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Supramolecules **Hot Paper**

Metal-Deficient Supramolecule Based on a Fivefold-Symmetric Building Block

*Jana Schiller, Eugenia Peresypkina, Alexander V. Virovets, and Manfred Scheer**

Dedicated to Professor Maurizio Peruzzini on the occasion of his 65th birthday

Abstract: *An unprecedented cationic supramolecule* $[(Cp''Fe(\eta^5\text{-}P_5))_{12}\{CuNCMe\}_8]^{8+}$ *2.66 nm in diameter was selectively isolated as a salt of the weakly coordinating anion* $[Al\{OC(CF_3)_3\}_4]^-$ *for the first time and characterized by X-ray structure analysis, PXRD, NMR spectroscopy, and mass spectrometry. Its metal-deficient core contains the lowest possible number of Cu atoms to connect 12 pentaphosphaferrocene units, providing a supramolecule with fullerene topology which, topologically, also represents the simplest homologue in the family of metal-deficient pentaphosphaferrocene-based supramolecules* $[\{Cp^RFe(\eta^5\text{-}P_5)\}_{12}(CuX)_{20-n}]$*. The 12 vacant metal sites between the cyclo-*P_5 *rings, the largest number attained to date, make this compound a facile precursor for potential inner and outer modifications of the core as well as for functionalization via the substitution of labile acetonitrile ligands.*

Giant self-assembled supramolecules based on metal cations and rigid bi- or multidentate organic ligands have been met with growing interest over the last decade.[1] They represent an attractive combination of solubility and functionality such as the selective encapsulation of enantiomers and catalytic as well as photochemical activity.[2] Generally, these supramolecules contain dozens of metal atoms in their hollow cores, as, for example, spherical $[Pd_{30}(L1)_{60}](BF_4)_{60}$, $[Pd_{48}(L1)_{96}](BF_4)_{60}$ (L1 = selenophene-based spacer), octahedral $[M_{24}\{\text{pyrogallol[4]arene}\}_6]$ (M = Cu, Fe, Mg, V), and icosahedral $[M_{48}\{\mu_3\text{-}L2\}_{18}\{TC4A\}_{12}]$ (M = Co, Ni; H_4TC4A = *p-tert*-butylthiacalix[4]arene; L2 = 1H-tetrazol-1-yl)isophthalate) (Figure S14 in the Supporting Information).[3] Although usually all positions of metal cations in the supramolecule are fully occupied, it is nonetheless entirely conceivable that some of these metal cations are absent without harming the integrity of the core of the supramolecule in any way. Such "metal-deficient" supramolecules might be interesting as precursors for the design of mixed-metal supramolecules via subsequent saturation of vacant coordination sites with heterometals, opening a way to tailor the total charge/spin state of the supramolecule or electronic structure of the spacers. Moreover, modification by additional ligands coordinated to heterometallic sites becomes possible. Nevertheless, the general principles of achieving such metal-deficient supramolecules have not yet been developed.

During our studies of the coordination chemistry of polyphosphorus ligand complexes, such as pentaphosphaferrocene, $[Cp^RFe(\eta^5\text{-}P_5)]$ ($Cp^R = C_5(CH_2Ph)_5$ (Cp^{Bn}, **1a**), $C_5(CH_3)_5$ (Cp*, **1b**), 1,3-$C_5H_3tBu_2$ (Cp″, **1c**)), we found a way to construct various giant supramolecules reaching 4.6 nm in size via the coordination of Cu cations to P atoms of the *cyclo*-P_5 rings.[4] In a homologous family of supramolecules with the formula $[\{Cp^RFe(\eta^5\text{-}P_5)\}_{12}(CuX)_{20}]$ (**2**: Cp^R = Cp*, Cp^{Bn}; X = Cl, Br, Figure 1a), all phosphorus atoms of all *cyclo*-P_5 rings coordinate towards Cu cations, ideally forming an 80-vertex $\{Cu_{20}P_{60}\}$ core with a fullerene I_h-C_{80} topology and a pentagonal dodecahedral arrangement of Cu ions (Figure 1b). However, the comprehensive study of **1a**- and **1b**-based supramolecules in the solid state and in solution revealed that some of the {CuX} sites are statistically vacant. Therefore,

