Inorganic Phosphate and Arsenate within New Tetranuclear Copper and Zinc Complexes: Syntheses, Crystal Structures, Magnetic, Electrochemical, and Thermal Studies

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Supporting Information

ABSTRACT: Three, PO₄³⁻/HPO₄²⁻ and AsO₄³⁻-incorporated, new tetranuclear complexes of copper(II) and zinc(II) ions have been synthesized and fully characterized. In methanol–water, reactions of H₃cpdp (H₃cpdp = N,N'-Bis[2-carboxybenzoylmethyl]-N,N'-Bis[2-pyridylmethyl]-1,3-diaminopropan-2-ol) with copper(II) chloride in the presence of either NaOH/Na₂HPO₄·2H₂O or KOH/Na₃H₂AsO₄·7H₂O lead to the isolation of the tetranuclear complexes Na₄[Cu₄(cpdp)₂(μ₄-PO₄)](OH)₂·14H₂O (1) and K₃[Cu₄(cpdp)₂(μ₄-AsO₄)](OH)·16H₂O (2), respectively. Similarly, the reaction of H₃cpdp with zinc(II) chloride in the presence of NaOH/Na₂HPO₄·2H₂O yields a tetranuclear complex, Na₅(H₂O)₂[Zn₄(cpdp)₂(μ₄-HPO₄)]Cl₂·12½H₂O (3). All complexes are characterized by single-crystal X-ray diffraction and other analytical techniques, such as Fourier transform infrared and UV–vis spectroscopy, thermogravimetric and electrochemical studies. The solid-state molecular framework of each complex contains two monocationic [M₂(cpdp)]⁺ (M = Cu, Zn) units, which are exclusively coordinated to either phosphate/hydrogen phosphate or arsenate groups in a unique mode. All three complexes exhibit a μ₄:η¹:η¹:η¹:η¹ bridging mode of the PO₄³⁻/HPO₄²⁻/AsO₄³⁻ groups, with each bridging among four metal ions. The thermal properties of all three complexes have been investigated by thermogravimetric analysis. Low-temperature magnetic studies of complexes 1 and 2 disclose moderate antiferromagnetic interactions mediated among the copper centers through alkoxide and phosphate/arsenate bridges. Electrochemical studies of complexes 1 and 2 in dimethylformamide using cyclic voltammetry reveal the presence of a fairly assessable one-electron metal-based irreversible reduction and one quasi reversible oxidation couple.

INTRODUCTION

Polynuclear transition metal complexes have attracted interest as mimics of active sites of several biological systems and in materials chemistry, especially in the field of molecular magnetism. In this regard, the use of polyoxoanions of group 15 (P and As) in the synthesis of polynuclear metal complexes has increased significantly not only due to their biological implication, as the metal ions of this group are greatly involved in phosphate metabolism, but also due to their potential role as mediators of magnetic exchange interactions. Tetrahedrally disposed polyoxoanions of group 15 propagate ferromagnetic coupling between copper centers, as proposed by Hendrickson and co-workers. These oxo-anions, such as phosphate and arsenate, have a strong binding capability with transition metal ions. The presence of four oxygen donor sites may allow phosphate and arsenate to coordinate to as many as 12 metal ions (Scheme 1), although several different coordination modes are possible. Despite their potential binding competency, the transition metal complexes/clusters involving inorganic phosphate/hydrogen phosphate and arsenate are still sparse, mainly due to the difficulties in preparation, tendency to form layered complexes, and low crystalline properties of such reaction products. Thus, inorganic phosphate/hydrogen phosphate- and arsenate-based molecular clusters involving copper(II) and zinc(II), with attractive topologies, are very limited. A literature search also shows that some diphosphonate- and triphosphonate-based transition metal complexes featuring interesting luminescence and magnetic properties have been investigated very recently.© 2017 American Chemical Society

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Scheme 1. Maximum Possible Coordination Modes of PO₄³⁻ and AsO₄³⁻ Groups

X = P, As

Kruger and co-workers²⁰ have reported the synthesis and characterization of a μ₃-PO₄-bridged tetrancular copper(II) complex possessing a butterfly topology. Recently, synthesis, structural characterization, and evaluation of the magnetic properties of PO₄⁻ and AsO₄⁻-bridged tetrancular copper complexes of a phenol-based multidentate ligand have been carried out systematically by Schindler and co-workers.¹⁵

Gahan and co-workers²¹ have reported an octanuclear zinc cluster of carboxylate containing a multidentate ligand, which is a tetramer of dinuclear complexes, bridged by two phosphate groups and bifurcating acetic acid arms. Our recent interest has been the preparation of tetra- and hexanuclear complexes of nickel, copper, and zinc using several alkoxide and carboxylate-based multidentate ligands and their characterization and applications.²²–²⁰ These ligands consist of a flexible backbone with several carboxylate groups, which may offer extra possibilities toward the formation of frameworks with interesting topologies. Taking this into consideration, two isostructural oxo-anions, that is, phosphate and arsenate, have been investigated and the results are reported herein.

RESULTS AND DISCUSSION

Syntheses and General Characterization. The polydentate ligand H₅cdpd was prepared and characterized following our previously published procedure.²⁶ Reactions of H₅cdpd with copper(II) and zinc(II) in the presence of phosphate and arsenate salts have been systematically investigated to explore the roles of these oxo-anions in the formation and stabilization of polymeric complexes, as depicted in Scheme 2. A mixture of CuCl₂·2H₂O, H₅cdpd, and Na₃HPO₄·2H₂O in a 4:2:1 molar ratio, respectively, in the presence of NaOH, in methanol−water (4:1; v/v) was allowed to react for 1 h at room temperature. The produced blue solution was then filtered and evaporated naturally, yielding a blue tetrancular complex, Na₃[Cu₅(cdpd₂)(μ₃-PO₄)]·(OH)₂·14H₂O (1). The blue tetrancular complex K₃[Cu₅(cdpd₂)(μ₃-AsO₄)]·(OH)·16·H₂O (2) was synthesized in a similar manner except that Na₃HPO₄·2H₂O and NaOH were replaced by Na₃HAsO₄·7H₂O and KOH as reagents in the reaction. However, the pale yellow tetrancular complex Na₃[Cu₅(cdpd₂)(μ₃-PO₄)]Cl·12·H₂O (3) was formed by the reaction of ZnCl₂ with H₅cdpd and Na₃HPO₄·2H₂O in a 4:1 molar ratio, respectively, in the presence of NaOH, in methanol−water (4:1; v/v) under refluxing conditions followed by cooling of the reaction solution to room temperature. X-ray quality single crystals of 3 were obtained by slow evaporation of the light yellow filtrate.

The complexes were fully characterized by elemental analysis, Fourier transform infrared (FT-IR), UV−vis,¹³ H and¹⁵ C NMR spectroscopy, and single-crystal X-ray crystallography. Elemental analysis and single-crystal X-ray diffraction study established the compositions of complexes 1−3.

