt–N vectors in purine complexes has meanwhile been confirmed in a number of structurally related adenine complexes, including such with one of the chloride ligands substituted by a guanine model nucleobase. Angles of the Pt–N vectors in all cases are again close to 90°, namely between 86.7(3) and 88.4(3)° [10]. For N7,N1 bridged guaninato complexes, a similar situation can be envisaged, but the number of examples is limited. In two structurally characterized complexes containing 9-methylguaninate, angles of 87.4(4) and 83.9(3)° have been observed [11]. Inspection of structural details reveal that the flexibility of the external ring angles at N7 primarily accounts for variations in the angle formed between the Pt–N vectors. Thus any decrease in the C5–N7–Pt angle at the expense of the C8–N7–Pt angle decreases the angle between the two vectors.

Approximately 120° angles are formed by metal–donor site vectors in the case of pyrimidine nucleobases. Depending on the sites considered and on the substitution patterns of the base N3,C5, N3,N1 and C5,N1 bridging leads to these angles (**5**).



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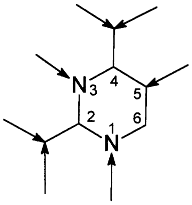
These patterns become more versatile, if metal binding also to the exocyclic groups is considered (**6**) or if the pyrimidine base is carrying additional substituents capable of metal binding, e.g. as in 6-amino-3-methyl-5-nitrosouracilate [12].



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In this account, only two examples will be discussed, namely compounds derived from unsubstituted uracil (Section 4.1) and 1-methylcytosine (Section 4.2), respectively.

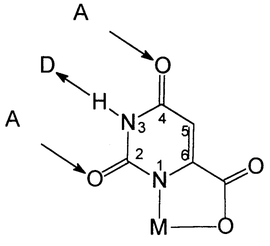
2.2. Metal electrophiles applied

As a consequence of the general slow reaction kinetics of Pt^{II} species, self-assembly processes leading to large molecules from small precursors are rather the exception than the rule for this metal ion. They are, however, still possible (see Section 4.3.1 and [13]). This situation is in contrast to analogous Pd^{II} complexes [14], where many examples exist for self-assembled macromolecules with regular shapes. We have applied in particular *trans*-a_2Pt^{II} ($a = NH_3$ or amine) entities, occasionally in conjunction with Hg^{II} for our work, and in one case *cis*-$(NH_3)_2Pt^{II}$.

2.3. Hydrogen bonding

Design strategies of supramolecular assemblies concentrate, among other things, on the usefulness of hydrogen bond formation [15]. In order to fully take advantage of this approach, a maximum number of sites capable of hydrogen bond formation is desirable. The natural nucleobases and their models (N1 site of pyrimidine blocked; N9 site of purine blocked) are not particularly helpful in this context in that metal coordination to Watson–Crick binding sites not only reduces the number of potential H bonding sites by one but also, it frequently sterically blocks the sites immediately adjacent to the metal entity. With metal binding to the Hoogsteen site of the purine (N7), this problem is less severe. Still, unless the complementary base utilizes an uncommon metal binding pattern, formation of larger aggregates is inhibited. Thus, for example, a metalated cytosine can interact with a guanine base to form three H bonds according to Watson–Crick only if the metal is either at N4 (*anti* with respect to N3), at C5, or at N1 of cytosine and if the N3 and O2 positions remain non-protonated.

Consequently, the approach to include H bond formation in the generation of supramolecular species has focused on modified nucleobases such as orotate **7** [16] or 5-aminoorotate **8** [17].



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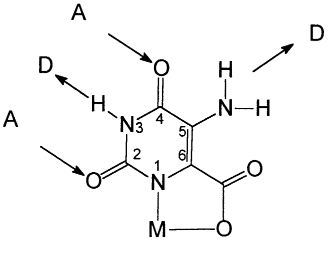

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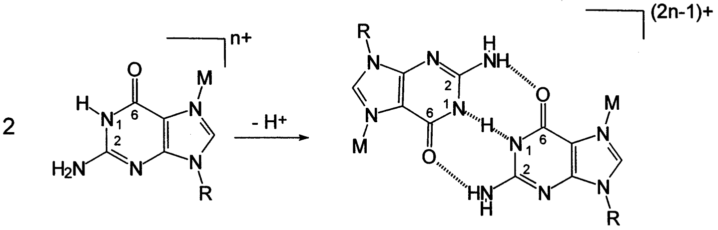
Metal complexes with these relatives of the natural pyrimidine nucleobases can either self-aggregate or aggregate via suitable other components such as 2,6-diaminopyridine, for example.

