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Use of a cyclo-P₄ building block – a way to networks of host-guest assemblies
Use of a cyclo-P₄ building block – a way to networks of host–guest assemblies†

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Despite the proven ability to form supramolecular assemblies via coordination to copper halides, organometallic building blocks based on four-membered cyclo-P₄ ligands find only very rare application in supramolecular chemistry. To date, only three types of supramolecular aggregates were obtained based on the polyphosphorus end-deck complexes Cp⁸Ta(CO)₂(P₄) (1a: Cp⁸ = Cp⁸; 1b: Cp⁵ = Cp⁵), with none of them, however, possessing a guest-accessible void. To achieve this target, the use of silver salts of the weakly coordinating anion SbF₆⁻ was investigated as to their self-assembly in the absence and in the presence of the template molecule P₃Se₄. The two-component self-assembly of the building block 1a and the coinage-metal salt AgSbF₆ leads to the formation of 1D or 3D coordination polymers. However, when the template-driven self-assembly was attempted in the presence of an aliphatic dinitrile, the unprecedented barrel-like supramolecular host–guest assembly P₃Se₄@[{(Cp⁸Ta(CO)₂(P₄))₆(CuI)₅}] (3) and ‘pear’-like {[{(Cp³P₄)}₅Cu₃(C₂H₅CN)₅]} (4) scaffolds. Unlike many supramolecules based on cyclo-P₄ building blocks, none of these four-membered ring-based spheres feature guest inclu-
sions or even possess a guest accessible void. A way to realize host-guest chemistry is to use a larger Lewis-acidic metal cation free of any additional ligand occupying a coordination site. Moreover, the introduction of a fourth reaction component stimulating the degree of freedom in a self-organising process might create an extra chance of host–guest ability. Such a fourth component could be a linker that enables flexible aggregation. Herein we report on the self-assembly reaction of P₃Se₅, {Cp³Ta(CO)₂(P₄)} (1a), AgSbF₆ and the flexible dinitrile NC(CH₃)₂ CN to give a 2D coordination network in which a barrel-like supramolecular host–guest P₃Se₅@[{(Cp²Ta(CO)₂(P₄))₆Ag₈}]₈⁺ assemblies of 2.49 nm in size are connected by dinitrile linkers.

Results and discussion

To approach the task of host-guest chemistry starting with a four-membered building block, the two-component self-assembly of 1a and AgSbF₆ was studied beforehand.
colourless solution of AgSbF₆ in CH₂Cl₂ was layered with a yellow solution of 1a in toluene with a CH₂Cl₂ : toluene middle-layer (2 : 1). During the diffusion process, two different crystalline phases are formed (Fig. 1): orange plates of 5 and a few orange octahedra of 6. Unfortunately, the change of neither the stoichiometry nor the concentration of the starting materials nor the layering of the reaction solution after a complete diffusion with hexane, pentane or Et₂O led to a selective formation of one of the products.

According to X-ray diffraction studies, the main product of the reaction of 1a with AgSbF₆ is a 1D coordination polymer \([\{\text{Cp}^+\text{Ta(CO)}_2\}^{1+}\text{Ag}^+\text{SbF}_6}^{2-}\]_2\] (5) consisting of chains with \[\{\text{Ag}(1a)\}^{2+}\] repeating units (Fig. 2a). The Ag ions show a distorted tetrahedral coordination by four P atoms of four different cyclo-P₄ ligands \(\text{P}–\text{Ag}–\text{P} 90.3–140.5°\), which, in turn, coordinate to another \(\text{Ag}(\text{P}₄)\) moiety in a 1,2-fashion (Fig. 2b). This structural motif, \(\{\text{Ag}(\text{P}₄)\}^{2+}\), has been known for other supramolecular aggregates based on polyphosphorus complexes and \(\text{M}(\text{s}) = \text{Cu, Ag, Au}\) but has not been found for the cyclo-P₄ derivatives. The P–P bond lengths vary in a range between 2.149(5) and 2.179(5) Å and are in agreement with those in the free complex 1a \(\text{P}–\text{Ag}–\text{P} 2.150(2)–2.173(3) Å\), whereas the Ag–P bond lengths range between 2.494(3) and 2.563(3) Å. The SbF₆⁻ counter anions and the CH₂Cl₂ solvent molecules separate the chains.