X-ray Structural Characterization of the Complexes. The molecular structures of 1−3 were determined by single-crystal X-ray crystallography. Whereas complexes 1 and 2 crystallized in an orthorhombic system and their structures were solved in the Pbn space group, complex 3 crystallized in a monoclinic system and its structure was solved in the P2₁/a space group. Crystallographic parameters of the complexes are given in Table 1. Selected interatomic distances and angles are summarized in Tables 2 and 3.

Crystal Structure of Na₃[Cu₅(cdpd₂)(μ₃-PO₄)]·(OH)₂·14H₂O (1). The structural representation, with atom connectivity, of complex 1 is depicted in Figure 1. The X-ray crystal structure of 1 consists of a neutral core complex, [NaCu₅(cdpd₂)(μ₃-PO₄)]², two Na⁺ and two OH⁻ ions as counterions, and 14 lattice water molecules. The OH⁻ ions are associated with solvent water molecules and cannot be localized properly. The core of complex 1 is composed of one sodium(I) and four copper(II) ions, two cdpd⁻⁻⁻⁻ ligands, and one μ₃-PO₄⁻⁻⁻⁻ group. Two dicopper units, [Cu₂(cdpd)⁺], in 1 are coordinated exclusively by a bridging phosphate group in a μ₃η¹η¹η¹η¹η¹η¹tetradentate manner. Both dicopper units exhibit identical coordination geometries, bond distances, and bond angles around the metal centers and the cdpd⁻⁻⁻⁻ ligand. As indicated by the values of structural indices (τ = 0.273 for Cu1 and τ = 0.038 for Cu2), Cu1 is in a highly distorted square pyramidal geometry and Cu2 is in a slightly distorted square pyramidal geometry. The basal plane of the coordination geometry around each copper center is formed by a bridging alkoxy oxygen, a tertiary amine nitrogen, a pyridyl nitrogen of cdpd3⁻, and a phosphate oxygen atom. The apical position around each copper center is occupied by a benzoate oxygen atom of cdpd⁻⁻⁻⁻.

The deviations of the copper centers from the basal planes are 0.166 (Cu1) and 0.222 Å (Cu2). The equatorial Cu−O alkoxy and axial Cu−O carbonate bond distances range from 1.924(4) to 1.932(4) Å and 2.232(4) to 2.262(4) Å, respectively. The μ₃-bridging mode of the phosphate group with four copper centers forms four Cu−O−P bonds, with an average Cu−O−P bond angle of 129.04°. The P−O bond distances and O−P−O bond angles are in the range of 1.533(4)−1.537(4) Å and 110.7(2)−112.0(2)°, respectively. The intramolecular separation between the copper centers bridged by the alkoxy oxygen atom of cdpd⁻⁻⁻⁻ is much shorter, whereas the separation between the copper centers bridged by the phosphate anion is considerably longer (3.5297(5) Å vs 5.2974(5) Å). It is interesting to note that the four copper centers in the tetrancular unit assemble at the corners of a parallelogram (Figure 2).

A substantial number of dicopper complexes bridged by organic phosphates are known in the literature.²⁹−³⁴ However, neither the dicopper nor the tetrancular complexes with...
bridging inorganic phosphate have appeared to significantly cover all aspects of interactions between the copper ion and phosphate. Thus, the $\mu_4\eta^1\eta^1\eta^1\eta^1$ binding mode of inorganic phosphate is quite exceptional, and until now, only few structurally characterized copper complexes with the $\mu_4$-PO$_4$—Cu$_4$ coordination mode are known in the literature.$^{15,20,35,36}$

Crystal Structure of $\text{K}_2[\text{Cu}_4(\text{cpdp})_2(\mu_4-\text{AsO}_4)](\text{OH})\cdot16\frac{2}{3}\text{H}_2\text{O}$ (2). The X-ray crystal structure of 2 is presented in Figure 3. Analysis of the structure reveals that the molecular core of complex 2 is isostructural to that of complex 1, with two K$^+$ ions and one OH$^-$ ion present as the counterions. This OH$^-$ ion is associated with the solvent water molecules and cannot be localized properly. Similar to 1, complex 2 is produced by the self-assembly of two dinuclear $[\text{Cu}_2(\text{cpdp})]^+$ units bridged by an arsenate group in a $\mu_4\eta^1\eta^1\eta^1\eta^1$ tetradentate manner. Calculation of the structural indices$^{27}$ indicates that the coordination geometry around the Cu1 center ($\tau = 0.007$) is square pyramidal and that around the Cu2 center ($\tau = 0.350$) is highly distorted square pyramidal. The N$_2$O$_3$ coordination environment around Cu1 and Cu2 is provided by a bridging alkoxide oxygen, a tertiary amine nitrogen, a pyridyl nitrogen of cpdp$^3^-$, an arsenate oxygen atom.
Table 1. Crystallographic Parameters for Na₃[Cu₄(cpdp)₂(μ₄-PO₄)](OH·)·14H₂O (1), K₂[Cu₄(cpdp)₂(μ₄-AsO₄)](OH·)·16²/H₂O (2), and Na(H₂O)₆[Zn₄(cpdp)₂(μ₄-HPO₄)]Cl₁·12½H₂O (3)³,⁴,⁶

| 1 | 2 | 3 |
|---|---|---|
| empirical formula | C₆₆H₸₀N₁₈O₁₅PN₅Na₄Cu₄ | C₆₆H₸₀N₁₈O₁₅AsK₅Cu₄ | C₆₆H₸₀N₁₈O₁₅Cl₁PN₅NaZn₄ |
| formula weight | 1779.525 | 1863.854 | 1825.297 |
| space group | orthorhombic | orthorhombic | monoclinic |
| a, Å | 22.9275(11) | 23.4332(6) | 32.2177(15) |
| b, Å | 10.7050(4) | 10.3864(3) | 13.3500(6) |
| c, Å | 30.4859(10) | 30.7434(9) | 39.051(2) |
| α, deg | 90 | 90 | 90 |
| β, deg | 90 | 90 | 90 |
| γ, deg | 90 | 90 | 90 |
| volume, Å³ | 7482.4(5) | 7482.5(3) | 15967.3(15) |
| Z | 4 | 4 | 8 |
| density, mg/m³ | 1.585 | 1.655 | 1.267 |
| wavelength, Å | 0.71073 | 0.71073 | 1.54184 |
| temperature, K | 100(10) | 100(10) | 100(10) |
| F(000) | 3680 | 3847 | 7544 |
| absorption coefficient, mm⁻¹ | 1.250 | 1.764 | 3.236 |
| θ range for data collection | 1.604–28.161° | 1.738–26.371° | 3.518–66.627°³ |
| reflections collected | 8197 | 7610 | 13918 |
| independent reflections | 5687 | 6826 | 10940 |
| R(Fobsd data) [1 > 2σ(I)] | 0.0726 | 0.0479 | 0.0977 |
| wR²(Fall data) | 0.1750 | 0.1321 | 0.2794 |
| goodness-of-fit on F² | 1.061 | 1.109 | 1.043 |

