Engineering Coordination and Supramolecular Copper−Organic Networks by Aqueous Medium Self-Assembly with 1,3,5-Triaza-7-phosphaadamantane (PTA)

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ABSTRACT: The aqueous medium self-assembly reactions of copper(II) nitrate with 1,3,5-triaza-7-phosphaadamantane (PTA) as a main ligand and sodium azide or iodide as an auxiliary ligand lead to the new water-soluble Cu(I) coordination polymer $[Cu(\mu-N_3)(\mu-PTA)]_n$ (**1**) and monomer $[CuI(PTA)(PTAH)_2]I_2 \cdot H_2O$ (**2**) (PTAH = N-protonated form of PTA), with the PTA cages exhibiting the rare P,N- or the conventional P-coordination mode, respectively. Another hydrosoluble P-bound PTA derivative $[Cu(PTA)_4](NO_3) \cdot 6H_2O$ (**3**) is furnished in the absence of any auxiliary ligand. The compounds have been characterized by IR and NMR spectroscopy, elemental and single crystal X-ray diffraction analyses which feature the formation of a unique one-dimensional (1D) coordination network in **1** composed of the $\{Cu_2(\mu-N_3)_2\}$ cores and PTA spacers, as well as 1D (in **2**) and three-dimensional (3D) (in **3**) supramolecular structures built from multiple N−H···N (PTAH/PTA) and O−H···N (H_2O/PTA) H-bonds, respectively. The study broadens the still limited use of PTA as a spacer or building block for crystal engineering of metal−organic coordination and supramolecular networks, their nature being also dependent on the type of auxiliary ligand. Compound **1** represents the first example of a copper coordination polymer with PTA.

The design of novel coordination and supramolecular metal−organic networks is an intensively growing research area in crystal engineering, coordination, inorganic, and materials chemistry.[1] Among the great variety of coordination and supramolecular networks reported to date, those assembled from metal-containing building blocks and organic spacers represent the most typical examples.[1,2] Aromatic organic molecules with at least two N- and/or O-donor atoms such as various polypyridine and polycarboxylate derivatives are the most common spacers used in crystal engineering,[2] while the application of N,P-type aminophosphine spacers remains poorly explored.

The water-soluble aminophosphine 1,3,5-triaza-7-phosphaadamantane (PTA) and its derivatives have recently become important ligands in aqueous organometallic chemistry, namely, toward the preparation of new transition metal complexes and the search for their diverse applications, ranging from aqueous phase catalysis to medicinal chemistry and photochemistry.[3−5] Although a significant number of PTA complexes is known to date (structurally characterized examples approach ca. 200 hits),[6] in the vast majority of cases PTA and derivatives act exclusively as monodentate P-donor ligands, in spite of the availability of several potential N-coordination sites. Rare exceptions that have been recently discovered concern N-,[7] P,N-,[7b,8] or P,N,N-coordination modes[9] of the PTA core. Among this tiny group of compounds, the metal−organic networks where PTA acts as a spacer are limited to one-dimensional (1D) heterometallic Ru/Ag[8a] and Ru/Au[8b] chains, as well as to two-dimensional (2D) homometallic Ag[9] and Cu[8c] layers. Hence, bearing also in mind the hexagonal diamondoid-like geometry of PTA, further research on widening its application as a spacer (or building block) in crystal engineering and supramolecular chemistry appears to be a promising topic, namely, toward the synthesis of aqua-soluble organometallic materials, which constitutes a main aim of this study.

In pursuit of our general interest on the development of aqueous medium self-assembly synthetic methods[10] and their use in the synthesis of Cu[8c,11a] and Co[7c,11b] compounds with PTA and derivatives, we have recently reported[8c] a unique 2D Cu(I) coordination polymer $[Cu_2(\mu-I)_3(\mu-PTA-Me)]_n$ bearing the N-methylated PTA derivative (PTA-Me) that adopts a rare P,N-coordination. Taking into consideration that there are still no examples of Cu coordination polymers with PTA itself, the current work also aims at the extension of that study toward probing the multicoordination of PTA itself by self-assembly of copper ions in the presence of different auxiliary ligands.