Product 5 is insoluble in n-pentane and n-hexane, sparingly soluble in CH₂Cl₂ and fragmentises in N-donor solvents such as pyridine and CH₃CN. In the ESI-MS spectrum, fragments containing 1a, Ag⁺ and SbF₆⁻ are visible, with the highest peak at \(m/ z = 2604.7\), which can be assigned to \([\{1a\}^+\text{Ag}_2\text{SbF}_6}^{2-}\]²⁺. The ¹H and ³¹P NMR spectra of 5 in CD₃CN show signals corresponding to free 1a that corroborates with the expected fragmentation of 5 in CD₃CN.

Interestingly, the other coordination polymer \([\{\text{Cp}^+\text{Ta(CO)}_2\}^{1+}\text{Ag}^+\text{SbF}_6}^{2-}\]_2\] (6) was formed as a minor byproduct in the same reaction. This solvent-free phase, crystallized as orange octahedra, proved to have the same 2 : 1 ratio of 1a : AgSbF₆ as 5 and therefore represented a structural isomer of 5 which precluded a selective isolation and characterisation of the individual compounds by applying the appropriate stoichiometry of the educts. In contrast to 5, single crystal X-ray structure analysis of 6 revealed a 3D coordination polymer crystallizing as a racemic conglomerate in the chiral space group \(\text{P}1\overline{1}2\overline{1}2\) or \(\text{P}4_12\overline{1}2\). In the 3D framework all cyclo-P₄ ligands coordinate to Ag⁺ cations in a 1,2,3-coordination mode (Fig. 3), occurring only once in the peanut-like supramolecule. The tetrameric repeating \(\{\{1a\}^2\text{Ag}_4\}^{2+}\) units in 6 are constructed by the edge-sharing of the three-membered rings of \(\{\text{Ag}(\text{P}₄)\}^{2+}\). The tetramers possess a curved shape due to a distorted trigonal coordination environment of Ag (the P–Ag–P angles are in the range of 103.4–130.5°, Fig. 3a). Each unit is joined to four other neighbouring units (Fig. 3b) via one Ag–P coordinative bond to form a chiral 3D diamond-like network (dia⁹) with expanded channels (Fig. 3c). Despite being large (1.2–1.3 nm³), these channels do not provide accessible voids.
and are occupied by Cp" and CO ligands of 1a as well as by SbF₆⁻ anions. The P–P bond lengths range from 2.146(3) to 2.180(4) Å, being in agreement with the bond lengths in 5 and 1a, whereas the Ag–P bond lengths vary in a range between 2.446(3) and 2.493(3) Å.

Interestingly, the curved tetrameric repeating unit in the structure of 6 can potentially be extended to some kind of a cylindrical core similar to previously reported non-classical fullerene-like cores 2. However, in 6 the {Cp"Ta(CO)₂} units point out alternatively on the different sides of the cyclo-P₄ ligands of the concave tetramer. While in any possible cylindrical core all {Cp"Ta(CO)₂} units should point outside.

To overcome this difficulty and to direct the self-assembly process to the formation of a convex shell based on Ag cations and complexes 1a, we used a cage molecule P₄Se₃ as a rather small template. Moreover, to induce coordinative freedom and flexibility to form potential host–guest cages, we targeted the introduction of a flexible aliphatic linker as e.g. the dinitriles NC(CH₂)nCN with n ≥ 7, because they deliver the needed distance to the next possible formed sphere. To interconnect potentially formed supramolecular assemblies of 1a and AgSbF₆ templated by P₄Se₃, we used the linker NC(CH₂)₇CN in a four-component self-assembly process.

A colourless solution of AgSbF₆ in CH₂Cl₂ is first layered with a mixture of CH₂Cl₂ and toluene (2 : 1) and then with a yellow solution of 1a, P₄Se₃, and NC(CH₂)₇CN in toluene. The intermediate layer of the mixed solvents is used to slow down the diffusion and thus facilitate the growth of crystals better suitable for X-ray structure analysis. The AgSbF₆, 1a, P₄Se₃ and NC(CH₂)₇CN were taken in a ratio of 1 : 1 : 1.5 : 10; the 10-fold excess of the dinitrile is required to avoid the formation of the insoluble polymers 5 and 6. By doing this, orange prismatic crystals of 7 in 29% yield were formed (Fig. 1). Variation of the stoichiometry only leads to the occurrence of by-products and the formation of 7 in lower yields.

