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

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

Abstract: An unprecedented cationic supramolecule [{(Cp*RFe(5-P5))]2(CuX)20}8+ has 2.66 nm in diameter was selectively isolated as a salt of the weakly coordinating anion [AlOC(CF3)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(5-P5))]2(CuX)20}8+. The 12 vacant metal sites between the cyclo-P5 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.

Figure 1. a) Spherical supramolecule [{(Cp*RFe(5-P5))]2(CuX)20}8+ (2), b) its inorganic core [Cu8P60]8+ corresponding icosahedral representation for centers of cyclo-P5 units and dodecahedral for copper, and coordination mode of cyclo-P5 units. c) Hypothetical 12-fold deficient [Cu6P30]6+ core and its respective polyhedral representation. d) Coordination environment of Cu.
instead of an individual compound, a solid solution of various \([\{1a\}n\{CuX\}_8]_{n-vacant}\) \(n\)-vacant supramolecules with \(0 < n < 4.8\) crystallizes in the solid state.\(^{[4i]}\) 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 \([\{1\}n\{CuX\}_8]_{n-vacant}\) 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 \([\{1\}n\{CuX\}_{80-vacant}\] (WCA) \(n\)-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 \([Al(OC_{4}F_{9})_4]\) (tellonate, TEF) with \([Cu(CH_3CN)_4][Al\{OC(CF_3)_3\}_4]\) (1c), allowing the isolation of the \(8+\) charged supramolecule \([\{1c\}_{20}\{CuNCMe\}_8][TEF]_8\) (3, Figure 2b) possessing the first metal-deficient 68-vertex \([CuP_{60}]^{-}\) core with the lowest possible number of copper atoms sufficient to bind 12 \(\text{cyclo-P}_5\) ligands as required by the fullerene topology.\(^{[4b,i]}\)

The reaction of two equivalents of 1c with three equivalents of \([Cu(CH_3CN)_2][AlOC(CF_3)_3]_2\) (2) in \(CH_2Cl_2\) at room temperature led to the formation of an olive-green solution. Layering the solution with \(n\)-pentane afforded green octahedra of \((CH_2Cl)_{12}@[Cu(CH_3CN)_2][Cu(CH_3CN)_2][TEF]_8\) (3, Scheme 1) and green plates of \([Cu(CH_3CN)_2][Cu(CH_3CN)_2][TEF]_8\) (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 \(\text{cyclo-P}_5\) units with \(N\)-units by adding \(Ni(cod)_2\) (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).

Compound 3 crystallizes as green octahedra in the trigonal space group \(R3\). Single-crystal X-ray structure analysis of 3 revealed a 68-vertex sphere \((CH_2Cl)_6@[Cu(CH_3CN)_2][Cu(CH_3CN)_2][Cu(CH_3CN)_2][TEF]_8\) (Figure 2), consisting of 12 units of 1c arranged in an icosahedron in which Cu ions systematically cap eight of the 20 available trigonal faces (Figure 1c). The remaining 12 trigonal faces furnish six 18-membered rings \([CuP_{18}]^{-}\) corresponding to a face of an
The molecular structure of the tetracationic dimer in 4.
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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 of the most separated Cp” ligands plus twice the van der Waals radius of H (1.2 Å). The outer diameter for the TEF anion was calculated as the distance between H atoms of two of 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-Pt unit and the centroid of the node minus twice the van der Waals radius of P (1.8 Å) according to M. Martina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. A 2009, 113, 5806–5812.

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