Inorganic Chemistry

Article

Tetranuclear Copper(II) Complexes Bridged by α-D-Glucose-1-Phosphate and Incorporation of Sugar Acids through the Cu₄ Core Structural Changes

Merii Kato,[†] Ajay Kumar Sah,[†] Tomoaki Tanase,*,[†] and Masahiro Mikuriya[‡]

Department of Chemistry, Faculty of Science, Nara Women's University, Kitauoya-higashi-machi, Nara 630-8285, Japan, and Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda-shi, Hyogo 669-1337, Japan

Tetranuclear copper(II) complexes containing α-D-glucose-1-phosphate (α-D-Glc-1P), $[Cu_4(\mu\text{-}OH)\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(bpy)_4(H_2O)_2]X_3$ [X = NO₃ (**1a**), Cl (**1b**), Br (**1c**)], and $[Cu_4(\mu\text{-}OH)\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(phen)_4(H_2O)_2](NO_3)_3$ (**2**) were prepared by reacting the copper(II) salt with Na₂[α-D-Glc-1P] in the presence of diimine ancillary ligands, and the structure of **2** was characterized by X-ray crystallography to comprise four $\{Cu(phen)\}^{2+}$ fragments connected by the two sugar phosphate dianions in 1,3-O,O′ and 1,1-O μ_4-bridging fashion as well as a μ-hydroxo anion. The crystal structure of **2** involves two chemically independent complex cations in which the C_2 enantiomeric structure for the trapezoidal tetracopper(II) framework is switched according to the orientation of the α-D-glucopyranosyl moieties. Temperature-dependent magnetic susceptibility data of **1a** indicated that antiferromagnetic spin coupling is operative between the two metal ions joined by the hydroxo bridge ($J = -52$ cm⁻¹) while antiferromagnetic interaction through the Cu–O–Cu sugar phosphate bridges is weak ($J = -13$ cm⁻¹). Complex **1a** readily reacted with carboxylic acids to afford the tetranuclear copper(II) complexes, $[Cu_4\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(\mu\text{-}CA)_2(bpy)_4](NO_3)_2$ [CA = CH₃COO (**3**), o-C₆H₄(COO)(COOH) (**4**)]. Reactions with m-phenylenediacetic acid [m-C₆H₄(CH₂COOH)₂] also gave the discrete tetracopper(II) cationic complex $[Cu_4\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(\mu\text{-}m\text{-}C_6H_4(CH_2COO)(CH_2COOH))_2(bpy)_4](NO_3)_2$ (**5a**) as well as the cluster polymer formulated as $\{[Cu_4\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(\mu\text{-}m\text{-}C_6H_4(CH_2COO)_2)(bpy)_4](NO_3)_2\}_n$ (**5b**). The tetracopper structure of **1a** is converted into a symmetrical rectangular core in complexes **3**, **4**, and **5b**, where the hydroxo bridge is dissociated and, instead, two carboxylate anions bridge another pair of Cu^II ions in a 1,1-O monodentate fashion. The similar reactions were applied to incorporate sugar acids onto the tetranuclear copper(II) centers. Reactions of **1a** with δ-D-gluconolactone, D-glucuronic acid, or D-glucaric acid in dimethylformamide resulted in the formation of discrete tetracopper complexes with sugar acids, $[Cu_4\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(\mu\text{-}SA)_2(bpy)_4](NO_3)_2$ [SA = D-gluconate (**6**), D-glucuronate (**7**), D-glucarateH (**8a**)]. The structures of **6** and **7** were determined by X-ray crystallography to be almost identical with that of **3** with additional chelating coordination of the C-2 hydroxyl group of D-gluconate moieties (**6**) or the C-5 cyclic O atom of D-glucuronate units (**7**). Those with D-glucaric acid and D-lactobionic acid afforded chiral one-dimensional polymers, $\{[Cu_4\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(\mu\text{-}D\text{-}glucarate)(bpy)_4](NO_3)_2\}_n$ (**8b**) and $\{[Cu_4\{\mu\text{-}(\alpha\text{-}D\text{-}Glc\text{-}1P)\}_2(\mu\text{-}D\text{-}lactobionate)(bpy)_4(H_2O)_2](NO_3)_3\}_n$ (**9**), respectively, in which the D-Glc-1P-bridged tetracopper(II) units are connected by sugar acid moieties through the C-1 and C-6 carboxylate O atoms in **8b** and the C-1 carboxylate and C-6 alkoxy O atoms of the gluconate chain in **9**. When complex **7** containing D-glucuronate moieties was heated in water, the mononuclear copper(II) complex with 2-dihydroxy malonate, $[Cu(\mu\text{-}O_2CC(OH)_2CO_2)(bpy)]$ (**10**), and the dicopper(II) complex with oxalate, $[Cu_2(\mu\text{-}C_2O_4)(bpy)_2(H_2O)_2](NO_3)_2$ (**11**), were obtained as a result of oxidative degradation of the carbohydrates through C–C bond cleavage reactions.