Hence, we report herein the facile synthesis,[12] characterization, and structural features of three new Cu(I) compounds: (i) the 1D coordination polymer $[Cu(\mu-N_3)(\mu-PTA)]_n$ (**1**) that represents the first example of a copper compound with P,N-coordination of PTA, and (ii) the discrete monomers $[CuI(PTA)(PTAH)_2]I_2 \cdot H_2O$ (**2**) (PTAH = N-protonated form of PTA) and $[Cu(PTA)_4](NO_3) \cdot 6H_2O$ (**3**), with PTA/PTAH adopting conventional P-coordination modes, which are extended by intermolecular H-bonds to 1D and three-dimensional (3D) supramolecular assemblies, respectively. Compounds **1** and **2** have been obtained by modifying our self-assembly synthetic approach,[10a,b,f] namely, by allowing the reaction in acidic aqueous medium, at room temperature in air, of a mixture composed of copper(II) nitrate (metal source), PTA (main ligand), and sodium azide or iodide (auxiliary ligand) (Scheme 1). The type of the latter ligand appears to be a key factor that affects the coordination mode of PTA and, as a consequence, the nature of the resulting compound.

A similar synthetic procedure, but in the absence of any auxiliary ligand, leads to the known[11a] nonpolymeric $[Cu(PTAH)_4](NO_3)_5$ compound. However, if this reaction is also undertaken in acid-free medium (thus avoiding the protonation of PTA), the related PTA complex $[Cu(PTA)_4](NO_3) \cdot 6H_2O$ (**3**) is formed (Scheme 1). Hence, the systems presented herein composed of copper(II) as a metal source and PTA as a main ligand, together with easily accessible and cheap auxiliary ligands, open a new and simple single-pot procedure for engineering of diverse metal−organic assemblies in aqueous organic-solvent-free medium. The use of water as a solvent is an important feature of our systems since, in spite of the hydrosolubility of PTA, the chemistry concerning

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Scheme 1. Simplified Representation of the Aqueous Medium Self-Assembly Syntheses with Molecular Structures of Compounds 1−3 (in 1, Numbers Correspond to Extensions of a 1D Polymeric Chain), Showing Also How a Slight Modification of the Auxiliary Ligand Leads to Compounds with Diverse Coordination or Supramolecular Assemblies
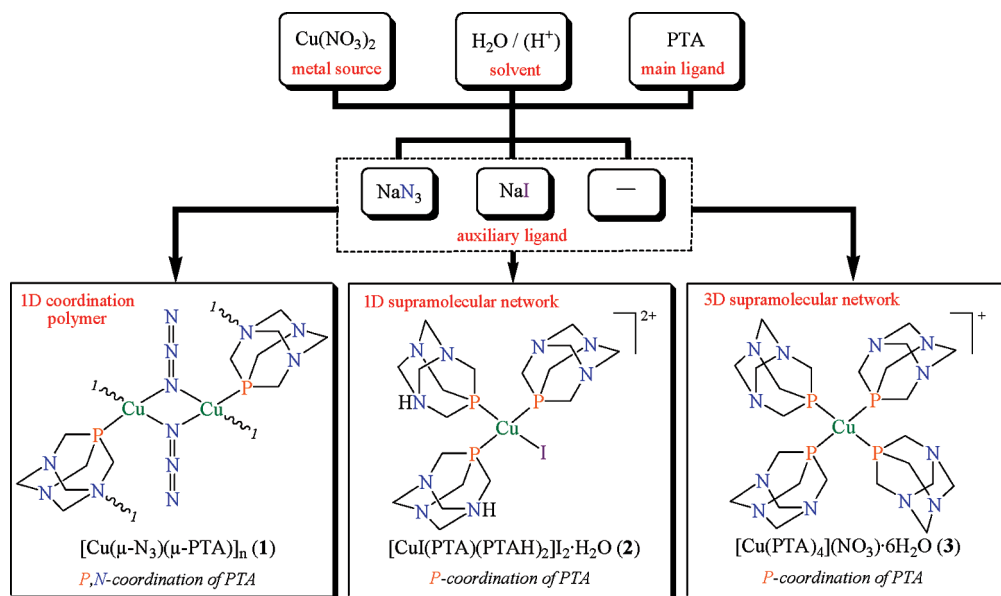
unusual coordination modes of PTA has been mostly developed in nonaqueous media.[7a,b,d,8a]