²wR² = [Σ[w(Fo² − Fe²)²] / Σ(Fo²)²]¹/², ³R₁ = [Σ|Fo| − |Fc|] / Σ|Fo|. ⁴The remaining two protons are most probably delocalized over the ammonium group, resulting in a μ₄-bridging of the HPO₄²⁻ unit. This is further supported by the values reported for some alkoxide-bridged di- and polynuclear zinc complexes.³⁷⁻⁴⁰

at the basal plane, and a benzoate oxygen atom of cpdp³⁻ at the apical position. The copper centers deviate from the basal plane by 0.198 Å (Cu1) and 0.158 Å (Cu2). The separation between the two copper centers within a cpdp³⁻-bridged dicopper unit is 3.5812(1) Å, which is similar to the distance found in complex 1. However, the separation between phosphate-bridged Cu–Cu found in complex 1. Similar to that observed in complex 1, the four copper centers in the core of complex 2 occupy the corners of a parallelogram (Figure 4). The average Cu–O–As bond angle is 123.79°, the As–O bond distance is 1.686(2) Å, and the O–As–O bond angles are in the range of 109.39(13)–112.56(11)°. The potassium ions in complex 2 reside in a distorted octahedral geometry surrounded by water oxygen atoms.

Careful search of the literature shows that only one structurally characterized tetranuclear copper complex with the μ₄-η¹:η¹:η¹:η¹ coordination mode of the AsO₄³⁻ ion is known.¹⁵ However, reports on some dinuclear copper(II) complexes and polyoxometallates that contain bridged arsenate or hydrogen arsenate ions with a Cu–O–As link are published in the literature.¹⁵⁻¹⁷ Hence, complex 2 represents the second example of a tetratenate copper complex with the μ₄-η¹:η¹:η¹:η¹ coordination mode of the AsO₄³⁻ group.

Crystal Structure of Na(H₂O)₆[Zn₄(cpdp)₂(μ₄-HPO₄)]Cl₁·12½H₂O (3). A representation of the molecular structure of complex 3 is presented in Figure 5. Close examination of the X-ray crystal structure reveals that the compound contains a Zn₄(cpdp)₂(μ₄-HPO₄) unit; one Na⁺, two H₂O⁺, and three Cl⁻ ions as counterions; and twelve and a half water molecules of crystallization. The core of complex 3 consists of two Zn₂(cpdp)⁺ units bridged by a HPO₄⁻⁻ ion in a μ₄-η¹:η¹:η¹:η¹ manner. Within each [Zn₂(cpdp)⁺]⁺ unit, the two zinc centers are bridged and chelated by an alkoxide oxygen of cpdp³⁻ and a —O—P—O— linkage of HPO₄²⁻. In the tetranuclear unit, four zinc centers sit at the corners of a quadrilateral feature, with edge lengths of 3.575(1), 3.195(3), 3.630(4), and 3.254(3) Å (Figure 6). The Zn1, Zn2, Zn3, and Zn4 centers assume a distorted trigonal bipyramidal geometry (Figure 6), as confirmed by the values of structural indices (τ = 0.935 for Zn1, τ = 0.528 for Zn2, τ = 0.775 for Zn3, and τ = 0.831 for Zn4).²⁷ The trigonal bipyramidal coordination environment around each zinc center is surrounded by a bridging alkoxide oxygen, a pyridyl nitrogen, and a carboxylate oxygen of cpdp³⁻ in the basal plane and a tertiary amine nitrogen of cpdp³⁻ at the apical positions. The coordination environment of the countercation, Na⁺, may be best explained by the distorted octahedral geometry, with water and carboxylate oxygen atoms. The Zn—O_alkoxide, Zn—O_carboxylate, and Zn—N_amine bond distances are comparable to the values reported for some alkoxide-bridged di- and polynuclear zinc complexes.²⁷⁻⁴⁰

To balance the total charge, three protons have to be present in the structure. However, the protons could not be located precisely from Fourier density map. This is because the basicity of the PO₄³⁻ group is much higher than that of water; most probably, one proton is located at the PO₄³⁻ unit. This is further supported by the inhomogeneous P—O bond distances. The P1—O12 bond, which is the shortest (1.427(9) Å), may be a P≡O double bond, whereas the P1—O14 and P1—O11 bonds (1.534(4) and 1.539(6) Å, respectively) may be P=O single bonds. The fourth bond, P1—O13, is much longer than the other bonds (1.603(8) Å), which supports bonding to a proton. The remaining two protons are most probably delocalized over...
Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Na₃[Cu₄(cpdp)₂(μ₃-PO₄)](OH)₂·14H₂O (1) and K₃[Cu₄(cpdp)₂(μ₃-AsO₄)](OH)₂·16H₂O (2)

| interatomic distances [Å] | 1                          | 2                          |
|--------------------------|-----------------------------|-----------------------------|
| Cu(1)—O(1)              | 1.924(4)                    | Cu(1)—O(1)                 | 1.942(3)       |
| Cu(1)—O(2)              | 2.262(4)                    | Cu(1)—O(6)                 | 1.921(2)       |
| Cu(1)—O(7)              | 1.922(4)                    | Cu(1)—O(2)                 | 2.245(3)       |
| Cu(1)—N(1)              | 2.046(5)                    | Cu(1)—N(1)                 | 2.082(3)       |
| Cu(1)—N(3)              | 1.989(4)                    | Cu(1)—N(3)                 | 2.002(3)       |
| Cu(2)—O(1)              | 1.932(4)                    | Cu(2)—O(1)                 | 1.930(3)       |
| Cu(2)—O(4)              | 2.232(4)                    | Cu(2)—O(7)                 | 1.931(2)       |
| Cu(2)—O(6)              | 1.911(4)                    | Cu(2)—O(4)                 | 2.253(3)       |
| Cu(2)—N(2)              | 2.029(5)                    | Cu(2)—N(2)                 | 2.046(3)       |
| Cu(2)—N(4)              | 1.998(5)                    | Cu(2)—N(18)                | 1.994(3)       |