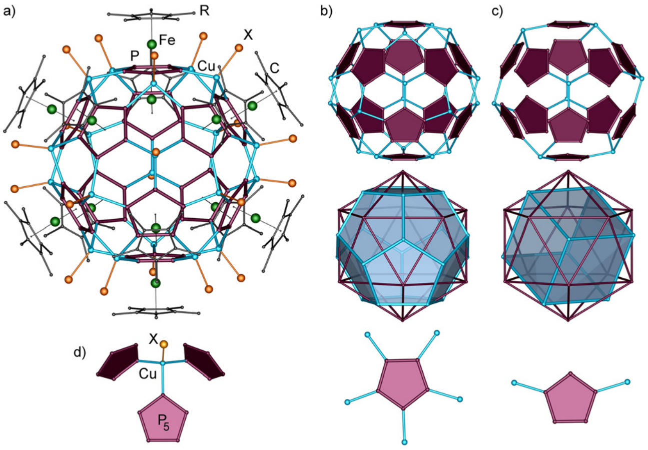

Figure 1. a) Spherical supramolecule $[\{Cp^RFe(\eta^5\text{-}P_5)\}_{12}(CuX)_{20}]$ (**2**), b) its inorganic core $\{Cu_{20}P_{60}\}$, corresponding icosahedral representation for centers of *cyclo*-P_5 units and dodecahedral for copper, and coordination mode of *cyclo*-P_5 units. c) Hypothetical 12-fold deficient $\{Cu_8P_{60}\}$ core and its respective polyhedral representation. d) Coordination environment of Cu.

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instead of an individual compound, a solid solution of various $[\{\mathbf{1a}\}_{12}(\mathrm{CuX})_{20-n}]$ *n*-vacant supramolecules with $0<n<4.8$ crystallizes in the solid state.[4f] The question arises as to how an individual compound containing a supramolecule with given *n* can be selectively obtained. Moreover, what is the maximally achievable value of metal deficiency *n*?

All $[\{\mathbf{1}\}_{12}(\mathrm{CuX})_{20-n}]$ 80-vertex supramolecules known so far are neutral due to the presence of copper-bonded halide anions X and are similar in size and shape as predefined by substituted cyclopentadienyl ligands of 12 units of **1**. Obviously, this is the reason why they readily co-crystallize. At the same time, molecular modeling of these spherical systems revealed that eight copper(I) cations is the minimum number to keep a sphere of this overall size together, if they are distributed in a cube-like arrangement (Figure 1c), leaving $20-8=12$ vacant metal sites. After numerous attempts, such a supervacant sphere was considered as unattainable in both **1a**/CuX and **1b**/CuX systems.[4b,f]

One of the possible approaches to control the formation of a Cu-deficient sphere with a given *n* is to obtain positively charged analogues of the supramolecule **2** using weakly coordinating anions (WCAs). As the stability of the ionic structure strongly depends on the mutual size and charge of the ions (function of *n* in the present case), the size of the WCA should play an important role. Firstly, every additional metal position will require an additional counter anion and, with a large WCA, different $[\{\mathbf{1}\}_{12}\mathrm{Cu}_{20\text{-}n}]^{(20-n)+}(\mathrm{WCA}^-)_{20-n}$ salts are not able to crystallize in the same structure type. In this way, an undesirable co-crystallization of salts with different *n* can be prevented. In addition, different salts are also expected to have different solubilities, which allows fractional crystallization. Secondly, the degree of metal deficiency can be controlled to a certain extent by the size of the WCA, because only a restricted number of large anions can surround multicharged cations, avoiding anion–anion repulsive interactions. Therefore, a larger WCA can afford a higher degree of metal deficiency. Following these considerations, herein we report on the synthesis of a Cu salt of a bulky WCA $[\mathrm{Al(OC_4F_9)_4}]^-$ (teflonate, TEF) with $[\mathrm{Cp''Fe}(\eta^5\text{-}\mathrm{P}_5)]$ (**1c**), allowing the isolation of the 8+ charged supramolecule $[(\mathbf{1c})_{12}\{\mathrm{CuNCMe}\}_8](\mathrm{TEF})_8$ (**3**, Figure 2b) possessing the first metal-deficient 68-vertex $\{\mathrm{Cu_8P_{60}}\}$ core with the lowest possible number of copper atoms sufficing to bind 12 *cyclo*-P_5 ligands as required by the fullerene topology.[4b,f]