Introduction

Carbohydrates are the most widely distributed naturally occurring compounds and are indispensable to living organ-isms as an energy source and building blocks. In a variety of biological events, interactions of metal ions with carbo-hydrates have been elucidated to be involved as key steps,[1] indicating the potential importance of bioinorganic chemistry with carbohydrates. In the development of their detailed molecular chemistry with metal ions, many difficulties have been encountered owing to the complicated stereostructures

* To whom correspondence should be addressed. E-mail: tanase@ cc.nara-wu.ac.jp.
    † Nara Women's University.
    ‡ Kwansei Gakuin University.

related with many isomers and their low affinity to metal ions through polyhydroxy groups under neutral conditions as well as hygroscopic nature in purification and isolation processes. From these reasons, the functional-group-tethered carbohydrate-derived ligands (amino, imino, and Schiff's base-type substituents on the C-1 position, phosphino pendants on hydroxy groups, etc.)[2-4] were prepared and used for isolation of the metal complexes with sugars; otherwise, strong basic conditions were applied to generate deprotonated hydroxo groups, which have a strong affinity to hard metal ions, occasionally leading to successful isolation of specific and interesting structures[5] but mostly resulting in polymeric uncharacterized compounds. In contrast, biological processes use the tagging system by phosphate groups in anchoring, orienting, and activating carbohydrates in stereospecific manners. In metabolism and biosyntheses of carbohydrates, sugar phosphate esters are known to play crucial roles as intermediate compounds in regulating biosystems.[6] Many

enzymes, which promote transformations of sugar phosphates, have been revealed to require metal ions with their functions; examples are fructose-1,6-bisphosphatase (dinuclear Mg^{II}, Mn^{II}, Co^{II}, and Zn^{II}),[7] phosphomannose isomerase (Zn^{II}),[8] phosphoglucose isomerase (Fe^{II}),[9] phosphoglucomutase (Mg^{II}),[10] and ribulose bisphosphate carboxylase (Mg^{II}, Mn^{II}, and Ca^{II}),[11] and so on.[12] In this regard, studies on the interaction of sugar phosphate esters with metal ions are of significant importance; however, no structurally characterized transition-metal complex has been reported thus far, except some structures of their alkali- and alkaline-earth-metal salts.[13]

In the present study, we utilized α-D-glucose-1-phosphate (α-D-Glc-1P) because it acts as a critical intermediate in the first step of glycolysis and glycogen synthesis and have prepared and characterized discrete tetranuclear copper(II) complexes bridged by α-D-Glc-1P with the help of diimine ligands $[Cu_4(\mu\text{-OH})\{\mu\text{-}(\alpha\text{-D-Glc-1P})\}_2(L)_4(H_2O)_2]^{3+}$ [L = bpy (**1**), phen (**2**)]. Furthermore, complex **1** was found to readily react with carboxylic acids, leading to the stable tetracopper(II) complexes $[Cu_4\{\mu\text{-}(\alpha\text{-D-Glc-1P})\}_2(\mu\text{-RCOO})_2(bpy)_4]^{2+}$, through the Cu_4 core structural changes. A similar reaction has been applied to accommodate sugar acids and successfully resulted in isolation of the discrete tetracopper complexes bridged by α-D-Glc-1P and sugar acids $[Cu_4\{\mu\text{-}(\alpha\text{-D-Glc-1P})\}_2(\mu\text{-SA})_2(bpy)_4]^{2+}$ [SA = D-gluconate (**6**), D-glucuronate (**7**), D-glucarateH (**8a**)] and, in addition, one-

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dimensional chiral coordination polymers in which the α-D-Glc-1P-bridged tetracopper(II) units are connected by D-glucarate (**8b**) and D-lactobionate (**9**). Sugar acids, possessing carboxylic functional substituents as well as polyhydroxy groups, play important roles in carbohydrate metabolism and are widely occurring as biological constituents in plant cell walls, glycosaminoglycans in mammalian tissues, and microbial polysaccharides.[14] They have also attracted practical attention as sequestering agents in relation to environmental and toxicological problems[15] and as potential candidates of renewable starting materials for biodegradable and green industrial products.[16] In these regard, the present accumulation of sugar acids as well as sugar phosphates onto the tetracopper(II) complexes could provide molecular-based fundamental information and methodology for green industrial materials with renewable carbohydrates.

We report herein full details of the synthesis and characterization for D-Glc-1P-bridged tetranuclear copper(II) complexes [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(L)$_4$(H$_2$O)$_2$]$^{3+}$ [L = bpy (**1**), phen (**2**)] and its Cu$_4$ core transformation through incorporation of a series of sugar acids to provide sugar-coated tetracupric complexes and their one-dimensional chiral coordination polymers. Part of the preliminary results have already been communicated.[17]

Results and Discussion

Tetranuclear Copper(II) Complexes with α-d-Glc-1P, [Cu$_4$(μ-OH){μ-(α-d-Glc-1P)}$_2$(L)$_4$(H$_2$O)$_2$]$^{3+}$ [L = bpy (1), phen (2)]. When cupric salts, CuX$_2 \cdot n$H$_2$O (X = NO$_3$, Cl, Br), were reacted in water with Na$_2$[α-D-Glc-1P] in the presence of bpy (2,2′-bipyridyl), tetranuclear copper(II) complexes with the sugar phosphate anions [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(bpy)$_4$(H$_2$O)$_2$]X$_3$ [X = NO$_3$ (**1a**), Cl (**1b**), Br (**1c**)] were isolated in good yields (35−63%). A similar reaction by using Cu(NO$_3$)$_2 \cdot$3H$_2$O and phen (1,10-phenanthroline) also afforded the analogous tetracopper(II) complex formulated as [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(phen)$_4$(H$_2$O)$_2$](NO$_3$)$_3$ (**2**) in a crystalline form. The UV−vis and circular dichroism (CD) spectral similarity of **1a**−**c** implied that the counteranions were not bound to the metal centers (Figure 1). In the electrospray ionization mass spectrometry (ESI-MS) spectra for methanolic solutions of **1a**−**c** and **2**, divalent parent peaks corresponding to {Cu$_4$(α-D-Glc-1P)$_2$(L)$_4$ − 2H}$^{2+}$ were observed in agreement with the simulated peak
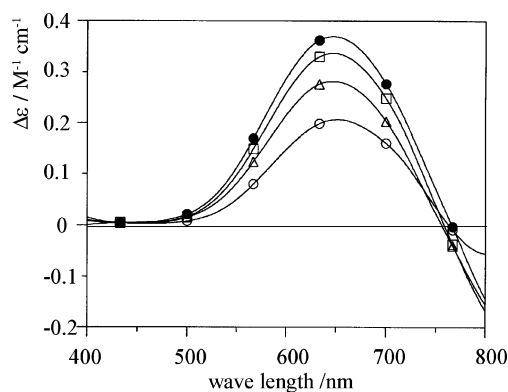
Figure 1. CD spectra of **1a** (black circle), **1b** (triangle), **1c** (square), and **2** (circle) in methanol.
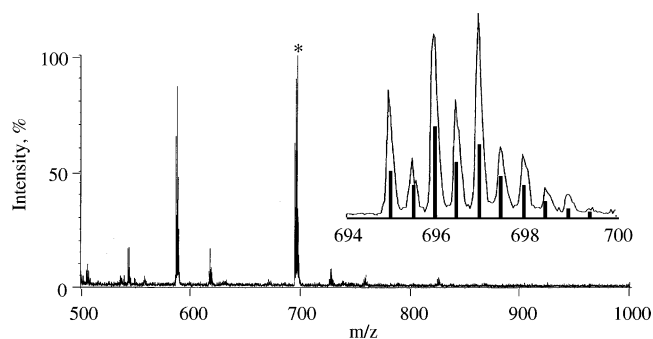