| interatomic angles [deg] | 1                          | 2                          |
|--------------------------|-----------------------------|-----------------------------|
| O(1)—Cu(1)—O(2)         | 99.83(17)                   | O(1)—Cu(1)—O(2)            | 93.43(14)      |
| O(1)—Cu(1)—N(1)         | 86.29(17)                   | O(1)—Cu(1)—N(1)            | 84.64(11)      |
| O(1)—Cu(1)—N(3)         | 160.63(19)                  | O(1)—Cu(1)—N(3)            | 165.32(12)     |
| O(7)—Cu(1)—O(1)         | 92.92(16)                   | O(6)—Cu(1)—O(1)            | 98.15(11)      |
| O(7)—Cu(1)—O(2)         | 93.04(15)                   | O(6)—Cu(1)—O(2)            | 98.82(11)      |
| O(7)—Cu(1)—N(1)         | 177.02(18)                  | O(6)—Cu(1)—N(1)            | 165.76(12)     |
| O(7)—Cu(1)—N(3)         | 96.73(18)                   | O(6)—Cu(1)—N(3)            | 91.87(11)      |
| N(1)—Cu(1)—O(2)         | 89.93(17)                   | N(1)—Cu(1)—O(2)            | 94.93(12)      |
| N(1)—Cu(1)—O(2)         | 96.39(17)                   | N(3)—Cu(1)—O(2)            | 95.62(14)      |
| N(3)—Cu(1)—N(1)         | 83.21(19)                   | N(3)—Cu(1)—N(1)            | 83.09(12)      |
| O(1)—Cu(2)—O(4)         | 93.89(17)                   | O(1)—Cu(2)—O(7)            | 93.18(11)      |
| O(6)—Cu(2)—O(4)         | 102.26(17)                  | O(1)—Cu(2)—O(4)            | 100.90(11)     |
| O(6)—Cu(2)—N(2)         | 162.8(2)                    | O(1)—Cu(2)—N(2)            | 86.99(11)      |
| N(2)—Cu(2)—O(4)         | 93.44(18)                   | O(1)—Cu(2)—N(18)           | 158.09(13)     |
| N(4)—Cu(2)—O(4)         | 95.02(18)                   | O(7)—Cu(2)—O(4)            | 89.09(10)      |
| N(4)—Cu(2)—N(2)         | 83.2(2)                     | O(7)—Cu(2)—N(2)            | 179.12(12)     |
| N(4)—Cu(2)—N(2)         | 83.2(2)                     | O(7)—Cu(2)—N(18)           | 96.81(12)      |
| O(1)—Cu(2)—N(2)         | 84.08(18)                   | N(2)—Cu(2)—O(4)            | 90.03(11)      |
| O(1)—Cu(2)—N(4)         | 165.07(19)                  | N(18)—Cu(2)—O(4)           | 98.72(12)      |
| O(6)—Cu(2)—O(1)         | 96.35(16)                   | N(18)—Cu(2)—N(2)           | 83.32(12)      |

all solvent water molecules. The Zn—O—P and O—P—O bond angles are in the range of 120.9(3)—132.5(5)° and 103.0(3)—116.1(4)°, respectively. The average Zn—Zn separation within the cpdp₃⁻ bridged dizinc unit is 3.602 Å, whereas the average separation between two zinc centers across a phosphate bridge is 5.224 Å.

Here, it is noteworthy that the X-ray structure of complex 3 features one coordinated benzoate arm and one coordinated pyridyl arm at one half of the dinuclear [Zn₃] unit facing toward one coordinated pyridyl arm and one coordinated benzoate arm at the other half of the dinuclear [Zn₃] unit. Because of such a face-to-face sequential arrangement of benzoate—pyridyl—pyridyl—benzoate functionalities, moderate intramolecular π···π stacking interactions (Figure S1, Supporting Information) have been observed between the adjacent benzoate—pyridyl, pyridyl—pyridyl, and pyridyl—benzoate rings, with average closest contacts of 3.680, 3.618, and 3.709 Å, respectively.

**Structural Comparison of the Complexes 1–3.** In all three complexes, two dinuclear [M₂(cpdp)]⁺ units (M = Cu and Zn) are assembled onto bridging PO₄³⁻/HPO₄²⁻ or AsO₄³⁻ groups. In all of the complexes, the PO₄³⁻/HPO₄²⁻ or AsO₄³⁻ ions display a μ₃-η¹⁻·η¹⁻·η¹⁻·η¹⁻·η¹⁻·η¹⁻ bridging mode, connecting all four copper or zinc centers. The occurrence of such a tetradeutate bridging mode of PO₄³⁻/HPO₄²⁻/AsO₄³⁻ groups helps stabilize the molecular structures of the complexes. Among the three sodium ions present in 1, one provides the necessary factors for stabilization of the core of the complex and the other two sodium ions act as countercations. On the other hand, the sodium ion present in 3 acts only as a countercation. All copper centers in complexes 1 and 2 adopt a distorted square pyramidal geometry, whereas all zinc centers in 3 exhibit a distorted trigonal bipyramidal geometry. Whereas the four copper centers in 1 and 2 are assembled at the corners of a parallelogram, the four zinc centers in 3 are assembled at the corners of an irregular quadrilateral. Moderate intramolecular π···π stacking interactions are observed in complex 3 due to face-to-face sequential arrangement of the benzoate—pyridyl—pyridyl—benzoate functionalities, but no such kind of interactions is present in complexes 1 and 2.

On comparing the structural features of 1–3 with those in the literature reports, one can say that the μ₃-bridging mode of inorganic phosphate/hydrogen phosphate is limited to polyoxometallates and layered infinite sheets. Generally, a phosphate ion is known to be able to bind two metal centers, and such structures are of particular interest for modeling the active site of purple acid phosphatases. In contrast to the μ₃-η¹⁻·η¹⁻·η¹⁻·η¹⁻·η¹⁻·η¹⁻ bridging
Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Na(H$_3$O)$_2$[Zn$_4$(cpdp)$_2$(μ$_4$-HPO$_4$)]Cl$_3$·12½H$_2$O (3)

| interatomic distances [Å] |  |
|---------------------------|--|
| Zn(1)—O(1)               | 1.987(4) Zn(3)—N(5) | 2.241(6) |
| Zn(1)—O(2)               | 2.026(4) Zn(3)—O(6) | 2.008(10) |
| Zn(1)—N(1)               | 2.220(5) Zn(3)—N(7) | 2.120(7) |
| Zn(1)—O(11)              | 2.025(4) Zn(3)—O(7) | 1.970(8) |
| Zn(1)—N(3)               | 2.072(6) Zn(3)—O(13) | 1.978(7) |
| Zn(2)—O(1)               | 1.974(4) Zn(4)—O(14) | 1.988(5) |
| Zn(2)—O(4)               | 2.020(7) Zn(4)—N(8) | 2.144(7) |
| Zn(2)—O(12)              | 2.041(8) Zn(4)—O(6) | 2.035(10) |
| Zn(2)—N(2)               | 2.262(6) Zn(4)—O(9) | 1.960(6) |
| Zn(2)—N(4)               | 2.083(6) Zn(4)—N(6) | 2.253(6) |