The reaction of two equivalents of **1c** with three equivalents of $[\mathrm{Cu(CH_3CN)_4}][\mathrm{Al\{OC(CF_3)_3\}_4}]$ (**2**) in $\mathrm{CH_2Cl_2}$ at room temperature led to the formation of an olive-green solution. Layering the solution with *n*-pentane afforded green octahedra of $(\mathrm{CH_2Cl_2})_{1.25}@[(\mathrm{Cp''FeP_5})_{12}\{\mathrm{Cu(CH_3CN)}\}_8](\mathrm{TEF})_8$ (**3**, Scheme 1) and green plates of $[(\mathrm{Cp''FeP_5})_2\mathrm{Cu_4}(\mathrm{CH_3CN})_{10}](\mathrm{TEF})_4$ (**4**). By changing the stoichiometry of the reaction, only the ratio of **3** to **4** could be varied, with **3** always being the major product.

Surprisingly, compound **3** was formed selectively during a first unsuccessful attempt to fill the free coordination sites at the *cyclo*-P_5 units with Ni^0 units by adding $\mathrm{Ni(cod)_2}$ (cod = 1,5-cyclooctadiene) to the reaction mixture. Within a few minutes, black metallic Ni precipitated. After filtration and layering the olive-green solution with *n*-pentane, **3** could be isolated in a moderate yield with its phase purity confirmed by PXRD (Figure S12 in the Supporting Information).

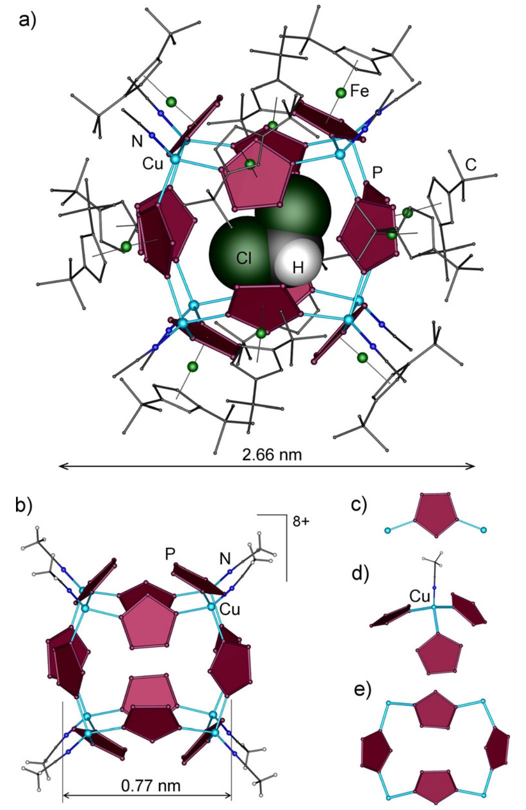
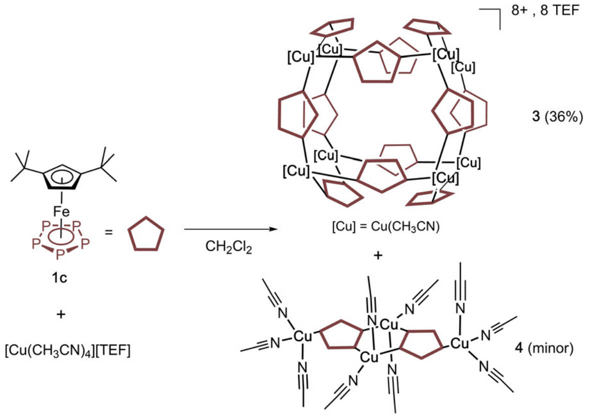


Figure 2. a) The cationic supramolecular assembly of **3**: b) the 68-vertex cube-like inorganic core, c) 1,3-coordination mode of the **1c** unit, d) coordination environment of Cu, and e) 18-membered $\{\mathrm{Cu_4P_{14}}\}$ cycle.