We have repeatedly demonstrated that hemideprotonation of guanine as a consequence of N7 metal binding leads to guanine, guanine self-pairing **9** of considerable strength [18,19] and, as outlined below, this feature can be used to generate larger aggregates.



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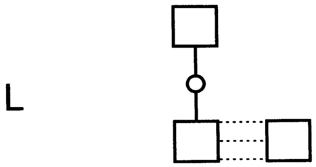
3. Purine complexes

3.1. Producing letters of the alphabet with trans-a_2Pt^{II} and H bonds

The use of purine bases as corners in regularly shaped molecules yields a variety of species that can be considered letters of the alphabet, e.g. L, S, Z, U or O, with bars formed by either the linear metal entity or H bonds (**10** [20], **11** [21], **12** [10], **13** [19], **14** [22], **15** [23], **16** [22]).



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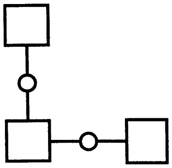

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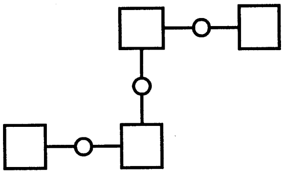

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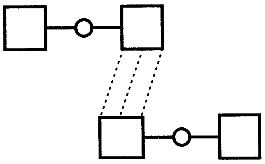

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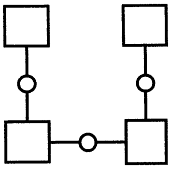

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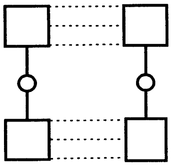

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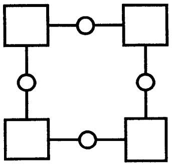

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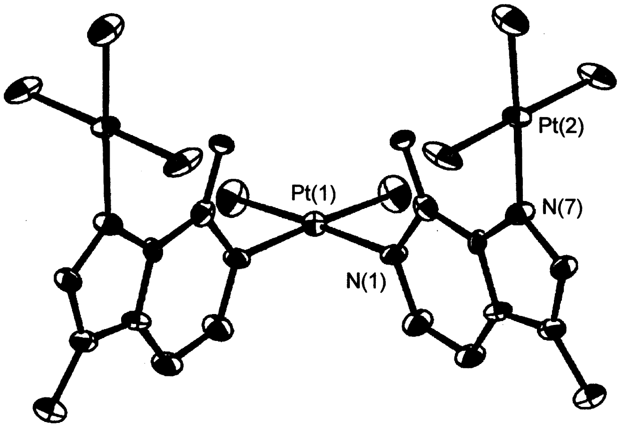
While some of the letters, S and U, are to be considered different rotamers, the situation in fact is not that simple since the way in which the central purine bases are cross-lined, e.g. via two N1 or two N7 positions, has an effect on the overall structure [10].

3.2. Going three-dimensional

Compound **17**, previously reported by us [24] and prepared by cross-linking two 9-methyladenine entities $[(9\text{-MeA-}N7)Pt(NH_3)_3]^{2+}$ via a *cis*-$(NH_3)_2Pt^{II}$, which binds at the N1 sites of the 9-MeA purine bases, is unique in that (i) the *cis*-$(NH_3)_2Pt^{II}$ provides a right angle (ii) the N1 bond adenines are perpendicular to the plane of *cis*-$(NH_3)_2Pt(N1)_2$ (iii) the 9-MeA ligands provide 90° angles as far as the Pt–N1