Figure 2. ESI-MS spectrum for a methanolic solution of **1a** with an inset view for the observed and calculated peaks corresponding to the dication of {Cu$_4$(α-D-Glc-1P)$_2$(bpy)$_4$ − 2H}$^{2+}$.

patterns (Figure 2). These spectral features suggested that the tetranuclear structures of **1a**−**c** and **2** are analogous to each other; the detailed structures of **2** as well as **1c** were determined by X-ray crystallography.

Perspective drawings for the complex cations of **2** with the atomic numbering scheme are illustrated in Figure 3, and selected bond distances and angles are listed in Table S3 (Supporting Information). The asymmetric unit contains 2 independent complex cations, abbreviated as cations **A** and **B**, 6 nitrate counteranions, and 30 solvent water molecules. Both of the cations consist of tetranuclear copper(II) ions bridged by two phosphate groups of α-D-Glc-1P dianions and a hydroxo group together with auxiliary four phen and two water molecules. The four Cu^{II} ions are arranged in a trapezoidal framework with a pseudo-C_2 axis passing through the μ-hydroxo O atom. The upper two Cu ions are clipped by the hydroxo O atom with average Cu−O = 1.928 Å and average Cu−O−Cu = 119.6 ° and are separated at 3.2537-(8) Å (Cu1···Cu2) and 3.4091(8) Å (Cu5···Cu6). The distinct Cu···Cu distances of cations **A** and **B** may result from different orientations of the α-D-glucopyranosyl moieties as described later. The two basal Cu atoms are 4.2577(8) Å (Cu3···Cu4) and 4.2341(8) Å (Cu7···Cu8) apart with double bridges of the phosphate anions in a 1,3-O,O′ mode. The pairs of upper and basal Cu atoms [3.4243(8)−3.6687(9) Å; average 3.5612 Å) are also doubly bridged by the phosphate anions in 1,3-O,O′ and 1,1-O fashion. The monoatom-bridging O atom of the phosphate group is bound to the upper Cu atom at its apical site and to the basal Cu atom at an

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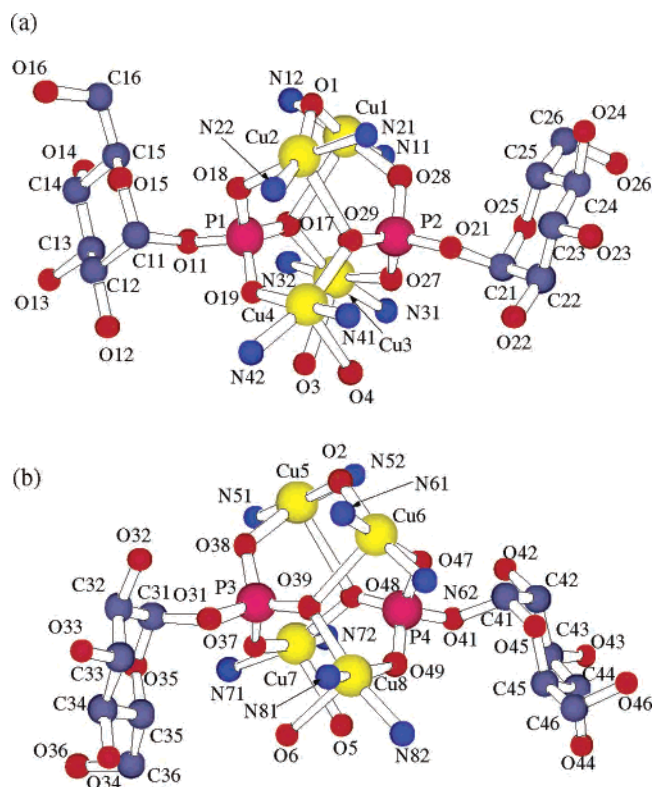
Figure 3. Perspective drawings for the complex cations of **2**: (a) cation **A**; (b) cation **B**. The C atoms of the phen ligands are omitted for clarity. Color code: Cu, yellow; P, violet; O, red; N, blue; C, gray.