| interatomic angles [deg] |  |
|--------------------------|--|
| N(3)—Zn(1)—N(1)         | 78.4(2) O(6)—Zn(3)—N(5) | 81.4(3) |
| O(1)—Zn(1)—N(3)         | 120.1(2) O(6)—Zn(3)—N(7) | 128.1(3) |
| O(1)—Zn(1)—O(11)        | 96.40(19) N(7)—Zn(3)—N(5) | 77.7(2) |
| O(1)—Zn(1)—O(2)         | 121.9(2) O(7)—Zn(3)—N(5) | 91.5(3) |
| O(1)—Zn(1)—N(1)         | 81.85(19) O(7)—Zn(3)—O(6) | 112.8(3) |
| O(11)—Zn(1)—N(3)        | 103.4(2) O(7)—Zn(3)—N(7) | 114.7(3) |
| O(11)—Zn(1)—O(2)        | 87.75(18) O(7)—Zn(3)—O(13) | 93.9(3) |
| O(11)—Zn(1)—N(1)        | 178.0(2) O(13)—Zn(3)—N(5) | 174.6(3) |
| O(2)—Zn(1)—N(3)         | 114.87(19) O(13)—Zn(3)—O(6) | 96.4(3) |
| O(2)—Zn(1)—N(1)         | 92.33(19) O(13)—Zn(3)—N(7) | 100.0(3) |
| O(1)—Zn(2)—N(2)         | 81.76(19) O(13)—Zn(4)—N(8) | 97.3(3) |
| O(1)—Zn(2)—N(4)         | 130.0(2) O(14)—Zn(4)—O(6) | 100.1(3) |
| O(1)—Zn(2)—O(4)         | 109.8(2) O(14)—Zn(4)—N(6) | 174.9(3) |
| O(1)—Zn(2)—O(12)        | 97.9(2) N(8)—Zn(4)—N(6) | 78.1(2) |
| N(4)—Zn(2)—N(2)         | 77.7(2) O(6)—Zn(4)—N(8) | 125.0(3) |
| O(4)—Zn(2)—N(2)         | 90.7(3) O(6)—Zn(4)—N(6) | 81.0(3) |
| O(4)—Zn(2)—N(4)         | 115.6(3) O(9)—Zn(4)—O(14) | 92.7(2) |
| O(4)—Zn(2)—O(12)        | 106.4(4) O(9)—Zn(4)—N(8) | 117.5(3) |
| O(12)—Zn(2)—N(2)        | 161.7(3) O(9)—Zn(4)—O(6) | 113.3(3) |
| O(12)—Zn(2)—N(4)        | 88.9(3) O(9)—Zn(4)—N(6) | 91.5(2) |

Figure 1. Molecular structure of complex 1, with the atom numbering scheme. Hydrogen atoms are omitted for clarity.
modes of $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ groups observed in various transition metal complexes, the $\mu_4:\eta^1:\eta^1$ bridging mode is less known. Again, the $\mu_4$-bridging mode of the inorganic $\text{AsO}_4^{3-}$ ion is less common, and compared with those with the $\mu_2:\eta^1$ bridging mode, only a small number of transition metal complexes containing the $\mu_4:\eta^1:\eta^1$ bridging mode are known in the literature.

**Spectroscopic Investigation of the Complexes.** In the FT-IR spectra (Figures S2–S4), the $\nu_{\text{C}=\text{N}}$ stretching frequencies are observed at $\sim 1608 \text{ cm}^{-1}$ for all three complexes, indicating the presence of pyridyl functionality of the ligand backbone. The occurrence of metal-bound carboxylate groups is manifested by the strong asymmetric
ν\textsubscript{as}(COO\textsuperscript{−}) and symmetric ν\textsubscript{s}(COO\textsuperscript{−}) vibrations at 1588 and 1378 cm\textsuperscript{−1} for 1, 1586 and 1377 cm\textsuperscript{−1} for 2, and 1592 and 1382 cm\textsuperscript{−1} for 3. The relatively higher differences of Δ (Δ = ν\textsubscript{as}(COO\textsuperscript{−}) − ν\textsubscript{s}(COO\textsuperscript{−})) of ~210, 209, and 210 cm\textsuperscript{−1} for 1, 2, and 3, respectively, are indicative of terminal binding of carboxylate groups.\textsuperscript{56} Strong bands at 1028 and 890 cm\textsuperscript{−1} for 1, 936 and 841 cm\textsuperscript{−1} for 2, and 1024 and 910 cm\textsuperscript{−1} for 3 are detected in the FT-IR spectra due to the Cu−O−P, Cu−O−As, and Zn−O−P asymmetric and symmetric stretching vibrations, respectively.\textsuperscript{57−60}

All three complexes are fairly soluble in methanol, and we carried out their spectroscopic characterization by recording electronic absorption spectra (Figures S5−S7) in the range of 200−900 nm. The broad absorption bands with maxima at 719 nm (ε, 452 M\textsuperscript{−1} cm\textsuperscript{−1}) and 716 nm (ε, 377 M\textsuperscript{−1} cm\textsuperscript{−1}) for complexes 1 and 2, respectively, correspond to d−d transitions. Intense absorption bands at 261 nm (ε, 41 484 M\textsuperscript{−1} cm\textsuperscript{−1}), 260 nm (ε, 39 524 M\textsuperscript{−1} cm\textsuperscript{−1}), and 264 nm (ε, 15 090 M\textsuperscript{−1} cm\textsuperscript{−1}) are observed for complexes 1, 2, and 3, respectively, and are due to metal ion-bound ligand-based charge-transfer transitions. The electronic absorption spectra of the complexes have been compared to those of the free ligand, H\textsubscript{3}cpdp. In methanol, the spectrum of free H\textsubscript{3}cpdp shows three highly intense absorption bands at 254 nm (ε, 218 835 M\textsuperscript{−1} cm\textsuperscript{−1})\textsuperscript{sh}, 261 nm (ε, 240 441 M\textsuperscript{−1} cm\textsuperscript{−1}), and 268 nm (ε, 182 728 M\textsuperscript{−1} cm\textsuperscript{−1})\textsuperscript{sh} in the charge-transfer region (Figure S8). Upon binding of metal ions, the bands at 254 nm (ε, 218 835 M\textsuperscript{−1} cm\textsuperscript{−1})\textsuperscript{sh} and 268 nm (ε, 182 728 M\textsuperscript{−1} cm\textsuperscript{−1})\textsuperscript{sh} disappeared.

Furthermore, to gain insight into the behavior of the complexes in aqueous solution, the UV−vis spectra of 1−3 in water (pH ~ 7.5), acidic (pH ~ 5)/alkaline (pH ~ 9) solutions, and in the solid state were recorded. The solid-state UV−vis spectra (Figures S9a, S10a, S12a, and S13a). Moreover, the bands at ~262, 260, and 261 nm in the charge-transfer region for 1, 2, and 3, respectively, in the solid state are in accordance with the bands observed in water (Figures S9b, S10b, S11, S12b, S13b, and S14). In contrast, the solid-state UV−vis spectra of 1−3 indicate minor changes in both the d−d and charge-transfer regions when compared to the spectra obtained for acidic/alkaline solutions (Figures S15 and S16). To check the stability of the complexes in water, the absorbances at 715 and 713 nm for representative complexes 1 and 2, respectively, were monitored with time for ~24 h. As shown from the absorbance versus time plots (Figures S17 and S18).
S18), there is no decay of these absorption bands. On the other hand, the absorbance versus time plots (Figures S19 and S20) obtained upon monitoring the absorbances at 715 and 713 nm for 1 and 2, respectively, in acidic/alkaline solutions with time for ~24 h show a gradual decay of these absorption bands. Hence, it can be concluded that the solid-state structures of complexes 1–3 are retained for an extended period of time only in water but not in acidic/alkaline solutions. Therefore, all three complexes are stable in water, whereas they are relatively unstable in acidic/alkaline solutions. Careful search of the literature has shown that the stability of some metal clusters has been established by electronic spectroscopy in solution.61,62

In the 1H NMR spectrum (Figure S21), complex 3 shows broad multiplets in the range of 2.72–4.53 ppm, corresponding to the 2 —CH2— and 2 >CH— protons. The presence of 32 aromatic protons has been demonstrated by broad multiplets in the range of 6.79–8.33 ppm. In the 13C NMR spectrum of complex 3 (Figure S22), one resonance peak at 176.35 ppm is observed in the downfield region due to the presence of a monodentate terminal benzoate carbon. 13C NMR signals appeared in the range of 51.81–63.72 and 122.88–157.57 ppm, corresponding to aliphatic and aromatic carbons, respectively.