The choice of azide as an auxiliary ligand was governed by its broad coordination versatility and affinity to form coordination networks,[6] while the iodide was found to be a bridging ligand in the recently obtained $[Cu_2(\mu\text{-}I)_3(\mu\text{-}PTA\text{-}Me)]_n$ polymer[8c] and other Cu-phosphine complexes.[6] The formation of 1−3 also involves the reduction of the starting Cu(II) to Cu(I) ions, with a partial oxidation of PTA to phosphine oxide and, additionally in the case of 2, with a partial oxidation of I^- to I_2.[8c,11a] It should be noted that the simple copper(I) salts (e.g., CuCl, CuI) could not be used as starting materials under the described reaction conditions due to their almost insolubility in water. All the compounds 1−3 have been isolated in good yields as air-stable water-soluble crystalline solids. Their molecular structures have been unambiguously established by X-ray crystallography,[14] and supported by elemental analysis, IR and NMR spectroscopies.[12]

The solution ^1H NMR spectra of 1−3 show two types of methylene protons: (i) the $P\text{-}CH_2\text{-}N$ occurring as singlets at δ 4.1−4.2 and (ii) the $N\text{-}CH_2\text{-}N$ displaying an AB spin system centered at δ 4.56 in 1 and 3 (assigned to the $N\text{-}CH_{ax}\text{-}N$ and $N\text{-}CH_{eq}\text{-}N$ protons), and a broad singlet in 2. The $^{31}P\{^1H\}$ NMR spectra exhibit broad singlets at δ −85.4 and −84.4 for 1 and 2, respectively, whereas 3 shows the 1:1:1:1 quartet ($^1J_{P-Cu}$ = 761 Hz) centered at δ −78 similar to that of $[Cu(PTA)_4](NO_3)\cdot 2H_2O$.[11a] The different multiplicity signals and the shifted δ values in $^{31}P\{^1H\}$ NMR, in comparison with uncoordinated PTA/PTAH, support the preservation of the coordination environments around the Cu(I) atoms upon dissolution in D_2O (1, 3) or DMSO-d_6 (2). In general, the NMR spectra of 1−3 exhibit features typical for copper species with PTA and derived ligands.[5d,8c,11a]

The crystal structure of 1 (Figure 1a) is composed of the neutral symmetry equivalent $[Cu(\mu\text{-}N_3)(\mu\text{-}PTA)]$ units, which are held into infinite 1D double chains (Figure 2a) with the repeating period of 6.543(3) Å, equal to the *a* unit cell dimension.[14] Fragments of the crystal packing diagram of 1 showing the relative spatial arrangement of four neighboring metal-organic chains represented by different colors are displayed in Figure S1, Supporting Information. These chains bear the $\{Cu_2(\mu\text{-}N_3)_2\}$ cores and the bidentate cage-like PTA spacers that adopt alternating P- or N-coordination, thus leading to the formation of repeating 12-membered rings (i.e., A in Figure 2a). The coordination environment of each tetracoordinated Cu1 atom is filled by two μ-PTA and two μ-1,1-azide ligands,

arranged in a significantly distorted tetrahedral geometry with the bond angles [avg. 107.9(7)°] ranging from 87.31(7)° [N11−Cu1−N11^{ii}] to 128.90(5)° [P1−Cu1−N11] (hereafter all the symmetry codes are those of Figures 1 and 2). The square-like Cu1−N11−Cu1^i−N11^i fragment is planar and has the Cu1···Cu1^i and N11···N11^i separations of 3.063(2) and 2.923(2) Å, respectively. Within the $\{Cu_2(\mu\text{-}N_3)_2\}$ core, the azide moieties are essentially linear [N11−N21−N31 178.17(16)°] and adopt the "up-down" spatial orientation. PTA is bound through slightly different Cu1−P1 [2.1753(10) Å] and Cu1−N2^i [2.1455(14) Å] bonds and its cage-like geometry is almost unaffected by the unconventional P,N-coordination mode, featuring bonding parameters comparable to those reported previously for other coordination polymers with PTA spacers, that is, $[\{CpRu(PTA)_2(dmso)\}\{AgCl_2\}]_n$ (Cp = cyclopentadienyl),[8a] $[\{Cp(PTA)_2Ru\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2\}\{Au(CN)_4\}]_n$,[8b] $[Ag(PTA)(H_2O)]_n(NO_3)_n$,[9] and $[Cu_2(\mu\text{-}I)_3(\mu\text{-}PTA\text{-}Me)]_n$.[8c] Compound 1 represents the first example of a copper coordination polymer bearing PTA spacers.