Single crystal X-ray structure analysis revealed the formation of a 2D polymeric network of interconnected supramolecular aggregates of P₄Se₃@[{(Cp"Ta(CO)₂)(η⁴-P₄)}Ag]₈(NC(CH₂)₇-CN)₄.₃][SbF₆]₆ (7) (Fig. 4). In this square lattice coordination network the nodes represent novel self-assembled aggregates [[{(1a)Ag₈}₄]₈ of 2.49 nm in size (Fig. 4a, see ESI† for details). In the inorganic core of the nodes, eight cyclo-P₄ units and eight Ag ions are assembled in a square-antiprismatic arrangement of eight joined six-membered [Ag₄P₄] rings (Fig. 4b). This 40-vertex arrangement closely resembles two fused tetrameric units of 6; every cyclo-P₄ ligand (P–P: 2.131(5)–2.177(5) Å) coordinates to three Ag cations, again in a 1,2,3-mode. However, the Ag environment is tetrahedral, as every silver cation, in addition to three P atoms of three 1a units, is also coordinated by one dinitrile linker (2.179(17) to 2.305(14) Å). The Ag–P bond lengths vary from 2.477(3) to 2.528 (3) Å. The similarity of the inorganic cores in 6 and 7 is underlined by P–Ag–P angles that vary from 97.3(1) to 127.4(1)° being similar to those in 6 despite the difference in the coordination number of Ag.

These supramolecular assemblies represent the first doughnut-like cyclo-P₄-based structure open at two sides. Cyclic or cylindrical molecules are rather abundant in different classes of coordination compounds. Among them, the closest analogues of cylindrical ligand-based supramolecules usually do not act as molecular containers. A doughnut-shaped Ti-oxo clusters with a permanent MOF-like porosity and high CO₂ adsorption capacity was recently reported. Two bowl-like

Fig. 4 (a) Supramolecular node, (b) its 40-vertex inorganic core (c) containing a P₄Se₃ guest molecule. (d) node with outgoing linkers, (e) 2D network of interconnected nodes in 7. The guest is depicted in the space-filling model. Non-coordinating linker units are highlighted in green. (Cp"Ta(CO)₂) fragments and counter-anions are omitted for clarity.
supramolecules based on pentaphosphaferrocene and Cu(i) halides were just recently obtained in our group, which are open only at one side, \([\text{[CP}^*\text{Fe}(\text{η}^5-P_5)]_{11}[\text{CuX}]_{15-}\text{-}x] \) \(X = \text{Cl}, \text{Br}; x = 0.45-1.55\). This makes the ‘doughnut’ in 7 the second example only of the open architectures among all supramolecules based on polyphosphorus cyclo-P\(_n\) ligands \((n = 4, 5)\). Additionally, each supramolecular node contains a P\(_4\)Se\(_3\) molecule as a guest (Fig. 4c) in its inner void of 0.60 \(\times\) 0.68 nm. The guest is disordered over two positions with 80 and 20% probability. The fact that the guest is disordered suggests that there are no significant intermolecular host–guest interactions. The shortest intermolecular contacts amount to 3.54–3.77 Å for the \(P_{\text{host}}\cdots\text{Se}\) contacts and 3.41–3.65 Å for the \(P_{\text{host}}\cdots\text{P}_{\text{guest}}\) contacts \(^{13}\) (see the ESI for more details). Nevertheless, the tendency of the self-assembly, without the guest, is towards the formation of the supramolecular host assembly.

Every Ag cation is coordinated by one dinitrile linker, however, only seven dinitriles are linked to another supramolecular node, whereas one is terminal. Three nodes are double-brided by linkers, while the fourth one is linked by a single dinitrile ligand. The positive charge of the eight Ag(I) cations is balanced by eight SbF\(_6^-\) anions which occupy both the interlayer space and the meshes of the network. The presence of a terminal dinitrile possessing a non-coordinated donor cyano group shows the conceptual possibility to expand the structure in the third dimension. The separation of the nodes in the resulting layer, represented by Ag····Ag distances, amounts to 12.44–13.99 Å. The corresponding N····N distances in the bridging dinitrile ligands vary in the range between 9.24 and 10.31 Å, which demonstrates the shortening of the ligands that possess a folded configuration, as compared to 11.76 Å for the calculated length of the linear linker. \(^{12}\) This correlation demonstrates that the use of a shorter dinitrile with \(n = 6\) (10.73 Å in the linear configuration) might also give similar polymers of host–guest agglomerates for 1a-based supramolecules.

