**Abstract:** The cyclo-P₄ complexes [CpTa(CO)₅(η⁴-P₄)] (Cp*: C₃₅H₆₅Bu₅, Cp*¹ = 1,3-C₃₅H₆₅Bu₅, Cp*² = 1,2,4-C₃₅H₆₅Bu₅) turned out to be predestined for the formation of hollow spherical supramolecules with non-classical fullerene-like topology. The resulting assemblies constructed with CuX (X = Cl, Br) showed a highly symmetric 32-vertex core of solely four- and six-membered rings. In some supramolecules, the inner cavity was occupied by an additional CuX unit. On the other hand, using CuI, two different supramolecules with either peanut- or pear-like shapes and outer diameters in the range of 2–2.5 nm were isolated. Furthermore, the spherical supramolecules containing Cp¹⁻⁻ ligands at tantalum are soluble in CH₂Cl₂. NMR spectroscopic investigations in solution revealed the formation of isomeric supramolecules owing to the steric hindrance caused by the third tBu group on the Cp¹⁻⁻ ligand. In addition, a 2D coordination polymer was obtained and structurally characterized.

**Fullerenes**, defined as spherical carbon clusters, are prime examples of discrete nanosized supramolecules. Owing to their unique optic and electronic properties, they have gained increasing attention in materials science and nanotechnology.[1] However, the majority of reports on fullerenes are restricted to the most stable derivatives such as C₆₀ and C₇₀, which can be prepared on a reasonable scale. Consisting solely of five- and six-membered rings, they are so-called classical fullerenes. Some time ago, we succeeded in showing that [CpFe(η⁴-P₃)] (Cp* = C₅Me₅) containing a cyclo-P₃ ligand self-assembles with copper(I) halides to give supramolecules with fullerene-like topology. These unprecedented carbon-free analogues of the I₈-C₄₀ (Figure 1) and I-C₄₀ frameworks represent less stable fullerene-like congeners.[2]

Figure 1. a) Supramolecule with 80 vertices based on [Cp²Fe(η⁴-P₃)] and CuX (X = Cl, Br). b) The molecular scaffold illustrating the I₄-C₈₀ fullerene topology.

Some time ago, we were interested to see whether non-classical fullerenes of various ring sizes[3] are also accessible using the metallasupramolecular approach. The cyclo-P₄ complex [CpTa(CO)₅(η⁴-P₄)] (1a; Cp* = 1,3-C₃₅H₆₅Bu₅) seems to be predestined for the formation of spheres comprising the four-membered ring motif. First investigations of the reactivity of 1a with CuCl revealed the formation of the spherical supramolecule [[CpTa(CO)₅(η⁴-P₃)]₈(CuCl)₈] (2a), which consists exclusively of four- and six-membered rings.[4] Its scaffold consists of 32 inorganic core atoms and exhibits O₈ symmetry; this non-classical fullerene framework has not been obtained in fullerene chemistry thus far.[5]

This single result led to some decisive questions as to whether the concept of structural arrangements of four- and six-membered rings in supramolecules could be extended to unprecedented spherical structural motifs as it was possible for the five-membered ring of pentaphosphaferrrocene.[2,7] Moreover, further information on the formation process and the structural stability in solution was required as the insolubility of the formerly obtained 32-vertex ball 2a did not allow for any investigations of its behavior in solution. Thus a third tert-butyl group was introduced into the cyclopenta-dienyl ring to increase the solubility, and the complex...
[ Cp"Ta(CO)₅(η⁴-P₄)] (1b: Cp" = 1,2,4-C₆H₃(C₂H₅)₂) was synthesized, structurally characterized, and examined in terms of its reactivity towards copper(I) halides.