In contrast to the case of 1, the structure of 2 (Figure 1b) is not polymeric and bears the discrete $[CuI(PTA)(PTAH)_2]^{2+}$ cation, two iodide anions, and one crystallization H_2O molecule per formula unit. The Cu(I) atom exhibits distorted tetrahedral coordination geometry that involves two symmetry equivalent N-monoprotonated PTAH ligands, one PTA moiety, and one terminal iodide ligand. The average bond angle around the Cu atom is ca. 107.8°, while the major deviation from the idealized tetrahedral geometry concerns the P1−Cu−I1 angle of 96.61(2)°. Both PTAH and PTA ligands exhibit the most common P-coordination mode with the Cu−P1 and Cu−P2 bond distances of 2.2259(7) and 2.2198(9) Å, respectively, which are slightly longer than the corresponding Cu1−P1 bond length in 1 (Figure 1). The Cu−I1 distance of 2.6993(9) Å is comparable to those in related compounds, that is, $[Cu_2I_2(\mu\text{-}I)_2(PTA\text{-}Me)_2]$ and $[Cu_2(\mu\text{-}I)_3(\mu\text{-}PTA\text{-}Me)]_n$.[8c] Although in 2 the cage-like PTA/PTAH moieties do not act as spacers of a coordination network, an extensive interlinkage of neighboring $[CuI(PTA)(PTAH)_2]^{2+}$ cations takes place via only one type of strong intermolecular H-bonds, thus giving rise to 1D supramolecular cationic chains running parallel to the [010] direction (Figure 2b). Hence, each protonated N13 atom of PTAH acts as an H-bond donor bridging to the N21^i atom of PTA in the neighboring unit [N13−H13···N21^i 2.77(1) Å, 176.7(1)°]. The resulting H-bonded chains feature the 16-membered centrosymmetric rings (i.e., B in Figure 2b) with the Cu···Cu separation of 9.418(2) Å. Besides, two types of voids are found in the structure of 2, which are filled
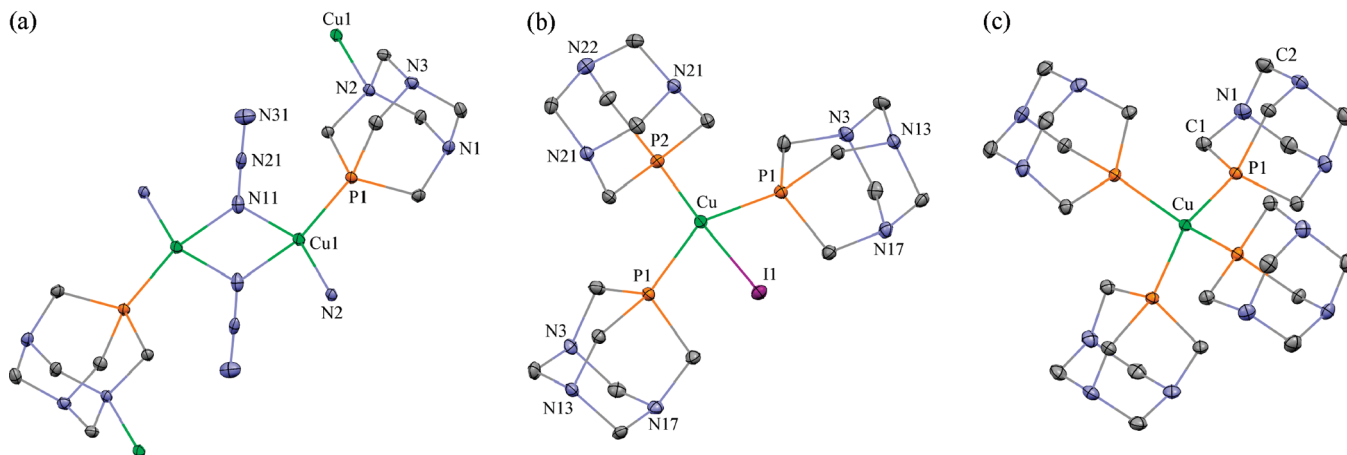
(a) (b) (c)