equatorial site (average Cu−O−Cu = 105.1°). Consequently, the phosphate group of the α-D-Glc-1P dianion connects three Cu atoms at equatorial sites and additionally attaches to the fourth Cu atom at its axial site with one 1,1-O monoatom-bridging and four 1,3-OPO′ triatom-bridging structures, acting as an efficient supporting ligand to form the tetra-copper core (Chart 1). This type of bridging structure of phosphate monoesters is extremely scarce, merely involved only in the pentanuclear molybdenum complex [Mo₅O₁₅-(HAMP)₂]²⁻ (AMP = adenosine-5′-monophosphate),[18] and, further, the examples in which a phosphate monoester bridged three metal centers in three 1,3-O,O′ bridging ways are also limited.[19−24] The {Cu₄(μ-OH)(μ-PO₄)₂(phen)₄(H₂O)₂} core structures of cations **A** and **B** are chemically similar and approximately enantiomeric to each other in relation to the pseudo-C_2 symmetry mentioned above. In contrast, the orientations of the D-glucose moieties are entirely different; in cation **A**, the C-6 hydroxymethyl parts of the D-glucose moieties are directed upward, near the hydroxo bridge, and in cation **B**, those parts are directed downward, far from the
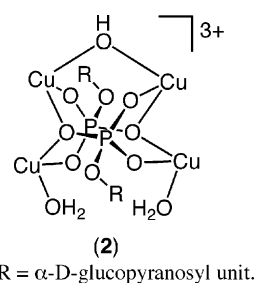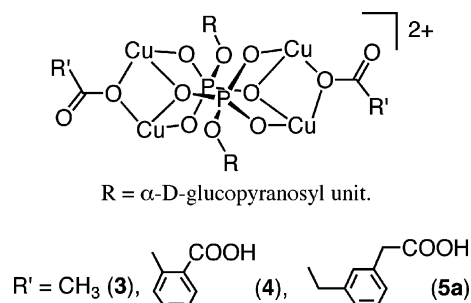
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Chart 1

(2)

R = α-D-glucopyranosyl unit.

Chart 2

R = α-D-glucopyranosyl unit.

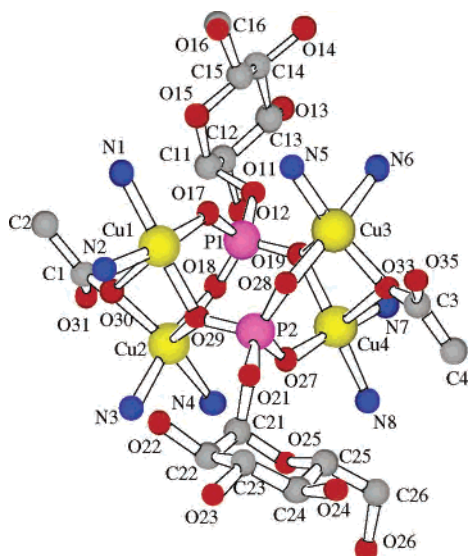R' = CH₃ **(3)**, [o-COOH structure] **(4)**, [m-COOH structure] **(5a)**

hydroxo unit. These structures implied that the sugar residues are easily rotated around the α anomeric C−O and P−O single bonds depending on the C_2 configurational switch of the tetracopper cluster core.

Complex **1c** was also characterized by X-ray crystal-lography on a block-shaped crystal of **1c·7H₂O** to involve the tetracopper cations **A** and **B** similar to those in **2** (see Figure S12 in the Supporting Information). The crystal-lographic data are deposited as a CIF file. A detailed structural discussion is not performed because the crystal-lographic analysis is somewhat low grade as a result of the seriously disordered structures of bromide anions and sol-vated water molecules.

Tetranuclear Copper(II) Complexes with α-D-Glc-1P and Carboxylic Acids. The hydroxo-bridged dicopper(II) unit involved in complexes **1** and **2** is regarded as an important functional bioinorganic motif, and some attempts to react complex **1a** with hydrogen peroxide were made in relation to oxidase/oxygenase activities of some copper-containing metalloproteins. Although no specific oxidation of the sugar phosphate was observed, the hydroxo group was easily protonated to be dissociated from the metal centers, which could further be utilized to introduce organic car-boxylate groups into the sugar phosphate bridged tetracopper-(II) framework. Treatments of **1a** with an excess amount of acetic acid, *o*-pthalic acid, or *m*-phenylenediacetic acid in dimethylformamide (DMF) at room temperature afforded the carboxylate-bridged tetracopper(II) complexes [Cu₄{μ-(α-D-Glc-1P)}₂(μ-CA)₂(bpy)₄](NO₃)₂ [CA = CH₃COO (**3**), *o*-C₆H₄(COO)(COOH) (**4**), *m*-C₆H₄(CH₂COO)(CH₂COOH) (**5a**)] in moderate yields (10−43%; Chart 2).

The structures of **3** and **4** were determined by X-ray crystallography. A perspective drawing for the cluster core of complex **3** is illustrated in Figure 4, and selected bond lengths and angles are listed in Table S4 (see the Supporting

Figure 4. Perspective drawing for the complex cation of **3**; Cu (yellow), P (violet), O (red), N (blue), and C (gray). The carbon atoms of bpy ligands are omitted for clarity.