Crystals of 7 are stable in the mother solution for several weeks. 7 is insoluble in hexane and pentane, sparingly soluble in CH\(_2\)Cl\(_2\) and shows fragmentation in CH\(_3\)CN and pyridine. In the ESI-MS spectrum of 7, fragments containing 1a, Ag, NC[CH\(_2\)]\(_n\)-CN and SbF\(_6^-\) are observed, with the highest peak at \(m/z = 2604.7\), which can be assigned to the same molecular ion \(\text{[1a}\cdots\text{Ag}\cdots\text{SbF}_6]}^+\) as in the case of 5. Similarly to 5 and 6, in CD\(_3\)CN 7 undergoes fragmentation. Therefore, the \(^1\)H and \(^{31}\)P NMR spectra show only signals of the starting materials.

Conclusions

The self-assembly of the 1a complex and the coinage metal salt Ag\(_2\)SbF\(_6\) was studied, and the possibility of forming host–guest complexes based on cyclo-P\(_4\) ligands was demonstrated for the first time. Moreover, these host–guest agglomerates can be linked in a coordination network, thus representing new polymeric matrices in which unprecedented barrel-like silver-polypnictogen-containing supramolecules serve as molecular containers. This finding opens new frontiers in the coordination chemistry of cyclo-P\(_4\) ligand complexes suggesting the design of new supramolecular architectures and exploring the influence of different coinage metal salts, the template effect of different guests as well as the variation of the nature of the linker and its lengths.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 X-ray structure analysis: compound 5: \(C_{102.13}H_{72.17}AgCl_{2.7}F_{20.17}O_{2.17}SbT_{2.09}\), orange plate, \(M_r = 1449.64\) g mol\(^{-1}\); triclinic, sp. gr. \(P1\), \(a = 10.4796(5), b = 14.2670(6), c = 17.0118(8)\), \(\alpha = 96.742(4), \beta = 90.464(4), \gamma = 101.225(4)\), \(V = 2476.3(2)\) Å\(^3\), \(Z = 2\), \(T = 90\) K, \(R_1 = 0.067, wR_2 = 0.182, GOF = 1.00\); compound 6: \(C_{12.16}AgF_5O_7P_4SbTa_{0.68}\), orange octahedron, \(M_r = 881.77\) g mol\(^{-1}\), tetragonal, sp. gr. \(P4_2\), \(a = 19.2268(9), c = 26.5819(2)\), \(V = 9825.98(13)\) Å\(^3\), \(Z = 16\), \(T = 90\) K, \(R_1 = 0.030, wR_2 = 0.062, GOF = 0.95\), Flack parameter = 0.009(5); compound 7: \(C_{128.13}H_{24.17}N_7\text{O}_{2.17}F_2\text{P}_{2.17}Cl_{13}\text{Ag}_{12.17}\text{Sb}_{6.17}\text{Ta}_{13.17}\text{Se}_{6.17}\), orange prism, \(M_r = 16.818.72\) g mol\(^{-1}\); triclinic, sp. gr. \(P1\), \(a = 17.9594(1), b = 22.5635(2), c = 38.3494(4)\), \(\alpha = 81.1581(7), \beta = 78.4160(7), \gamma = 71.7720(7)\), \(V = 14\) 534.6(2) Å\(^3\), \(Z = 2\), \(T = 80\) K, \(R_1 = 0.0895, wR_2 = 0.287, GOF = 1.09\). See ESI for more information.

2 The size of the channel in 6 is estimated as the minimal distance between the closest non-bonded P atoms minus doubled van der Waals radius of P. \(^{15}\)

3 The outer diameter in 7 is calculated as the distance between the H atoms of two of the furthermore Cp\(^3\) ligands plus twice the van der Waals radii of H. \(^{14}\)

4 The size of the void in 7 is calculated as the distance between the centroids of every individual cyclo-P\(_4\) unit and the centroid of the node minus twice the van der Waals radius of P (1.8 Å). \(^{14}\)

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