Figure 1. Ellipsoid plots of **1** (a), **2** (b), and **3** (c) with partial atom labeling scheme. Thermal ellipsoids are drawn at the 50% (a, b) or 10% (c) probability level. Hydrogen atoms, counterions, and crystallization water molecules are omitted for clarity. Symmetry operators were used to generate equivalent atoms. Cu green, N blue, P orange, C gray, I purple. Selected bond lengths (Å) and angles (°): **1**: Cu1−P1 2.1753(10), Cu1−N2^i 2.1455(14), Cu1−N11 2.0484(15), Cu1−N11−Cu1^{ii} 92.69(7), N11−Cu1−N2^i 104.38(6), P1−Cu1−N11 128.90(5), N11−Cu1−N11^{ii} 87.31(7), P1−Cu1−N2^i 119.24(5), P1−Cu1−N11^{ii} 112.30(5), N2^i−Cu1−N11^{ii} 95.03(6), N11−N21−N31 178.17(16) [symmetry codes: (i) $x + 1$, y, z; (ii) $-x + 2$, $-y$, $-z + 1$]; **2**: Cu−P1 2.2259(7), Cu−P2 2.2198(9), Cu−I1 2.6993(9), P1−Cu−P1^i 115.01(3), P1−Cu−P2 120.18(2), P2−Cu−I1 98.28(4), P1−Cu−I1 96.61(2) [symmetry code: (i) x, $-y + 1/2$, z]; **3**: Cu−P1 2.2581(9), P1−Cu−P1^i 109.47(7) [symmetry code: (i) $1/4 - x$, y, $1/4 - z$].
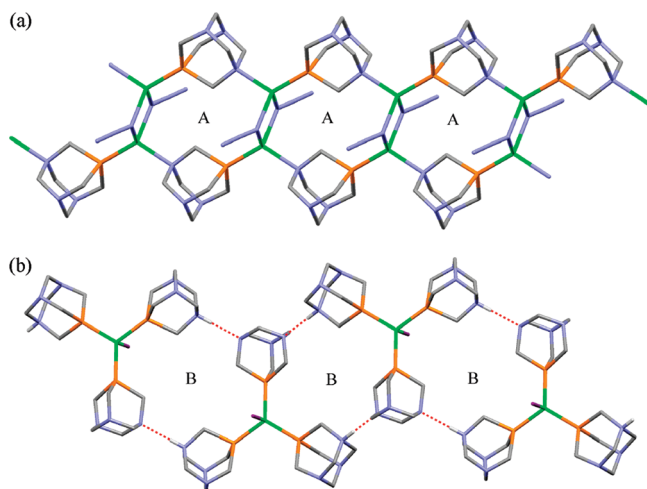
(a)

(b)

Figure 2. Fragments of the crystal packing diagrams of **1** (a, view along the [100] direction) and **2** (b, slightly rotated view along the *a* axis) showing: (a) 1D metal−organic chain composed of the {Cu$_2$(μ-N$_3$)$_2$} cores and PTA spacers; (b) 1D supramolecular chain built from the [CuI(PTA)(PTAH)]$^{2+}$ units assembled through repeating N13−H13···N21^i hydrogen bonds [2.77(1) Å, 176.7(1)°, symmetry code: (i) x, $-y + 1/2$, z] (red dotted lines). Letters A and B correspond to the equivalent 12-membered Cu-N$_3$-Cu-PTA-Cu-N$_3$-Cu-PTA (in **1**) and 16-membered Cu-PTAH-PTA-Cu-PTAH-PTA (in **2**) rings, respectively. Hydrogen atoms (except for those involved in H-bonds), counterions, and crystallization water molecules are omitted for clarity. Cu green, N blue, P orange, C gray, I purple, H pale gray.

by either iodide anions or the 1D hybrid water-iodide anionic networks {[(H$_2$O)(I)]$^-$}$_n$ (for a more detailed description, see Supporting Information, Figure S2).