Herein, we report on a systematic investigation of the reactivity of the cyclo-P₄ ligand tantalum complexes 1a and 1b towards CuX (X = Cl, Br, I), which led to the isolation and structural characterization of three novel representatives of spherical C₃₂ analogues [(Cp"Ta(CO)₅(η⁴-P₄))₃]Cu₂I₄ (2b: Cp" = Cp", X = Br; 2c: Cp" = Cp"", X = Cl; 2d: Cp" = Cp"", X = Br). For the first time, the solubility of the Cp" derivatives (2c and 2d) enabled a characterization in solution. Furthermore, we succeeded in the isolation of two spheres containing singular scaffolds. [(Cp"Ta(CO)₅(η⁴-P₄))]₃Cu₂I₄ isomorphous with 1c (2b and 2c) (3) and [(Cp"Ta(CO)₅(η⁴-P₄))]₃Cu₂I₄(μ-I)(μ-1)(μ-1)(CH₂CN)]²⁻ (4a, 4b). The unprecedented double sphere of 3 shows potential for subsequent aggregation according to the spherical building block concept. Their structures give insight into the formation pathway of the 32-vertex balls as the spherical C₃₂ analogue as CuI, unlike other copper(I) halides, tends to form extended Cul aggregates. By carefully layering a solution of CuI in CH₂CN over a solution of 1a in toluene, orange prisms of [(Cp"Ta(CO)₅(η⁴-P₄))]₃Cu₂I₄(μ-I)(μ-I)] were formed within four days (Figure 2). After approximately two weeks, a new crop of yellow prisms appeared as the second fraction, representing another spherical cluster, namely [(Cp"Ta(CO)₅(η⁴-P₄))]₃Cu₂I₄(μ-I)(μ-I)(CH₂CN)]²⁻ (4a, 4b). The crystallization of cluster 4 was delayed during the synthesis of 3 owing to its higher solubility, which was concluded from an optical examination of the crystalline material and the unit cells of dozens of different crystals. The formation of 3 and 4 in the same reaction is due to the very similar ratios of 1a/CuI in the composition of both products (3: 1:2.33; 4: 1:2.40). Interestingly, the direct synthesis of compound 4 was possible under similar reaction conditions in the presence of [Cp*Fe(η⁴-P₄)]₃. The formation of 4, albeit as another solvatomorph (4a), was accompanied by the formation of brown needles of the earlier reported 2D coordination polymer [(Cp*Fe(η⁴-P₄))(CuI)]₄. Apparently, the presence of [Cp*Fe(η⁴-P₄)] in the reaction mixture inhibits the preliminary formation of 3 and favors the formation of 4.

Compound 3 crystallizes in the monoclinic space group C2/m, and structural analysis revealed an unprecedented nanocapsule that consisted of ten cyclo-P₄ complexes 1a bound to eight Cul units and two CuI₄ units (Figure 3b). Six complexes 1a bind in a 1,2,3,4- and four in a 1,2,3,4-coordination mode. The whole supramolecule 3 can be described in terms of two [(Cp"Ta(CO)₅(η⁴-P₄))(CuI)]₄ fragments connected by two CuI₄ units. The two cluster fragments have similar inorganic frameworks, which can be derived from those of 2a and 2b by removing one cyclo-P₄ complex 1a and coordinating four CuX units to it. Therefore, it seems that on the way to the formation of the regular 32-vertex spheres of 2, two incomplete spheres were fused by two CuI₄ units to give the double sphere 3. The resulting inner scaffold of 3 has a peanut-like shape and consists of 38 inorganic core atoms, 40 P, 14 Cu, and 4 I atoms (Figure 3). The iodine atoms only support the scaffold as its connectivity can be achieved with Cu–P bonds. As expected, the Cu–I bonds with terminal iodides (average: 2.53(1) Å) are shorter than to μ-I (2.598(3) Å) and μ-I (average: 2.69(2) Å) atoms. The P–P

![Figure 2: Reactions of [Cp"Ta(CO)₅(η⁴-P₄)]] (1a: Cp" = Cp"; 1b: Cp" = Cp") with copper(I) halides yield the supramolecules 2–4 and the coordination polymer 5 (yields in parentheses).](image-url)
Molecular structures of is tetracoordinated, 4a, 1b, 2b and towards CuX (X = I) atoms (2.6(1) Å in 4b). The P–P bonds in 4a (2.129(3)–2.168(3) Å) and 4b (2.128(4)–2.166(4) Å) are shorter than in 1a and 3, respectively. The spherical cluster 4 has an outer diameter of 2.35 nm. Like in 3, the inner cavity of 4 is occupied by iodide, which here belongs to the [CuI₄]⁻ unit. Interestingly, the supramolecules 4a and 4b are isomers: The structural difference between their scaffolds was traced back to two positions occupied by either an iodide or a CH₂CN molecule.