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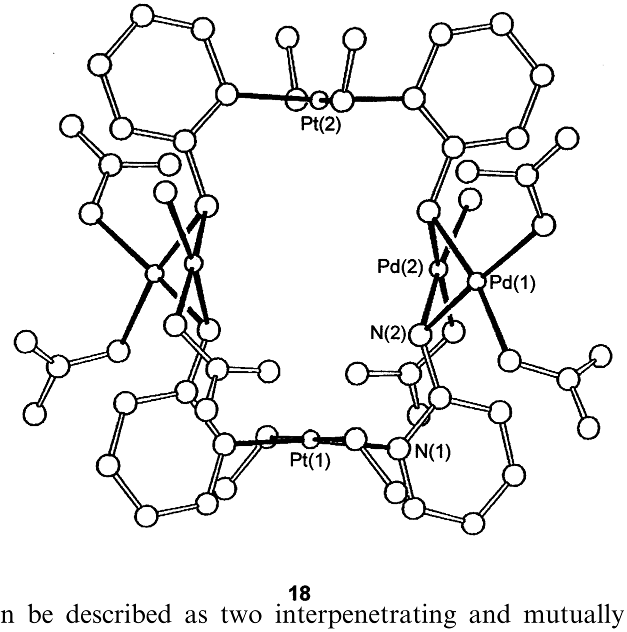
It is obvious that if the $(NH_3)_3Pt^{II}$ moieties are to be replaced by *trans*-$(NH_3)_2Pt^{II}$ units and bridging ligands eventually, closed, open or penetrating systems with numerous 90° angles will form.

The successive reaction of 2-aminopyridine (Hampy) with first a *trans*-$(CH_3NH_2)_2Pt^{II}$ entity and then an excess of a *cis*-L_2Pd^{II} species ($L = OH_2, NO_3^-$) leads to a cyclic hexanuclear complex $[\{Pt(CH_3NH_2)_2(ampy)_2\}_2Pd_4(NO_3)_6(H_2O)_2]^{2+}$ **18**, which is likewise three-dimensional as far as the six metals are concerned [25].



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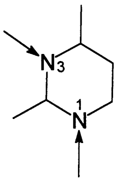
The cation can be described as two interpenetrating and mutually perpendicular rectangles which consist of a rectangle of four Pd^{II} ions (ca. 2.9 × 6.3 Å) and another one formed by the two Pt atoms and the four ampy planes (ca. 4.1 × 7 Å).

4. Pyrimidine complexes

4.1. Uracil quartet

The combination of two endocyclic sites in relative *meta* positions of a pyrimidine nucleobase, e.g. N1 and N3 (**19**) or N3 and C5 (**20**) or C5 and N1 (**21**) of uracil or cytosine leads to 120° angles as far as the N–M and C–M vectors are concerned. As will be outlined in Section 4.3. for **19**, this feature leads nevertheless to an open box as long as the metal entity has *cis*-geometry, and two sides which are approximately perpendicular to each other.



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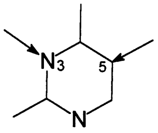

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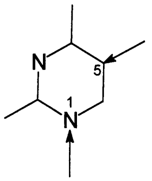

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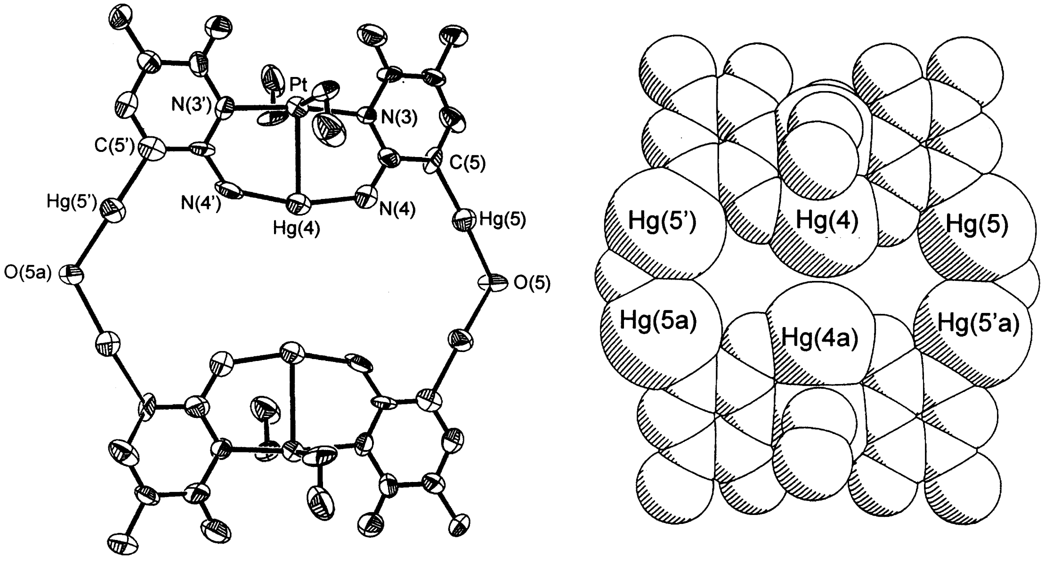
4.2. Cytosine hexagon