The cubic crystal structure of **3** (Figure 1c) comprises the discrete [Cu(PTA)$_4$]$^+$ cation that exhibits a very high symmetry, being generated from only five symmetry nonequivalent atoms (Cu, P1, N1, C1, and C2). The four P-bound PTA ligands are arranged in a perfect tetrahedral coordination geometry. Complex **3** appears to be isostructural to the recently reported [Cu(PTA)$_4$]Cl·6H$_2$O,[13] exhibiting similar unit cell dimensions and bonding parameters, and therefore is not discussed further. One should only mention the formation of a regular 3D supramolecular network by means of
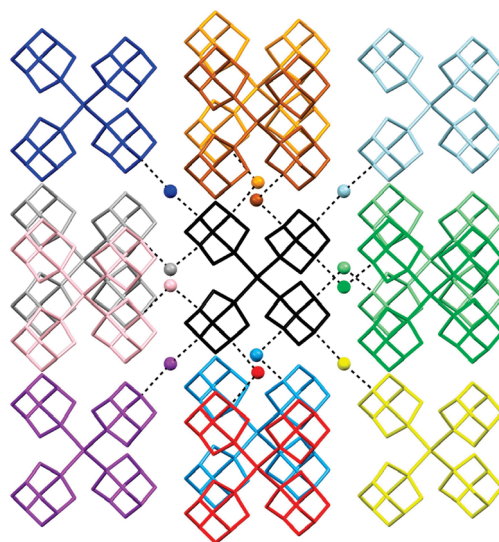
Figure 3. Partial representation of the crystal packing diagram of **3** exhibiting the three-dimensional binding of the central [Cu(PTA)$_4$]$^+$ unit (black colored) with 12 neighboring ones (each represented by a different color) via repeating OW−HW1···N1 hydrogen bonds (black dotted lines) between crystallization H$_2$O molecules (colored balls) and PTA nitrogen atoms. Hydrogen atoms and nitrate anions are omitted for clarity.

extensive equivalent O−H···N hydrogen bonds [2.92(1) Å, 167.0(1)°] between crystallization water molecules (six per formula unit) and PTA nitrogen atoms (Figures 3 and S3).

The above self-assembly syntheses took advantage of the versatile PTA coordination and H-bond modes of interaction. PTA can act (i) as a bridging P,N-ligand (spacer) to generate a coordination polymer as in **1**, or (ii) as a H-bonded building block toward supramolecular assemblies either involving its protonated form as the H-donor, that is, the PTA/PTAH pair (as in the case of **2**) or another H-donor such as H$_2$O, in the PTA/H$_2$O pair (as in the case of **3**).

The PTA interaction modes have thus a key role in determining the type of metal−organic assembly, and appear to be dependent on the number of PTA ligands. Hence, in the more open {Cu(μ-

N$_3$)(μ-PTA)} core (in **1**) with only one PTA per Cu atom, the P-coordinated PTA can N-bind to another Cu center and the auxiliary ligand (N$_3$) can also act as a bridge. In the more sterically demanding [CuI(PTA)(PTAH)$_2$]$^{2+}$ (in **2**) and [Cu(PTA)$_4$]$^+$ (in **3**) units, with three or four PTA moieties per Cu, respectively, neither PTA nor the auxiliary ligand (in **2**) can bind to another metal atom, but the H-bond ability of PTA (and of its protonated form, PTAH) drives the formation of the supramolecular assembly. PTA then acts as an intermolecular H-bonded building block, by interacting with its own protonated form (in **2**) or, in its absence, with crystallization solvent (H$_2$O) molecules (in **3**).