In the IR spectra of all products, the two CO stretching vibrations (2a: 2040 cm⁻¹, 1974 cm⁻¹; 2b: 2042 cm⁻¹, 1972 cm⁻¹; 3: 2011 cm⁻¹, 1969 cm⁻¹; and 4: 2017 cm⁻¹, 1976 cm⁻¹) all display a significant shift to higher wavenumbers compared to those of 1a (1983 cm⁻¹, 1952 cm⁻¹). Furthermore, all compounds obtained from the Cp⁺ derivatives 1a were completely insoluble in n-hexane, toluene, CH₂Cl₂, and THF.

Certainly, NMR spectroscopic characterization would be desirable to confirm the existence of the superspheres in solution. A promising approach for this is based on increasing the steric demand on the Cp⁺ ligand by introducing a third tert-butyl group on the Cp⁺ ring. For this reason, [Cp⁺Ta-(CO)₅(n⁴-P₃)] (1b) was synthesized in analogy to the preparation of 1a in good yields (73%). The comprehensive characterization of 1b in solution as well as in the solid state by X-ray crystallography showed almost identical structural features to those of 1a.

The reactivity of 1b towards CuX (X = Cl, Br) was investigated by adding a solution of CuX in CH₂Cl₂ to a solution of 1b in toluene or benzene and stirring it for ten minutes. Subsequently, the red solution was layered with Et₂O, and after three weeks, red prisms of 2c and 2d had formed (Figure 2). These products were also formed when 1b/ CuX ratios ranging from 1:1 to 1:2 were used.

Both 2c and 2d crystallized in the monoclinic space group P2₁/m, and X-ray structural analysis revealed the supramolecules [{Cp⁺Ta-(CO)₅(n⁴-P₃)}][CuX₄]ₙ⁻ (2c: X = Cl, x = 0.6; 2d: X = Br, x = 0.3; Figure 3a). The molecular structures of 2a–2d are similar; with the exception of the additional tert-butyl group, they exhibit the same spherical supramolecules and alternating patterns of four- and six-membered rings in the 32-vertex core (Figure 3e). The Ox symmetry of the inorganic scaffold is violated by the organic substituents at the Ta atoms, which leads to overall C₃v (2b) or C₃ symmetry (2c, 2d) for the supramolecules in the solid state. The P–P bonds of 2.144(3)–2.176(3) Å in 2d are only slightly shorter than those in the free complex 1b and supramolecule 2a (2.156(2)–2.180(2) Å).[15] The inner cavities of 2c and 2d have the same size (dₘₙₙ = 0.6 nm) whereas the maximum outer diameters of 2.50 nm (2c) and 2.54 nm (2d) are larger by about 0.35 nm than those of the Cp⁺ derivatives 2a and 2b, which is due to the third butyl group in the Cp⁺ ligands.

Attention needs to be drawn to the co-existence of the supramolecules 2b–2d with isomeric and slightly incomplete

![Figure 3. a–c) Molecular structures of 2c (a), 3 (b), and 4a (c). d) Section of the 2d polymeric network in 5. Hydrogen atoms omitted for clarity. e–g) Scaffolds of the supramolecules 2a–d (e), 3 (f), and 4a (g). h) Repeating unit of 5.](Image 52x86)
inorganic scaffolds in the solid state. One CuX unit is missing in the 32-vertex scaffold for 20–50% of the supramolecules. In 10% of the spheres, an additional CuX unit is present, which points into the cavity. In this case, the Cu ion is coordinated to two cyclo-P₄ units in η²-mode while the terminal X ion is located at the center of the cavity. This CuX unit can either co-exist with adjacent Cu ions α-coordinated to the cyclo-P₄ unit or neighbor a CuX vacancy in the 32-vertex scaffold. It thereby forms two or one Cu–Cu contacts of 2.81–2.95 Å.