Scheme 1. Reaction of **1c** with $[\mathrm{Cu(CH_3CN)_4}][\mathrm{TEF}]$ (**2**) leading to **3**.

Compound **3** crystallizes as green octahedra in the trigonal space group $R\bar{3}$. Single-crystal X-ray structure analysis of **3** revealed a 68-vertex sphere $[(\mathrm{CH_2Cl_2})@[\{\mathrm{Cp''Fe}(\eta^5{:}\eta^1,\eta^1\text{-}\mathrm{P}_5)\}_{12}\mathrm{Cu}_8]^{8+}$ (Figure 2), consisting of 12 units of **1c** arranged in an icosahedron in which $\mathrm{Cu^I}$ ions systematically cap eight of the 20 available trigonal faces (Figure 1c). The remaining 12 trigonal faces furnish six 18-membered rings $\{\mathrm{Cu_4P_{14}}\}$ corresponding to a face of an underlying cube of the inorganic core (Figure 2e). Each ring edge-shares four analogous rings and carries two positions potentially available to metal coordination. Every *cyclo*-P_5 ligand coordinates to Cu in a 1,3-mode with Cu–P distances of 2.287(2)–2.314(2) Å and P-Cu-P bond angles of 99.53(8)–103.80(8)°. A spherical assembly solely composed of two-coordinated units of **1** was predicted but never observed before.[4b,f] The Cu atoms are tetrahedrally coordinated by three units of **1c** and one acetonitrile molecule (Cu–N: 1.98(1)–1.974(7) Å, Figure 2d). The twofold coordinated pentaphosphaferrocene unit allows a restricted rotation around all Cu–P coordinative bonds and thus provides some adaptability to the inorganic core. The Cu⋯Cu separation in this cube-like arrangement amounts to 7.53–7.59 Å, which points to a certain deformation of the core along one of the body diagonals.

Another feature of the inorganic core is a guest-accessible inner cavity of 0.77 nm (Figure 2). In **3**, the cavity is statistically occupied by one or two CH_2Cl_2 molecules. Therefore, guest encapsulation of small molecules appears feasible.[4f,5]

The metal-deficient supramolecule possesses an outer diameter of 2.66 nm, which is twice that of a TEF anion (1.32 nm).[6] Charge balance requirements in **3** dictate a 1:8 ratio of the supramolecule to the outersphere TEF anions. Therefore, each supramolecule is completely isolated from any contacts with neighboring supramolecules by TEF anions as well as solvent CH_2Cl_2 molecules (Figure S11 in the Supporting Information).

Notably, the formation of **3** is not accompanied by the more metal-rich $[(\mathbf{1b})_{12}\{CuNCMe\}_{8+m}]^{8+m}$ salts. It is possible that these phases with $m>0$ are less favorable because of electrostatic repulsion of $8+m$ large anions per supramolecule in the crystal.

The minor product **4** crystallizes as green plates in the triclinic space group $P\bar{1}$. In the crystal structure of $[\{Cp''Fe(\eta^5{:}\eta^1,\eta^1,\eta^1\text{-}P_5)\}_2Cu_4(CH_3CN)_{10}](TEF)_4$ (**4**) (Figure 3), tetracationic dimers are surrounded by bulky TEF anions and solvent molecules. The complexes $[(\mathbf{1c})_2Cu_4(CH_3CN)_{10}]^{4+}$ consist of two units of **1c** coordinating three copper cations in a 1,2,4-mode. Two Cu^I ions are coordinated by two units of **1c** each to give a four-membered $\{Cu_2P_4\}$ cycle with Cu−P bond lengths of 2.2592(9)–2.278(1) Å and P-Cu-P angles of 107.11(4)–108.13(4)° falling in the usual range.[7] Two acetonitrile ligands coordinate the copper ions to complete their tetrahedral environment with Cu−N bond lengths of 1.997(3)–2.019(3) Å. Two more Cu cations are coordinated to the *cyclo*-P_5 in the position 4 (Cu−P: 2.216(1)–2.224(1) Å); their coordination sphere is saturated by three acetonitrile ligands with Cu−N bond distances of 1.974(3)–2.008(3) Å (Figure 3).