Information). The phosphate-bridged trapezoidal tetracopper structure of **1a** was converted into a symmetrical rectangular framework, in which the hydroxo group disappeared and, instead, two acetate anions bridge another pair of Cu ions with 1,1-O monoatom-bridging fashion [Cu1−O30−Cu2 = 100.2(3)°, Cu3−O33−Cu4 = 99.2(3)°]. The four {Cu^{II}(bpy)} fragments are bridged by two α-D-Glc-1P dianions and two acetate anions, and each Cu^{II} ion adopts [N₂O₃] square-pyramidal geometry. The {Cu₄(μ-PO₄)₂(μ-CH₃COO)₂(bpy)₄} core essentially possesses C_i symmetry, where the Cu pairs, (Cu1, Cu4) and (Cu2, Cu3), are mutually related with a pseudocentrosymmetry, whereas the actual introduction of α-D-glucopyranosyl residues onto the phosphate units reduced its symmetry to C_1. The sugar phosphate anion connects the four metal ions with four 1,3-O,O′ and one 1,1-O bridging structures in a mode similar to that observed in complex **2**, resulting in a symmetrical ring-fused system containing four eight-membered {CuOPOCuOPO} and two six-membered {CuOPOCuO} metallomacrocyclic rings. The basal coordination planes around the Cu1 and Cu4 atoms are comprised of two N atoms of bpy (average Cu−N = 1.998 Å), one phosphate O atom involved in the 1,3-OPO bridge [Cu1−O17 = 1.915(7) Å; Cu4−O27 = 1.915(7) Å], and the monoatom-bridging phosphate O atom [Cu1−O29 = 1.947(5) Å; Cu4−O19 = 1.960(5) Å]. The apical site is occupied by the monoatom-bridging carboxylate O atom with Cu1−O30 = 2.364(8) Å and Cu4−O33 = 2.291(8) Å. The Cu2 and Cu3 atoms are surrounded by two imino N atoms (average Cu−N = 1.989 Å), a 1,3-O,O′ bridging O atom [Cu2−O18 = 1.931(6) Å; Cu3−O28 = 1.928(7) Å], and the carboxylate O atom [Cu2−O30 = 1.979(6) Å; Cu3−O33 = 1.973(5) Å], forming the basal plane, and the monoatom-bridging phosphate O atom is bound to the axial position of the Cu center [Cu2−O29 = 2.519(9) Å; Cu3−O19 = 2.352(8) Å]. The [Cu1O29Cu2O30] and [Cu3O19Cu4O33] four atoms are arranged in a parallelogram, slightly bending toward a butterfly form with

Chart 3

(5b)
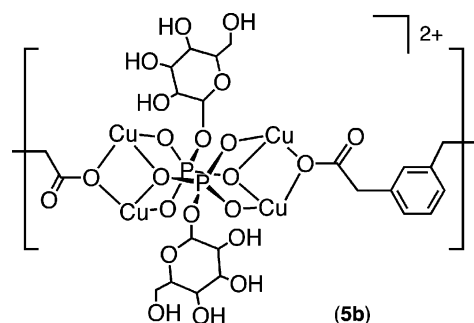
respect to the O$_b$O$_c$ axis; average O$_b$−Cu−O$_c$ = 77.9°, average Cu−O$_b$−Cu = 96.8°, and average Cu−O$_c$−Cu = 99.7° (Table S5 in the Supporting Information). In the structure of **3**, intramolecular π−π stacking interaction between the bpy ligands is not appreciable, unlike the structures observed in **2** (see Figure S2 in the Supporting Information).

The structure of **4** with *o*-pthalic acid is analogous to that of **3**, consisting of four {Cu(bpy)}²⁺ units bridged by two α-D-Glc-1P anions and two single-deprotonated *o*-pthalic acid ligands, *o*-C₆H₄(COO)(COOH). The structural parameters for **4** are summarized in Table S5 (in the Supporting Information), and an ORTEP diagram for the complex cation is deposited as Supporting Information (Figure S3). The carboxylate O atom bridges two Cu ions in a 1,1-η^1,η^1 fashion, and the other carboxylic group is H-bonded to a solvent methanol. The phenyl ring of the acid is oriented so as to develop an intramolecular π−π stacking interaction with the neighboring bpy ligand on the Cu$_a$ atom (see the schematic structure in Table S5 in the Supporting Information).

When complex **1a** was treated with a regulated amount of *m*-phenylenediacetic acid (1:1) in DMF, a one-dimensional coordination polymer formulated as {[Cu₄{μ-(α-D-Glc-1P)}₂-(μ-*m*-C₆H₄(CH₂COO)₂)(bpy)₄](NO₃)₂}$_n$ (**5b**; Chart 3) was isolated as single crystals suitable for X-ray crystallography (Figure 5 and Table S5 in the Supporting Information). In the crystal structure of **5b**, the α-D-Glc-1P-bridged tetracopper(II) units, {Cu₄{μ-(α-D-Glc-1P)}₂(bpy)₄}⁴⁺, are linked by *m*-phenylenediacetate dianions to form the one-dimensional cluster polymer, as shown in Figure 5a. The two terminal carboxylate groups of the *m*-C₆H₄(CH₂COO)₂ linker act as 1,1-O monatomic bridges to complete the rectangular Cu₄ structure similar to those of **3** and **4** (Figure 5b). The dicationic polymer units [Cu₄{μ-(α-D-Glc-1P)}₂-(μ-*m*-C₆H₄(CH₂COO)₂)(bpy)₄]²⁺ are linearly repeated with a unit length of 13.84 Å, and the linear orientation is further supported by the characteristic π−π stacking interaction between the phenyl ring of *m*-phenylenediacetate and both of the neighboring pyridyl rings of bpy ligands, as indicated in Figure 5a.