Magnetic Properties. The susceptibilities of complexes 1 and 2 were investigated in the temperature range of 2–300 K under an applied magnetic field of 1 T. The χM/T versus T plots of complexes 1 and 2 are illustrated in Figures 7 and 8, respectively. The solid lines correspond to the best fitting of the curves.

Figure 7. Temperature dependence of χM/T for complex 1. The red solid line corresponds to the best fit obtained with the isotropic exchange Hamilton described in the text.

The χM/T product for complex 1 has a value of 1.17 cm^3 K mol^-1 at room temperature. This is lower than the expected value of 1.50 cm^3 K mol^-1 for four uncoupled spins with S1 = S2 = S3 = S4 = 1/2. As the temperature decreases, the χM/T product gradually decreases, reaching to a value of 0.02 cm^3 K mol^-1 at 40 K, which remains nearly constant upon further cooling. This behavior indicates the antiferromagnetic interactions among the copper centers. Two different coupling constants have been taken into account to model this susceptibility data (Scheme 3). Whereas J1 describes the interaction mediated via the alkoxide and phosphate bridges, J2 refers to the interaction mediated by only the phosphate bridge. The magnetic data were fitted satisfactorily by applying the isotropic exchange Hamilton operator $H = -2J1 \sum_i S_i \cdot S_j$. The best simulation was obtained with $J1 = -96.0$ and $J2 = -26.6$ cm^-1 and $g_{Cu} = 2.20$ (fix). The g-value was maintained fixed to avoid overparameterization, while a very small paramagnetic impurity of 6% with $S = 1/2$ was included during the simulation.

For complex 2, the $\chi_M/T$ product has a value of 1.09 cm^3 K mol^-1 at room temperature, which is lower than the expected value of 1.50 cm^3 K mol^-1 for the four uncoupled spins with $S1 = S2 = S3 = S4 = 1/2$. On lowering the temperature to 40 K, a gradual decrease in the $\chi_M/T$ value was documented, reaching to a value of 0.01 cm^3 K mol^-1, which remains nearly constant on further cooling. This behavior is indicative of antiferromagnetic interactions among the copper centers. Likewise, in complex 1, two different coupling constants have been taken into account to model the susceptibility data (Scheme 3). The interaction that occurred through alkoxide and arsenate bridges is defined as $J1$, and the interaction that occurred through only arsenate bridge is defined as $J2$. A best fit of the magnetic data was achieved by applying the isotropic exchange Hamilton operator: $H = -2J1 \sum_i S_i \cdot S_j$. The best simulation was accomplished with $J1 = -101.8$, $J2 = -18.4$ cm^-1, and $g_{Cu} = 2.089$. The magnetic results obtained for complex 2 are in very good agreement with those for complex 1.

Magnetostructural correlations between the Cu—O—Cu and Cu—O—X—O—Cu (X = P (1) and As (2)) exchange pathways and the coupling constant (J) have been established.
in \(\mu\)-alkoxide- and \(\mu\)-phosphate/arsenate-bridged dicopper and multicopper complexes showing antiferromagnetic interactions. Complexes 1 and 2 exhibit Cu—Obridging alkoxide—Cu angles of 131.87 and 135.29°, respectively, which are greater than 130°, hence, antiferromagnetic interactions having \(J\) values between −61.5 and −103.5 cm\(^{-1}\) would be expected. Furthermore, it deserves to be noted that magnetic coupling through the Cu—O—X—O—Cu (X = P (1) and As (2)) exchange pathways connecting the equatorial positions is weakly antiferromagnetic. Therefore, \(J_1\) accounts for the higher values of −96.0 and −101.8 cm\(^{-1}\) for complexes 1 and 2, respectively, containing bis(\(\mu\)-alkoxide)(\(\mu\)-phosphate) bridges between the two copper centers. The larger antiferromagnetic interaction of \(J_1\) in complex 2 is in very good agreement with the expected behavior via a larger Cu—Obridging alkoxide—Cu angle. On the other hand, \(J_2\) represents lower values of −26.6 and −18.4 cm\(^{-1}\) for complexes 1 and 2, respectively, holding only a \(\mu\)-phosphate/\(\mu\)-arsenate bridge between the two copper centers. The shorter P—O bonds (average 1.535 Å) in complex 1 compared with the As—O bonds (average 1.686 Å) in complex 2 account for a better overlap, resulting in a slightly higher value of \(J_2\).

**Electrochemical Properties.** The redox behaviors of complexes 1 and 2 were studied by cyclic voltammetry at room temperature in dimethylformamide (DMF) solutions containing 0.1 M \([n\text{-Bu}_4\text{N}][\text{PF}_6]\) as the supporting electrolyte, with a glassy carbon electrode and platinum wire as the working and auxiliary electrodes, respectively. The reduction potentials of 1 and 2 were measured for a part of the characterization of the complexes and to compare their redox chemistry with those of some of the other complexes reported in the literature. The cathodic scan of the solutions of complexes 1 and 2 within the potential window of 600 to −1600 mV, at a scan rate of 50 mV/s, showed electrochemical activity. The cyclic voltammograms of 1.0 mM solutions of complexes 1 and 2 in DMF solutions are shown in **Figure 9**. Under similar experimental conditions, cyclic voltammetry studies of the free ligand \(\text{H}_2\text{cpdp}\) revealed no electrochemical activity within the scanned potential window (Figure S23). Hence, the electrochemical waves observed in the cyclic voltammograms of the complexes can be characterized as metal-based electron transfer processes. The electrochemical properties of complexes 1 and 2 feature an irreversible one-electron reduction and one quasireversible oxidation couple. The irreversible reduction peak at −0.82 V is assigned to the \([1]^{−/2}−\) reduction couple (Figure 9a). Further scanning toward more a negative potential resulted in only the reduction of the solvent. Upon reversing the scan toward a positive potential, a quasireversible response at \(E_{1/2} = 0.467\) V and \(\Delta E_p = 0.091\) V was observed, and the response has been assigned to the \([1]^{1/2}−\) reduction couple. The cyclic voltammogram of complex 2 (Figure 9b) shows similar features to that of complex 1 but at different reduction potential values. The irreversible reduction peak at −0.93 V and the quasireversible peaks at \(E_{1/2} = 0.467\) V and \(\Delta E_p = 0.079\) V are assigned to the \([2]^{−/2}−\) and \([2]^{0/−}\) redox couples, respectively. The shift in the reduction potential values of the two similar complexes is partly attributed to the difference in the ability of the \(\mu\)-bridging anions, PO\(_4^{3−}\) and AsO\(_4^{3−}\), to influence the electrophilic nature of the copper(II) centers. The obtained reduction potential values of the complexes are comparable to that of other tetranuclear copper complexes reported in the literature.73,74