Apparently, the single tBu group also supports the formation of the spherical clusters. However, it induces the formation of even more isomeric forms in addition to the structural variation in the inorganic core. In the free complex 1b, the Cp” ligands can rotate freely. However, upon coordination to the copper halide units, the rotation is hindered as the halides are now situated in between the tBu groups. With increasing halide size, this immobilization becomes more pronounced. As a consequence, every molecule of complex 1b can appear in two enantiomeric conformations that differ in the orientation of the single tBu group, which again leads to isomeric clusters. In the crystal structure of 2c, only one isomer is observed. However, the crystal structure of 2d consists of co-crystallized epimeric clusters as indicated by the disorder of one tBu group. As the formation of the spherical clusters in solution should not be influenced by the orientation of the single tBu group, a freshly prepared solution of 2c and 2d should contain several isomeric clusters, which might inhibit the crystallization of the macromolecules. This specific property is in accordance with the experimental observation that even from concentrated mixtures of 1b with CuX (X = Cl, Br), single crystals of 2c and 2d were formed only within several weeks, whereas 2a and 2b crystallized within one day.

Compounds 2c and 2d are orange, air-sensitive solids, and are insoluble in hexane and Et₂O. As anticipated, they are sparingly soluble in toluene and have moderate solubility in CH₂Cl₂. In the ¹H NMR spectra of 2c and 2d in CD₂Cl₂, six broad resonances appear between 1 and 2 ppm for the tBu groups and two broad resonances at 6.4 and 7.4 ppm for the methine H atoms. The presence of two resonances for the methine protons indicates the inhibited rotation of the Cp” ligand. The distinct downfield shift of the resonance at 7.4 ppm was attributed to the proximity of the halide ligand. The presence of several broad resonances for the tBu groups is in accordance with the slow isomerization of the clusters in solution. In the ³¹P[¹H] NMR spectrum, very broad resonances were observed between –50 and –90 ppm, which were shifted upfield by approximately 100 ppm compared to the free complex 1b. This indicates that the P₄ cycle interacts with the Lewis acidic copper(I) halides. Furthermore, resonances of the free complex 1b could be detected neither in the ¹H nor in the ³¹P[¹H] NMR spectrum. The same observations were made in NMR spectroscopic investigations of a freshly prepared reaction mixture of 1b and CuX (X = Cl, Br). These results indicate that the spherical aggregates, such as 2c and 2d, are formed immediately and remain intact in solution. This hypothesis was also confirmed by diffusion ordered spectroscopy (DOSY) experiments. The hydrodynamic radii thus determined correlate well with the radii derived from the crystal structure analysis in the solid state.

In the ESI mass spectra of 2c and 2d, only fragments of the clusters were detected. In CH₂Cl₂ solutions, the cation [(Cp”Ta(CO)₅)(η²-P₄)(Cu₂Cl)]⁺ was observed. In CH₂Cl₂/CH₃CN mixtures, larger cluster fragments up to [(Cp”Ta(CO)₅)(η²-P₄)(Cu₂Cl)]⁺ could be detected. The IR spectra show two CO stretching vibrations (2c: 2019 cm⁻¹, 1979 cm⁻¹; 2d: 2015 cm⁻¹, 1973 cm⁻¹), which are located at significantly higher wavenumbers than those of 1b (1982 cm⁻¹, 1939 cm⁻¹); similar observations were made for the analog Cu” clusters 2a and 2b.