In summary, the present study shows that PTA can act as a convenient spacer or H-bonded building block for the design of hydrosoluble coordination and supramolecular metal−organic networks, whose syntheses can be easily accomplished by aqueous medium self-assembly. In this way, three new crystalline water-soluble Cu(I) compounds **1**−**3** (Scheme 1) were generated, their nature being also dependent on the type of used auxiliary ligand (or its absence) and on the number of PTA ligands. In the case of using sodium azide, an unprecedented 1D coordination polymer **1** with the rare P,N-coordination mode of PTA was obtained. This compound also represents the first example of a homometallic 1D coordination polymer bearing any cage-like PTA derivative. When using iodide as the auxiliary ligand or in the absence of any added such a ligand, 1D and 3D supramolecular networks are formed (in **2** and **3**) through extensive intermolecular PTA H-bonds. These features should be accounted for in further developments, namely, toward the exploration of the still rare P,N-coordination and H-bond abilities of the hexagonal diamondoid-like PTA core and its N-protonated form in aqueous medium crystal engineering.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure determinations of **1**−**3**, and Figures S1−S3 showing additional crystal packing diagrams of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Synthesis and analytical data of **1**−**3**: To an aqueous solution (5 mL) of Cu(NO$_3$)$_2$·2.5H$_2$O (23 mg, 0.10 mmol) in HNO$_3$ (0.02 M, 0.10 mmol) (the acid was added to avoid a spontaneous hydrolysis of the metal salt) was added slowly an aqueous solution (5 mL) containing PTA (63 mg, 0.40 mmol) and the auxiliary ligand [sodium azide (26 mg, 0.40 mmol) for **1**; or sodium iodide (60 mg, 0.40 mmol) for **2**] with continuous stirring in air at room temperature. After being stirred for 15 min, the resulting cloudy solution was filtered off and the filtrate was left to evaporate in a beaker at ambient temperature. Colorless crystals (including those of X-ray quality) were formed in 1−2 weeks, then collected and dried in air to give compounds **1** and **2** in ca. 70% yield, based on copper(II) nitrate. Compound **3** was obtained (ca. 60% yield) by following the above procedure for **1** and **2**, but (i) starting from a non-acidic Cu(NO$_3$)$_2$ solution and (ii) without using any auxiliary ligand. All characterization procedures of **1**−**3** were performed on the instruments and according to the techniques previously described.[7c,8c] Analytical data for **1**: compound is slightly soluble in H$_2$O ($S_{25°C} \approx$ 5 mg·mL^{-1}) and insoluble in common organic solvents. C$_6$H$_{12}$CuN$_6$P (262.7): calcd. C 27.43, N 31.99, H 4.60; found: C 27.40, N 31.87, H 4.61. IR (KBr): 2957 (w), 2932 (w) and 2916 (w) ν(CH), 2047 (vs br.) ν_{as}(N$_3$), 1469 (w), 1440 (w), 1415 (m), 1360 (w), 1324 (w), 1282 (m), 1279 (m), 1239 (s), 1103 (s), 1091 (m), 1019 (s), 969 (s), 944 (s), 891 (m), 811 (s), 793 (s), 755 (s), 723 (m), 605 (s), 574 (s), 567 (s), 459 (w) and 442 (w) cm^{-1}. ^{1}H NMR (300 MHz, D$_2$O, Me$_4$Si): δ = 4.65 and 4.57 (J(H^{A}H^B) = 15 Hz, 12H, NCH^{A}H^{B}N), 4.15 (br. s, 12H, PCH$_2$N) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, D$_2$O, 85% H$_3$PO$_4$): δ = −85.4 (br. s) ppm. Analytical data for **2**: compound is slightly soluble in H$_2$O ($S_{25°C} \approx$ 10 mg·mL^{-1}), MeOH and EtOH; well soluble in DMSO. C$_{18}$H$_{40}$CuI$_3$N$_9$OP$_3$ (935.8): calcd. C 23.10, N 13.47, H 4.31; found: 22.91, N 13.08, 4.38. IR (KBr): 3467 (s br.) + 3370 (sh) ν(H$_2$O + NH), 2938 (w) and 2900 (w) ν(CH), 1446 (m), 1403 (m), 1290 (s), 1252 (m), 1227 (s), 1111 (m), 1018 (s), 977 (s), 945 (s), 895 (s), 855 (s), 807 (m), 788 (m), 748 (s), 653 (w), 610 (s),