Magnetic Properties of Complexes 1a, 3, and 5b. Among the trapezoidal tetracopper complexes of **1a**−**c** and **2**, an appropriate amount of a pure crystalline sample for magnetic measurements was obtained only for complex **1a** because of their hygroscopic nature. The temperature-
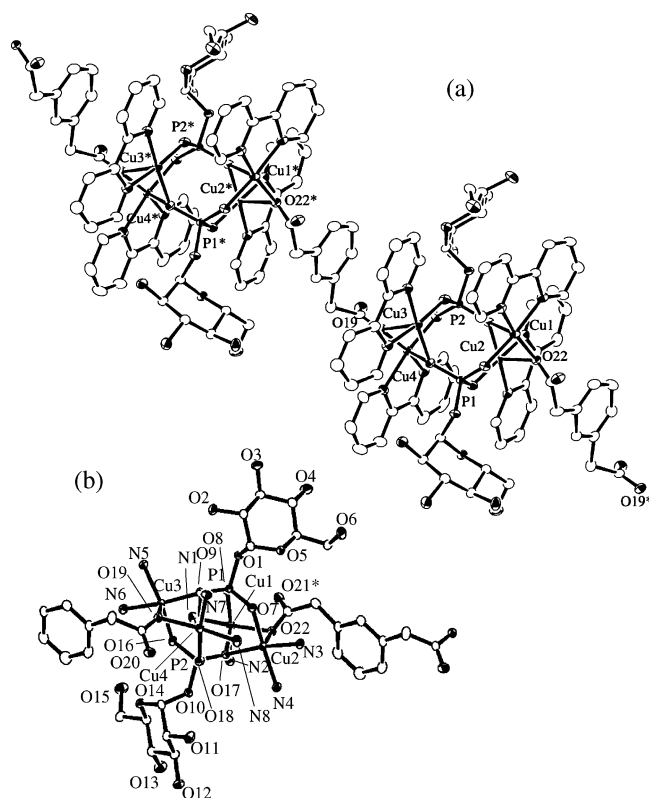
Figure 5. ORTEP plots for (a) the polymeric structure of **5b** and (b) its Cu₄ core structure, with the C atoms of the bpy ligands omitted for clarity.
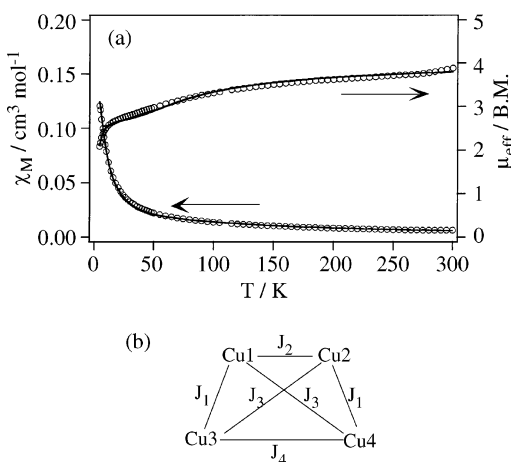
Figure 6. Plots of χ_M and μ_{eff} vs T for **1a** with the fitted lines (a) and scheme of the simplified spin-exchange coupling parameters (b).

dependent magnetic susceptibility data for **1a** are displayed as plots of χ_M and μ_{eff} vs T over the range of 4.5−300 K (Figure 6a). The curves revealed that the magnetism of the tetranuclear complex is reduced by an antiferromagnetic interaction; the room-temperature value of μ_{eff} per Cu₄ is 3.88 μ_B (300 K), which decreases with a lowering of the temperature to reach the value of 2.08 μ_B (4.5 K). Considering an idealized C_2-symmetrical structure of **1a**, the four exchange parameters, J_1-J_4 (Figure 6b), were introduced to simplify the Heisenberg spin-exchange Hamiltonian to $\mathbf{H} = -2J_1(\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4) - 2J_2\mathbf{S}_1 \cdot \mathbf{S}_2 - 2J_3(\mathbf{S}_1 \cdot \mathbf{S}_4 + \mathbf{S}_2 \cdot \mathbf{S}_3) - 2J_4\mathbf{S}_3 \cdot \mathbf{S}_4$. The magnetic susceptibility data were fitted by a theoretical expression derived from the van Vleck equation

with the resulting energy matrix (eq 1; see the Supporting Information). The best-fitted values are $g = 2.25$, $J_1 = -12.7$ cm⁻¹, and $J_2 = -51.8$ cm⁻¹, with J_3, J_4, and p parameters fixed at zero, where p is the fraction of mononuclear impurity. The temperature-independent paramagnetism $N\alpha$ was set to 60×10^{-6} cm³ mol⁻¹ for each Cu atom. The assignments of the two J values were confirmed by the structural parameters of the analogous complex **2**. Concerning bis(μ-hydroxo)dicopper(II) complexes, an empirical magnetostructural correlation has been developed as follows: the Cu−OH−Cu pathway with a Cu−O−Cu angle > 97.6° mostly transfers antiferromagnetic interactions, with an increasing antiferromagnetic interaction as the Cu−O−Cu angle increases, and the pathway with a Cu−O−Cu angle less than 97.6° transfers ferromagnetic interactions.[25,26] From these, the J_2 value (-51.8 cm⁻¹) corresponds to an antiferromagnetic exchange through the hydroxo-bridged dicopper-(II) unit because the average Cu1−OH−Cu2 angle of the analogous complex **2** is 119.6° (average Cu⋯Cu = 3.3314 Å). The value for J_1 (-12.7 cm⁻¹) indicated that weak anitiferromagnetic interactions are operative in the Cu1⋯Cu3 and Cu2⋯Cu4 pairs, which are connected by an O atom of the phosphate group with an average Cu−O−Cu angle of 105.1° (average Cu⋯Cu = 3.5612 Å) in **2**. It has been demonstrated that the unpaired electron of the square-pyramidal Cu^{II} center is in a magnetic orbital of $d_{x^2-y^2}$ involved in the basal plane, and when the magnetic orbitals of the Cu^{II} ions are favorably oriented to generate a considerable overlap on magnetic orbitals of bridging atoms, magnetic interactions between the two Cu ions are effectively transferred. In the present case, the average Cu−O−Cu angle of 105.1° is not as large as the Cu−OH−Cu angle, and the bridging Cu−O−Cu units involve the axial Cu−O bonds with d_{z^2} orbitals of the square-pyramidal Cu^{II} ions, with both of the structural features resulting in only a weak antiferromagnetic coupling.

The maganetic data for **3** and **5b** showed weak antiferromagnetic properties with μ_{eff} per Cu₄ of 3.67 μ_B (300 K) and of 2.44 μ_B (4.5 K) for **3** and those of 3.72 μ_B (300 K) and 2.54 μ_B (4.5 K) for **5b** (see Figure S13 in the Supporting Information). Although some attempts of curve-fitting analyses using eq 2 (see the Supporting Information) were made, reasonable magnetic parameters were not obtained because of the serious influence of a paramagnetic impurity at low temperature, preventing any further magnetostructural discussion.