Only if metal entities adopting linear coordination geometries are employed, will planar entities displaying 120° angles form. For example, a molecular hexagon **22**, consisting of four 1-methylcytosine bases, two *trans*-$(CH_3NH_2)_2Pt^{II}$ and in addition six Hg^{II} ions has been prepared in a stepwise fashion by (i) initially cross-linking two 1-methylcytosine rings via Pt^{II} (ii) orientation of the two nucleobases into a head–head arrangement by Hg^{II} cross-linking two exocyclic amino groups of cytosine (iii) substituting the C5 protons of the two bases by Hg^{II} and (iv) condensing two tetranuclear entities via OH bridges [25].



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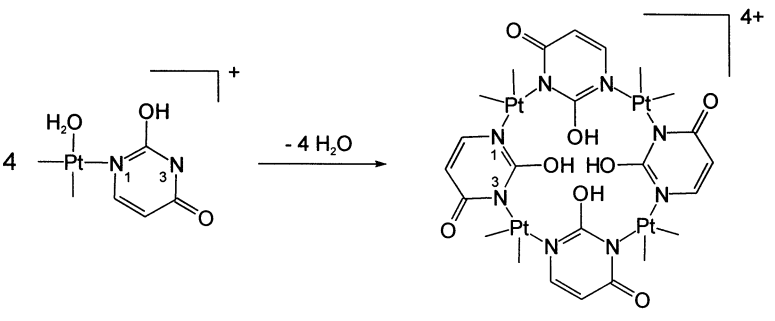
In this +6 cation, all four cytosine bases are dianionic. The six Hg^{II} ions are arranged in a coplanar fashion reminiscent of the surface of a metal salt.

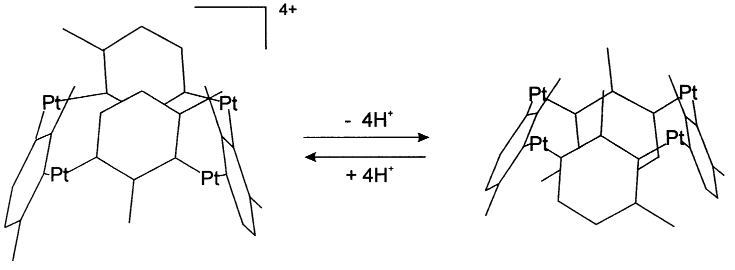
4.3. A calix[4]arene analogue

4.3.1. Synthesis and structural aspects

The combination of the 90° angle of the $enPt^{II}$ entity with the 120° angle between the vectors of the N1 and N3 sites of the uracil nucleobase leads to the spontaneous self-assembly of $[enPt(UH\text{-}N1)(H_2O)]^+$ (**23**) (UH = uracil monoanion) to the cyclic cation $[enPt(UH\text{-}N1,N3)]_4{}^{4+}$ (**24**) [26].



23 **24**



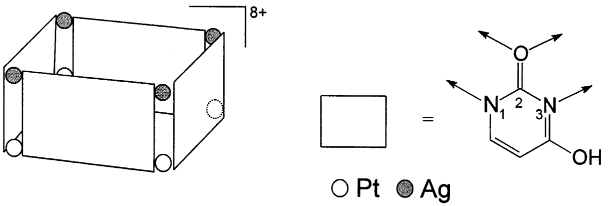
1,3-alternate conformer(**24a**) cone conformer(**24b**)

In contrast to the case of the cyclic complexes derived from purine nucleobases and trans-Pt^{II} (Section 3), the nucleobase planes are not parallel giving rise in this case to the formation of a 'molecular open box'. In addition, **24** can be considered a metal analogue of a classical calix[4]arene.

4.3.2. Solution dynamics

In the solid state, the cation **24** adopts a 1,3-alternate arrangement of the uracil nucleobases. This conformer appears to be strongly stabilized by the formation of a short hydrogen bond between the O2 and O4 exocyclic atoms of uracil [26]. In solution and after deprotonation to $[enPt(U\text{-}N1,N3)]_4$ a second major species (cone conformer) occurs.