587 (m), 564 (s), 462 (s), 438 (m) and 414 (w) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 4.80 (br. s, 18H, NC*H*$_2$N), 4.18 (br. s, 18H, PC*H*$_2$N) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, DMSO-d_6, 85% H$_3$PO$_4$): δ = −84.4 (br. s) ppm. Analytical data for **3**: colorless crystalline solid, well soluble in H$_2$O ($S_{25°C}$ ≈ 60 mg·mL^{-1}), MeOH, EtOH, DMSO, and slightly soluble in Me$_2$CO and THF. C$_{24}$H$_{60}$CuN$_{13}$O$_9$P$_4$ (862.3): calcd. C 33.43, N 21.12, H 7.01; found: 33.52, N 22.04, H 6.65. IR and NMR data are similar to those reported for [Cu(PTA)$_4$]Cl·6H$_2$O[13] and [Cu(PTA)$_4$](NO$_3$)·2H$_2$O.[11a]

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(14) Refinement details for the X-ray crystal structure analysis: Single crystals of **1**−**3** were mounted on a glass pin and transferred to an Oxford Xcalibur PX κ geometry diffractometer. The collection and integration of crystal data were performed with *CrysAlisCCD* and *CrysAlisRED* systems.[15] The structures were solved by direct methods with SHELXS-97 and refined using SHELXL-97.[16] All H atoms (apart from water H and amino H) were placed geometrically at idealized positions with C−H distances of 0.97−0.99 Å, and with U_{iso}(H) values of 1.2U_{eq}(C). Water H atoms in **2** and **3** were found from difference Fourier map and refined isotropically with U_{iso}(H) = 1.5U_{eq}(O) with the O−H distances fixed to 0.85−0.88 Å. In **2** the iodide anion was found to be disordered over three positions and refined with site occupancies of 0.36(1), 0.37(1), and 0.27(1). In **3** the NO$_3^-$ anion is disordered over multiple positions with oxygen atom site occupancies summing up to 3 and nitrogen atom to unity. The absorption correction was executed with CrysAlisRED[15] software giving T_{min}/T_{max} of 0.751/0.816, 0.432/0.838 and 0.760/0.811 for **1**, **2**, and **3**, respectively. Crystal data for **1**: C$_6$H$_{12}$CuN$_6$P, M = 262.74, λ = 0.71073 Å (Mo-$K\alpha$), T = 100(2) K, monoclinic, space group $P2_1/n$, a = 6.543(3), b = 12.190(5), c = 12.043(5) Å, β = 105.30(4)°, V = 926.5(7) Å^3, Z = 4, D_c = 1.884 g/cm^3, F_{000} = 536, μ = 2.50 mm^{-1}, 22496 reflections collected, 6307 independent, 3414 reflections with $I > 2\sigma(I)$ (R_{int} = 0.044), *GOF* = 0.908, $R1$ = 0.035, wR_2 = 0.085. Crystal data for **2**: C$_{18}$H$_{40}$CuI$_3$N$_9$OP$_3$, M = 935.75, λ = 0.71073 Å (Mo-$K\alpha$), T = 100(2) K, monoclinic, space group $P2_1/m$, a = 6.505(2), b = 16.128(5), c = 13.913(4) Å, β = 91.58(3)°, V = 1459.1(8) Å^3, Z = 2, D_c = 2.130 g/cm^3, F_{000} = 904, μ = 4.12 mm^{-1}, 36890 reflections collected, 10273 independent, 5509 reflections with $I > 2\sigma(I)$ (R_{int} = 0.057), GOF = 0.817, $R1$ = 0.033, wR_2 = 0.056. Crystal data for **3**: C$_{24}$H$_{60}$CuN$_{13}$O$_9$P$_4$, M = 862.28, λ = 0.71073 Å (Mo-$K\alpha$), T = 220(2) K, cubic, space group $Fd3m$, a = 20.117(4) Å, V = 8141(3) Å^3, Z = 8, D_c = 1.407 g/cm^3, F_{000} = 3648, μ = 0.76 mm^{-1}, 24920 reflections collected, 854 independent, 552 reflections with $I > 2\sigma(I)$ (R_{int} = 0.038), GOF = 1.006, $R1$ = 0.042, wR_2 = 0.118.

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