Incorporation of Sugar Acids into a Tetranuclear Copper(II) Framework Bridged by α-D-Glc-1P Ligands. The reaction of complex **1a** with carboxylic acids was applied to incorporate a series of sugar acids into the tetracopper(II) core. Sugar acids possess carboxylic functional moieties as well as polyhydroxy groups along the chiral backbones, which may lead to a variety of functions as potential candidates for sequestering agents in relation to

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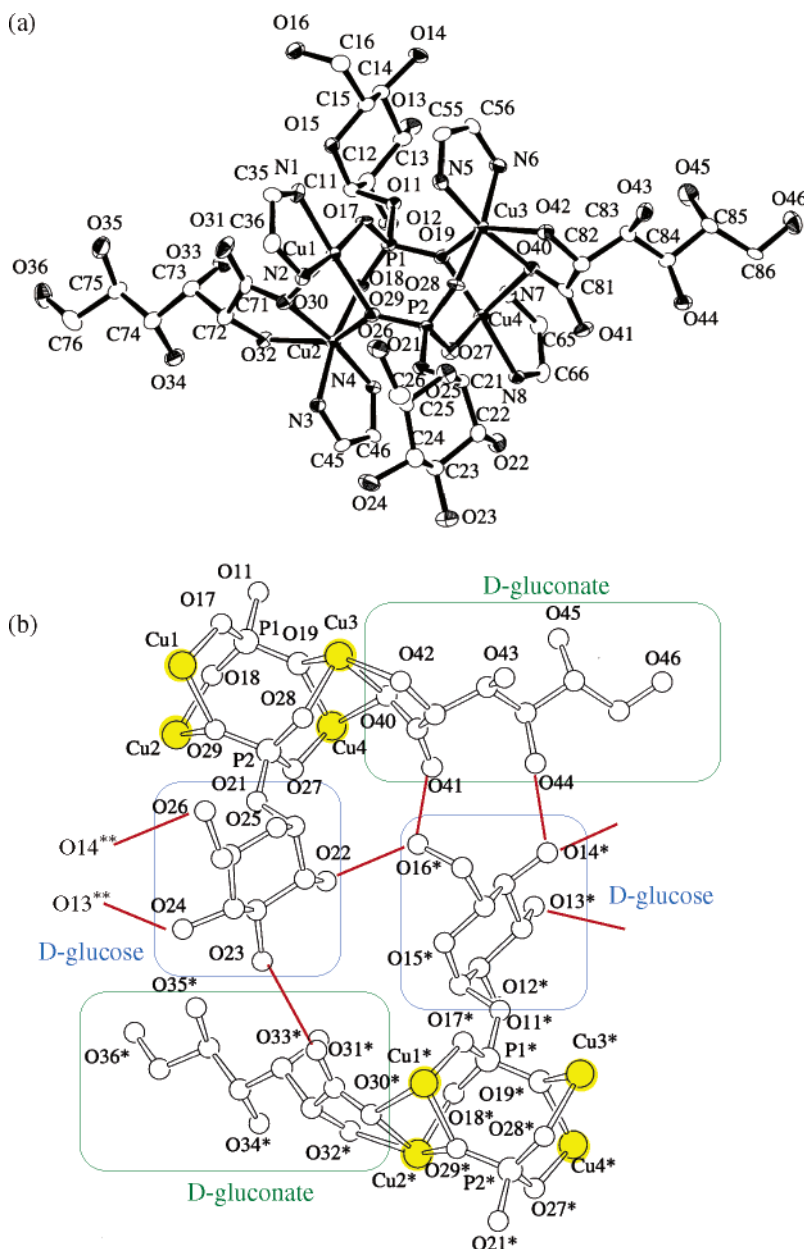
Chart 4
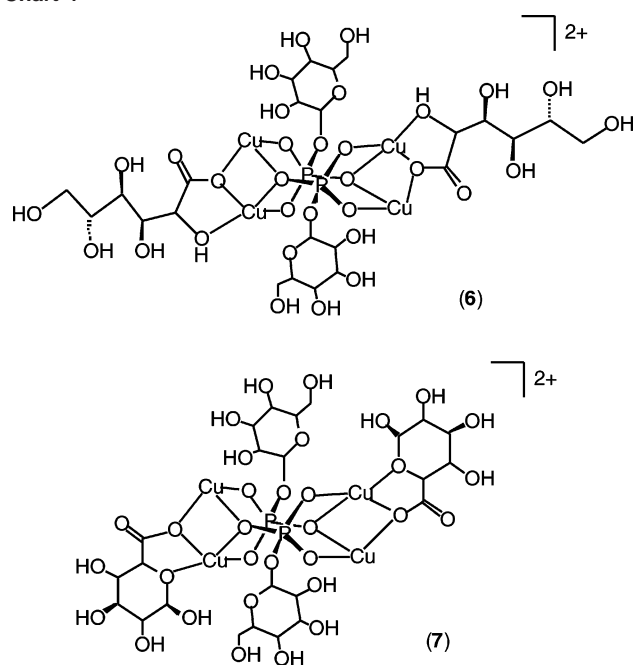
environmental and toxicological problems, bioactive molecular recognition agents in drug-delivery systems, and renewable starting materials for biodegradable industrial products. Whereas a number of earlier studies on the solution chemistry of sugar acids have been carried out,[15,27] structurally characterized transition-metal complexes containing sugar acids are scarce owing to their hygroscopic nature, which might lead to the lack of molecular-based information for metal–sugar acid interactions.[5a,28–31] When complex **1a** dissolved in DMF was reacted with an aqueous solution of sugar acids in a 1:2 ratio, the discrete tetracopper(II) complexes bridged by α-D-Glc-1P and sugar acids, [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-SA)$_2$(bpy)$_4$](NO$_3$)$_2$ [SA = D-gluconate (**6**), D-glucuronate (**7**), D-glucarateH (**8a**)], were isolated as crystalline forms in good yields (Chart 4). The detailed structures of **6** and **7** were determined by X-ray crystallography.