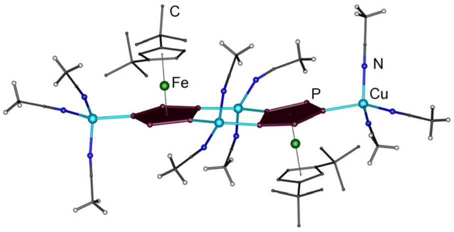


Figure 3. The molecular structure of the tetracationic dimer in **4**.

The supramolecular aggregate **3** and the by-product **4** are slightly soluble in CH_2Cl_2 and completely insoluble in other common organic solvents such as THF, toluene, and *n*-pentane. In donor solvents such as CH_3CN, **3** and **4** are well soluble at the cost of partial fragmentation. Therefore, all characterizations in solution were performed in a mixture of $CH_2Cl_2(CD_2Cl_2)/CH_3CN(CD_3CN)$. The ^1H NMR spectrum of **3** shows three singlets for the hydrogen atoms of Cp″ at 4.12 ppm (2H), 3.98 ppm (1H), and 1.18 ppm (18H). In the $^{13}C\{^1H\}$ NMR spectrum of **3**, five signals for the Cp″ ligands can be detected (31.35 ppm, 32.90 ppm, 72.37 ppm, 73.94 ppm, 111.84 ppm). The signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra are all shifted slightly to lower fields compared to the uncoordinated **1c**, which indicates a dynamic behavior of **3** in solution. The ^{31}P NMR spectrum of **3** exhibits one high-field shifted singlet at 163.2 ppm for the coordinated *cyclo*-P_5 ligand complex **1c** compared to free **1c** (168.9 ppm). The ESI mass spectra show peaks for the cationic fragments $[\{\mathbf{1c}\}_2Cu]^+$, $[\{\mathbf{1c}\}Cu(CH_3CN)]^+$, $[Cu(CH_3CN)_2]^+$, and $[Cu(CH_3CN)]^+$. Both compounds are air- and light-stable in the solid state for several days, but decompose within hours in solution when exposed to air.

In conclusion, a novel approach to metal-deficient pentaphosphaferrocene-based supramolecules was demonstrated relying on the usage of WCAs as counter anions, making it possible to control the metal deficiency of the inorganic core. In this way, the hollow supramolecule **3** was obtained based on 12 *cyclo*-P_5 rings and so far the smallest possible number (eight) of coinage metal atoms bearing labile acetonitrile ligands. These features open a way to using this promising multitasking precursor in supramolecular chemistry, which was beyond the scope of this first report about the fundamental accessibility of such metal-deficient spheres. The future perspectives are: (i) the presence of unprecedented 12 free metal sites makes it an interesting starting material for the further substitution of the supramolecule with heterometals or with metal complexes; (ii) the central cavity with a diameter of 0.77 nm, which is accessible for small molecules, allows inner functionalization; (iii) the terminal acetonitrile ligands could be substituted by various bridging N-donor ligands, opening the way to expanded networks of supramolecules. This approach will be fine-tuned in the future with respect to the nature of the corresponding Cp ligands and the coinage metals and further extended to any supramolecules having cores that are constructed from metal cations and neutral polydentate ligands.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: copper · pentaphosphaferrocene · self-assembly · supramolecular chemistry · weakly coordinating anions

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[6] The outer diameter in supramolecule **3** is calculated as the distance between H atoms of two the most separated Cp'' ligands plus twice the van der Waals radii of H (1.2 Å). The outer diameter for the TEF anion was calculated as the distance between H atoms of two the most separated F atoms (1.47 Å). The size of the void in **3** is calculated as the distance between the centroids of every individual *cyclo*-P_5 unit and the centroid of the node minus twice the van der Waals radius of P (1.8 Å) according to M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806 – 5812.

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