**Thermal Properties.** Thermogravimetric analyses (TGA) of the fully dried crystalline samples of the complexes were performed over a temperature range of 30–900 °C under a nitrogen atmosphere. The TGA plots of complexes 1–3 are presented in **Figures 10** and S24. For complex 1, the first weight loss of \(\sim 11.31\%\) (calcd: 11.47%) in the temperature range of 55–163 °C corresponds to the removal of 11 lattice water molecules. The residual amorphous complex is stable up to 210 °C. Then, complex 1 shows decomposition of metal-organic framework between 215 and 885 °C. In the case of complex 2, the first weight loss of \(\sim 12.68\%\) (calcd: 12.73%) in the temperature range of 57–128 °C corresponds to the loss of twelve and two-thirds lattice water molecules. The remaining substance is stable up to 200 °C, and further weight loss is observed between 210 and 815 °C due to the decomposition of the overall framework. Similarly, complex 3 shows a weight loss of \(\sim 13.59\%\) (calcd: 14.20%) in the temperature range of 33–205 °C, which is attributed to the loss of fourteen and a half water molecules. No further weight loss was observed up to 275 °C, followed by decomposition of metal-organic framework between 280 and 715 °C. Thermogravimetric analysis of the complexes indicates that complexes 1 and 2 are stable only up to \(\sim 200\) °C, whereas complex 3 is stable up to \(\sim 275\) °C. However, upon drying the crystal samples of the complexes in vacuum, 1 and 2 lose three and four water molecules of crystallization, respectively. Therefore, the thermogravimetric results agree with the compositions of 1, 2, and 3 being \(\text{Na}_3[\text{Cu}_4(\text{cpdp})_2(\text{\(\mu\)₆-PO}_4)](\text{OH})_2 \cdot 11\text{H}_2\text{O}\), \(\text{K}_2[\text{Cu}_4(\text{cpdp})_2(\text{\(\mu\)₄-AsO}_4)](\text{OH})_2 \cdot 12\text{H}_2\text{O}\), and \(\text{Na}_3[\text{H}_2\text{O}]_2[\text{Zn}_4(\text{cpdp})_2(\text{\(\mu\)₄-HPO}_4)]\text{Cl}_3 \cdot 12\text{H}_2\text{O}\), respectively, in the solid state, which is further supported by elemental analysis.
CONCLUSIONS

Three new $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ and $\text{AsO}_4^{3-}$-bridged tetranuclear complexes of copper(II) and zinc(II) with Cu$_4$($\mu_4$-$\text{PO}_4$)$_4$, Cu$_4$($\mu_4$-$\text{AsO}_4$)$_4$, and Zn$_4$($\mu_4$-$\text{HPO}_4$)$_4$ cores of the polydentate ligand H$_3$cpdp have been synthesized and fully characterized. All complexes show the $\mu_4$-$\eta^1$-$\eta^1$-$\eta^1$-$\eta^1$ coordination mode for the bridging of $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ and $\text{AsO}_4^{3-}$ ions to four metal centers. Among the complexes, 1 and 2 are rare examples of tetranuclear copper complexes showing the $\mu_4$-$\eta^1$-$\eta^1$-$\eta^1$-$\eta^1$ coordination mode of the $\text{PO}_4^{3-}$ and $\text{AsO}_4^{3-}$ groups. The presence of the $\mu_4$-coordination mode of the $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ or $\text{AsO}_4^{3-}$ ions in each complex appears to serve as a stabilizing factor for the tetranuclear Cu$_4$ and Zn$_4$ cores. Low-temperature magnetic studies of 1 and 2 reveal that $\mu$-alkoxide of cpdp$_3$- and the bridging $\text{PO}_4^{3-}$ or $\text{AsO}_4^{3-}$ ions act as moderate mediators of antiferromagnetic interactions among the copper centers. The TGA studies suggest that the decomposition temperature of the complexes range between 200 and 275 °C. Electrochemical studies of complexes 1 and 2 in DMF solution show the presence of fairly assessable metal-based irreversible one-electron reduction and one quasireversible oxidation couple. Isolation of these new tetranuclear assemblies showing the bridging potentials of phosphate and arsenate will certainly offer valuable insights into and directions toward the preparation of a variety of multinuclear transition metal complexes with fascinating topologies in the future.

EXPERIMENTAL SECTION

General Materials and Instrumentation. All reagents and chemicals were purchased commercially from Sigma-Aldrich Chemie GmbH, Germany, and Merck, India. These were reagent-grade materials and used without further purification. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 2400 CHNS/O Series II elemental analyzer. Quantitative analyses of the copper and zinc contents in the complexes were performed by iodometric titration (using Na$_2$S$_2$O$_3$) and complexometric titration (using Na$_3$H$_2$EDTA), respectively, in aqueous solution. Potentiometric titration of the ligand was carried out using a Mettler Toledo Seven Compact S220 digital ion/pH meter in aqueous solution. FT-IR spectra of the solid samples were recorded using a Perkin-Elmer L120-000A spectrometer. UV–vis spectra were recorded on a Shimadzu UV 1800 (200–900 nm) (1 cm quartz cell) spectrophotometer. $^1$H and $^{13}$C NMR spectra were obtained on a Bruker AC 400 NMR spectrometer. Mass spectra of the ligand were recorded using a Micromass Q-Tof Micro (Waters) mass spectrometer. TGA was carried out on powdered samples with a NETZSCH STA 449F3 thermal analyzer. Electrochemical measurements were made on a BAS-CV50 electroanalyzer, controlled with a Pentium III computer, with three-electrodes: a glassy carbon working electrode, a platinum wire counter electrode, and a Vycor-tipped Ag/AgNO$_3$ reference electrode. The working electrode was polished to a mirror finish on a microcloth of diamond or alumina (1.0 and 0.05 mm particles, respectively) and was cleaned electrochemically. Cyclic voltammograms were obtained at a 1.0 mM analyte concentration in DMF, using [n-Bu$_4$N][PF$_6$] as the supporting electrolyte. Data were analyzed using the software provided with this instrument. The solutions were degassed by purging with N$_2$ gas for 10 min, and a blanket of N$_2$ was maintained over the solution while making the measurements. iR compensation between the working and reference electrodes was accomplished by applying the positive feedback from the BAS-CV50 current follower. All potentials were measured at room temperature and scaled to NHE using Cp$_2$Fe/Cp$_2$Fe* (literature value of $E_{1/2}$ NHE = 0.40 V vs NHE in DMF) as an internal standard. Magnetic susceptibility data of complexes 1 and 2 were collected on powdered microcrystalline samples with a SQUID magnetometer (MPMS-7; Quantum Design) in the temperature range of 2–300 K under an applied field of 1 T. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal’s constant. The temperature-dependent magnetic contribution of the holder was determined experimentally and subtracted from the measured susceptibility data. The program phi$^2$ was used for spin Hamiltonian simulations of the data.