The 1,3-alternate cone conformer equilibrium can be affected by the presence of metal ions as has been found in the case of calixarenes [27]. For example, Ag^I is responsible for the spontaneous 1,3-alternate → cone conversion in acidic media to the formation of the octanuclear species [enPt(UH-*N*1,*N*3,*O*2)Ag]$_4^{8+}$ (**25**) [25].



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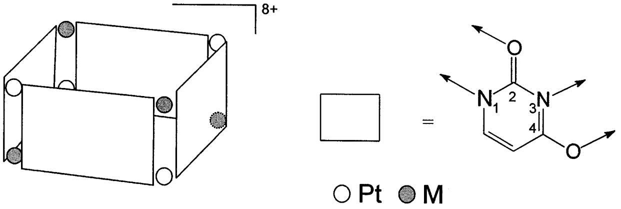
4.3.3. Coordination chemistry

Complex **24** is able to act as an efficient ligand as a consequence of the high basicity of the exocyclic oxygens of the *N*-platinated uracil rings. In related 1-methyluracil and 1-methylthymine systems an increase of 4–5 units in the pK$_a$ values is observed, which implies an enhanced metal affinity [28]. The 1,3-alternate and cone differ in preference for stoichiometries and binding sites. Complex **24a** is able to coordinate four divalent metals giving rise to the formation of octanuclear species [enPt(U-*N*1,*N*3,*O*2,*O*4)M]$_4^{8+}$ (M = Ni^{II}, Cu^{II}, Pt^{II}, Pd^{II}) (**26**) [25].



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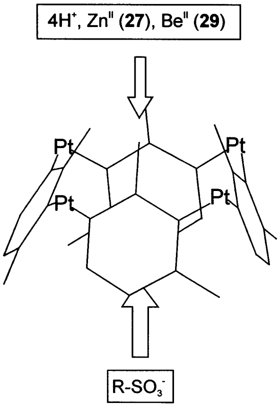
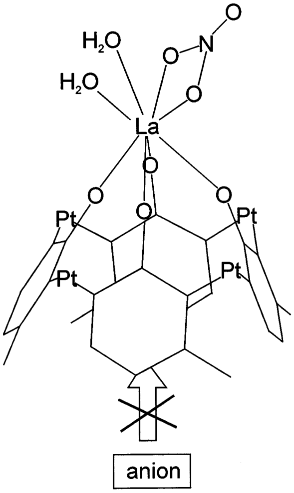
The behavior of **24b** as a ligand is, however, more versatile depending on the nature of the metal ion and preparation conditions. Thus, **24b** is able to incorporate four Ag^I metals in the oxo-surface formed by the O2 exocyclic atoms of uracil nucleobases in [enPt(UH-*N*1,*N*3,*O*2)Ag]$_4^{8+}$ (**25**). In the case of Zn^{II}, Be^{II} and La^{III} a lower number of metal entities are incorporated in the oxo-surface of **24b**, namely one in {[enPtU]$_4$Zn} $^{2+}$ (**27**), {[enPtU]$_4$La} $^{3+}$ (**28**) and {[enPtU]$_4$Be} $^{2+}$ (**29**) [29].





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4.3.4. Receptor properties

In addition to the noteworthy behavior of **24** as a versatile ligand towards various metal ions, **24** is also able to act as a receptor for organic anions when the cone conformation is present. Favorable behavior as a receptor is achieved in the protonated form of **24b**, as well as in the heteronuclear complexes **27** and **29** [29]. In the case of the protonated form of **24b** hydrogen bonding interactions between the O2 exocyclic atoms in a similar way as in the classic calix[4]arenes [30] accounts for an opening of the cone cavity which permits the facile incorporation of small molecules in the cavity. In compounds **27** and **29** the metal entities are responsible for a well structured cavity. The behavior of this set of compounds as receptors for anions can be considered a consequence of the positive charge of the species in contrast to non-substituted calixarenes which are neutral molecules and do not present anion-host properties [31]. In the case of compounds with the 1,3-alternate conformation (**24a** and **26**) or with **25**, which presents a pinched cone conformation, no behavior as receptors is observed in spite of the high positive charge of the species. This is a consequence of the absence of a sufficiently large cavity for guest inclusion. Complex **28** does not act as an anion receptor as a consequence of the coordination of the La^{III} centre to **24b**, which causes a marked flatening of the cone cavity.