Upon addition of a solution of CuI in CH₂CN to a stirred solution of 1b in CH₂Cl₂, an orange solution was obtained. After stirring the mixture for 4 hours, the ³¹P[¹H] NMR spectrum of the reaction mixture displayed no resonances corresponding to 1b, but very broad resonances appeared between –30 and –90 ppm, just like in the spectra of the CuCl/Br clusters 2c and 2d. However, the corresponding DOSY NMR experiment indicated that the spheres formed in solution have a smaller radius than derivatives 2c and 2d. In the ESI mass spectrum of the reaction mixture, the cation [(Cp”Ta(CO)₅)(η²-P₄)(Cu₂I)]⁺ represents the largest fragment, as found for isolated 2c. After removal of the solvent, two carbonyl bands (2013 cm⁻¹, 1971 cm⁻¹) appear in the IR spectrum of the obtained solid, which are similar to those of the clusters 2c (2019 cm⁻¹, 1979 cm⁻¹) and 2d (2015 cm⁻¹, 1973 cm⁻¹), but also correspond to those of 3 (2011 cm⁻¹, 1969 cm⁻¹) and 4 (2017 cm⁻¹, 1976 cm⁻¹). Both the solubility of these species and the analytical data indicate the presence of spherical aggregates in solution with structures similar to, but smaller than, those of the clusters 2c and 2d. Incomplete spheres thus seem to exist in solution that might be structurally comparable to fragments of 4 after CuI release or sections of 3. However, upon layering diethyl ether over the reaction mixture, yellow plates of the 2D polymer 5 were formed (Figure 2d), which were insoluble in hexane, Et₂O, toluene, CH₂Cl₂, and THF.

X-ray structure analysis of 5 revealed the 2D coordination polymer [(Cp”Ta(CO)₅)(η²-P₄)(Cu₂I)])n , in which cyclo-P₄ ligand complexes 1b link [Cu₂(I₂)]n heterocubane units in a 1,2,3,4-coordination mode (Figure 3b). Even though these complexes 1b feature the same coordination mode as in the spherical molecules 2c and 2d, the Cu₂I₄ units induce the formation of the layered structure in 5. Therefore, every second complex 1b is located on the opposite side of the polymeric layer. Compared with the free complex 1b, the average P–P bond is also shorter in 5 (2.150(6) Å). The Cu₂I₄ heterocubane structural motif is known in coordination chemistry. In 5, each iodine atom bridges three copper atoms with an average Cu–I distance of 2.66(4) Å, which lies in the typical range for such bonds. The resulting layers of Cu₂I₄ and cyclo-P₄ units are separated by the bulky Cp” ligands and the carbonyl ligands at the Ta atoms as well as co-crystallized CH₂CN solvent molecules.

In summary, a systematic study towards spherical supramolecules starting from the cyclo-P₄-containing tantalum complexes 1a and 1b as building blocks has yielded fascinating supramolecular assemblies with a non-classical fullerene.
topology. The CuX-based superspheres (X = Cl, Br; 2b–d) thus obtained mostly exhibit hollow 32-vertex scaffolds in the shape of a truncated octahedron that exclusively consists of alternating P₄ four- and Cu₄P₅ six-membered rings. In the solid state, isomeric and slightly incomplete supramolecules with lower symmetry were also observed. The higher steric demand in Cp²⁺ derivative 1b compared to 1a improved the solubility of these 2.5 nm large molecules. NMR spectroscopic studies confirmed that 1b-based spherical aggregates are immediately assembled and remain intact in solution. Although 1b did not give rise to molecular clusters in the reaction with CuI, 1a enabled the synthesis of the previously unknown supramolecules 3 and 4 with sizes of up to 2.2–2.8 nm. Cluster 3 consists of two open shells similar to those in 2 that are fused together by two Cu₄I₄ units to give an unprecedented peanut-shaped scaffold of 58 non-carbon atoms. The 41-vertex supramolecule 4 exhibits a completely new topology. A hemisphere of five cyclo-P₄ and four [Cu₄I₄] units closed by a Cu₄I₄ bowl results in a pear-shaped inorganic framework, where, in contrast to 3, the iodides are also involved in scaffold construction. However, both structures can be viewed as snapshots of the formation of the 32-vertex balls as the missing Ta₄P₂ unit of the 32-vertex ball can be replaced by a CuI network to form 4 or merged to a second incomplete ball via a (CuI), moiety to form peanut-shaped compound 3.

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[8] The diameters d of the inner cavities were calculated as the minimum distances between geometrically opposed atoms minus the van der Waals radii of the respective atoms (P: 0.180 nm, Cu: 0.140 nm, I: 0.198 nm). The d value was defined as the diameter of the largest sphere that can be inscribed in the cavity formed by the atoms. The outer diameter was taken as the maximum distance between two atoms the most distant from the center, plus twice the van der Waals radius for the H atom (0.12 nm).


[13] See the Supporting Information.

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