Preparation of Na$_3$[Cu$_4$(cpdp)$_4$($\mu_4$-$\text{PO}_4$)$_4$](OH)$_2$·14H$_2$O (1). A solution of CuCl$_2$·2H$_2$O (0.157 g, 0.92 mmol) in methanol (10 mL) was added to a solution of H$_2$cpdp (0.511 g, 0.46 mmol) and NaOH (0.055 g, 1.38 mmol) in methanol (10 mL) was added to a solution of H$_3$cpdp (1.0 mL) and NaOH (0.055 g, 1.38 mmol) in methanol (10 mL).
The reaction mixture was stirred for 1 h, resulting in a light yellow solution. Then, an aqueous solution of NaH2PO4 (0.041 g, 0.23 mmol) was added to this solution and the stirring was maintained for another 1 h. Upon complete stirring, the solution became blue. To remove any insoluble precipitate, the solution was filtered. The clear filtrate was left to evaporate at ambient temperature. Deep blue, block-shaped single crystals suitable for X-ray diffraction were obtained after 7–10 days. Yield: 0.350 g (87%). Anal. Calcld. for C62H84.33N8O27.67AsK2Cu4 {K2[Cu4(cpdp)2(μ4-AsO4)]·(C6H5)4}·2H2O, KOH, and Na2HAsO4·7H2O: C, 40.80; H, 4.74; N, 6.25; Cu, 14.33. Found: C, 40.69; H, 4.88; N, 6.31; Zn, 14.51. FT-IR (cm⁻¹): ν = 3409(b), 1608(s), 1592(s), 1567(s), 1547(s), 1486(s), 1438(s), 1382(s), 1303(s), 1271(s), 1210(s), 1158(s), 1091(s), 1024(s), 910(s), 884(s), 813(s), 762(s), 720(s), 676(s).

Preparation of Na(H3O)2[Zn4(cpdp)2(HPO4)]Cl3·12.5H2O (3). To a methanol (15 mL) solution of H3cpdp (0.511 g, 0.46 mmol) and NaOH (0.055 g, 1.38 mmol) was slowly added anhydrous ZnCl2 (0.125 g, 0.92 mmol) in methanol (10 mL) over a period of 10 min at ambient temperature. The reaction mixture was refluxed for 1 h, resulting in a light yellow solution. Then, an aqueous solution (5 mL) of NaH2PO4·2H2O (0.041 g, 0.23 mmol) was added to this solution and the reflux was continued for another 1 h. After completion of the reaction, the light yellow solution was cooled and filtered. Slow evaporation of the clear filtrate at room temperature produced light yellow block-shaped single crystals suitable for X-ray diffraction after 5–7 days. Yield: 0.338 g (79%). Anal. Calcld. for C62H84.33N8O27.67AsK2Cu4 {K2[Cu4(cpdp)2(μ4-AsO4)]·(C6H5)4}·2H2O, KOH, and Na2HAsO4·7H2O: C, 41.69; H, 4.89; N, 6.34; Cu, 13.97. FT-IR (cm⁻¹): ν = 3417(b), 1608(s), 1586(s), 1559(s), 1482(s), 1443(s), 1377(s), 1286(s), 1200(s), 1152(s), 1044(s), 1028(s), 941(s), 890(s), 857(s), 815(s), 762(s), 712(s), 675(s). UV–vis spectra (MeOH): λmax (ε, M⁻¹ cm⁻¹) = 716 (377), 260 (39 524).

Preparation of K2[Cu4(cpdp)2(μ4-AsO4)]·(C6H5)4·16/5H2O (2). This complex was prepared and crystallized following the above procedure using CuCl2·2H2O, KOH, and Na2HAsO4·7H2O. Yield: 0.340 g (81%). Anal. Calcld. for C62H84.33N8O27.67AsK2Cu4 {K2[Cu4(cpdp)2(μ4-AsO4)]·(C6H5)4}·12.5H2O: C, 41.56; H, 4.74; N, 6.25; Cu, 14.19. Found: C, 41.69; H, 4.97; N, 6.34; Cu, 13.97. FT-IR (cm⁻¹): ν = 3417(b), 1608(s), 1586(s), 1559(s), 1482(s), 1443(s), 1377(s), 1286(s), 1200(s), 1152(s), 1044(s), 1028(s), 941(s), 890(s), 857(s), 815(s), 762(s), 712(s), 675(s). UV–vis spectra (MeOH): λmax (ε, M⁻¹ cm⁻¹) = 719 (452), 261 (41 484).

X-ray Crystal Structure Determination and Refinement. Single crystals of 1 and 2 were mounted onto a diffractometer with a SuperNova, Dual, Cu at zero, Eos area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å), and the data were collected at 100 K. Similarly, crystal data for 3 were collected on a diffractometer with a SuperNova, Dual, Cu at zero, Eos area detector using graphite monochromated Cu Kα radiation (λ = 1.54184 Å). The orthorhombic space group of Pbcn for 1, orthorhombic space group of Pbcn for 2, and monoclinic space group of I2/a for 3 were determined by statistical tests. A total of 8197 data, with Miller indices hmin = −25, hmax = 28, kmin = −6, kmax = 14, lmin = −40, lmax = 16, in the range of 1.604 < θ < 28.161° for 1; 7610 data, with Miller indices hmin = −27, hmax = 29, kmin = −12, kmax = 11, lmin = −38, lmax = 25, in the range of 1.738 < θ < 26.371° for 2; and 13 918 data, with Miller indices hmin = −38, hmax = 38, kmin = −14, kmax = 15, lmin = −35, lmax = 46, in the range of 3.518 < θ < 66.625° for 3 were measured using ω oscillation frames. Absorption correction of the data was done by the multiscan method. Direct methods were employed to solve the structures with the help of SIR-97 software, and the refinement was completed by full-matrix least-squares methods on F² using the programs SHELXL80,81 and Olex2.82 A part of the structure of 3 is disordered over two positions, with a ratio of 0.75:0.25. Whereas the zinc ions and phosphate group were modeled over two positions, the cpdp⁻ ligand was not. In all three structures, some of the solvent water molecules/counterions are highly disordered over two or even three positions, which affects the quality of the single-crystal X-ray data and refining model. The difference Fourier map was used to locate the hydrogen atoms. Hydrogen atoms of the complexes were included in idealized positions (C—H, 0.96 Å) and refined as riding models. Hydrogen atoms of the solvent water molecules cannot be located precisely and were omitted.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00189.

UV–vis spectrum and CV plot of H3cpdp; FT-IR, NMR, and UV–vis spectra of 1, 2, and 3; view of intramolecular π–π stacking interactions and TGA plot of 3 (PDF) Crystallographic details for 1, 2, and 3 (CIF) (CIF) (CIF)

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Notes

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