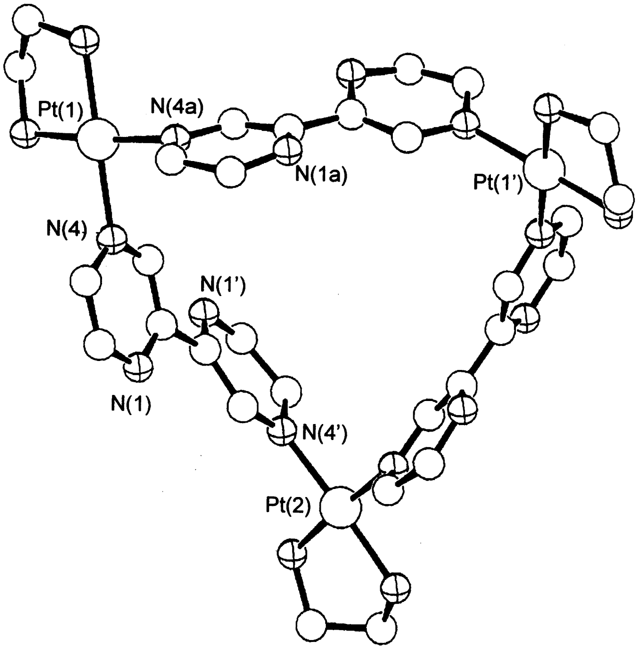
5. Triangles derived from 2,2′-bipyrazine and *cis*-a_2M^{II}

Much of the early work on molecular squares of Fujita and Stang type compounds relied on the 90° angle provided by the metal entity [2,3]. However, it is now clear, that the *cis*-geometry of a metal entity representing the corner stone of a macrocycle does not preclude formation of molecular triangles. The only prerequisite is a sufficient flexibility of the bridging organic ligand. As pointed out by Fujita [32] the molecular square derived from $\mathrm{enPd^{II}}$ and 4,4′-bipy can reversibly equilibrate with the corresponding triangle according to:

$$3\ (\text{square}) \rightleftharpoons 4\ (\text{triangle})$$

We have, in a different system with $\mathrm{enPt^{II}}$ and 2,2′-bipyrazine (2,2′-bpz) [33], confirmed the existence of cation **30**.

The compound **30** appears to be the kinetic product of the reaction, with the thermodynamically preferred one being the mononuclear compound containing the chelating 2,2′-bpz ligand via N1,N1′. The complex $\mathrm{enPd^{II}}$ forms this chelate preferentially [33]. In a similar self-assembly process, all be it from nine rather than six entities (three $\mathrm{enPt^{II}}$, three bridging ligands and three cucurbituril moieties), a molecular triangle has been very recently structurally characterized [34]. There are a number of other molecular triangles known where the metal ions provide 90° angles [35], including such with purine nucleobases [36]. Complex **30** behaves as a ligand toward additional metal species such as $\mathrm{enPd^{II}}$ [37], $\mathrm{enPt^{II}}$ or $\mathrm{Ag^{I}}$ [38]. These metal entities bind to the N1,N1′ positions of 2,2′-bpz, thereby forcing the two halves of the 2,2′-bpz to rotate about the 2,2′-bond to give hexanuclear $\mathrm{Pt_3Pd_3}$ vases [37] as well as larger aggregates, e.g. $\mathrm{[Pt_3]_2Ag_2}$ [38]. A common feature of these



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hexanuclear Pt_3Pd_3 and Pt_6 vases is their affinity for anions, which become incorporated in the cavity provided by the six heavy metals.

6. Summary

A simple concept—application of 90 or 180° angles at a metal entity and 90, 120, or 180° angles at a di- or multifunctional heterocyclic ligand, frequently a nucleobase—has led to a large variety of complexes of different topologies. Formation of these compounds occurs occasionally in a self-assembly process, even in the case of Pt^{II}, or alternatively in a stepwise fashion. Frequently the products formed represent aesthetically pleasing molecules, but they may also prove to be of further use. While this brief review essentially focused on synthetic and structural features, there is good reason to believe that because of the high positive charge of many of these compounds, a host–guest chemistry of anions may develop [39] and robust cationic molecular squares may prove of interest with respect to DNA telomers or the enzyme telomerase [40].

Acknowledgements

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