An ORTEP diagram for the complex cation of **6** is shown in Figure 7a, and selected bond distances and angles are summarized in Table S6 (in the Supporting Information). The structure consists of tetranuclear Cu^{II} ions bridged by two α-D-Glc-1P dianions and two D-gluconate anions,

(27) For example, see: (a) Frutos, A. A.; Escandar, G. M.; Peregrin, J. M. S.; Sierra, M. G.; Sala, L. F. *Can. J. Chem.* **1997**, *75*, 405. (b) Escandar, G. M.; Olivieri, A. C.; Sierra, M. G.; Sala, L. F. *J. Chem. Soc., Dalton Trans.* **1994**, 1189. (c) Escandar, G. M.; Sierra, M. G.; Peregrin, J. M. S.; Labadié, G.; Santoro, M.; Frutos, A.; Sala, L. F. *Polyhedron* **1994**, *13*, 909. (d) Frutos, A. A.; Signorella, S.; Sala, L. F.; Escandar, G. M.; Peregrin, J. M. S.; Moreno, V. *Polyhedron* **1998**, *17*, 3371. (e) González, J. C.; Daier, V.; García, S.; Goodman, B. A.; Atria, A. M.; Sala, L. F.; Signorella, S. *J. Chem. Soc., Dalton Trans.* **2004**, 2288. (f) Roldán, V.; Santoro, M.; González, J. C.; Peregrin, J. M. S.; Signorella, S.; Sala, L. F. *J. Inorg. Biochem.* **2004**, *98*, 347.
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resulting in a rectangular tetrametallic framework quite similar to those observed in **3** and **4**; Cu1···Cu2 = 3.337(1) Å, Cu3···Cu4 = 3.349(2) Å, Cu1···Cu3 = 4.098(2) Å, and Cu2···Cu4 = 4.075(2) Å. Namely, two D-gluconate moieties are successfully introduced into the Cu$^{II}_4$ core instead of the two carboxylate groups in **3** and **4**. The pairs of Cu1/Cu2 and Cu3/Cu4 centers are bridged by the carboxylate O atoms, O30 and O40, respectively, in a η^1,η^1 monatomic fashion, and, in addition, the hydroxy groups at the C-2 position of D-gluconates, O32 and O42, axially coordinate to the Cu2 and Cu3 atoms, respectively [Cu2−O32 = 2.346(8) Å; Cu3−O42 = 2.318(7) Å], to form five-membered chelate rings [O30−Cu2−O32 = 76.3(3)°; O40−Cu3−O42 = 77.6(3)°]. The Cu2 and Cu3 ions adopt a distorted [N$_2$O$_4$] octahedral geometry with the Jahn−Teller elongated axis seriously deformed [O29−Cu2−O32 =147.8(3)°; O19−Cu3−O42 = 149.7(3)°] owing to the chelating structure of D-gluconate units. The α-D-glucopyranosyl parts of the sugar phosphates take a stable $^4C_1$ chair conformation, and the D-gluconate moieties are stretched in a chain form. Whereas no intramolecular H-bonding interaction was observed between the sugar domains, the crystal packing structure involves H-bonding networks between the sugar parts, nitrate anions, and solvent water molecules. The characteristic sugar−sugar H-bonding interactions are depicted in Figure 7b. A pair of D-gluconate and D-glucopyranosyl units on the Cu$_4$ core interact with another pair of the sugar pendants on the neighboring Cu$_4$ cluster, related by a symmetry operation of (x, y − 1, z), through the H-bonding networks indicated by red lines (Figure 7b); O22···O16* = 2.764(9) Å, O23···O31* = 2.98(1) Å, O41···O16* = 2.671(9) Å, O44···O14* = 2.70(1) Å, O24···O13** = 2.87(1) Å, and O26···O14** = 2.809(9) Å [the atoms with * and ** are generated by the symmetry operators of (x, y − 1, z) and (x, y − 1, z − 1), respectively]. From these structural features, one can image a cartoon in which the sugar-coated Cu$_4$ clusters are self-assembled by sugar−sugar recognitions, providing a fundamental motif of a biomolecule-targeted metal−cluster delivery system.

Complex **7** has a structure analogous to that of **6**, where two D-glucuronate anions are introduced onto the tetracopper-(II) scaffold of {Cu$_4${μ-(α-D-Glc-1P)}$_2$(bpy)$_4$}$^{4+}$ (Figure 8a and Table S6 in the Supporting Information). Among the two D-glucuronate ligands, one adopts an α-D-pyranosyl form, bridging the Cu1 and Cu2 ions, and the other takes a β-D-pyranosyl one, connecting the Cu3 and Cu4 atoms. The C-2 and C-3 parts of the β-D-pyranosyl moiety are disordered in two positions with each 0.5 occupancy, both having a stable $^4C_1$ chair conformation. The C-6 carboxylate group of each D-glucuronate connects the two Cu atoms with a η^1,η^1 monatom bridging mode and completes the five-membered chelation by axial coordination of the C-5 cyclic O atom [Cu2−O35 = 2.32(2) Å; Cu3−O45 = 2.40(1) Å]. The orientation of the two D-glucuronate pyranoid rings could further be supported by an intrasugar H bond between the C-6 carbonyl and the C-4 hydroxy O atoms of the same D-glucuronate moiety: O31···O37 = 2.60(3) Å and O44···O47 = 2.67(2) Å. The ESI-MS spectrum for a DMF/
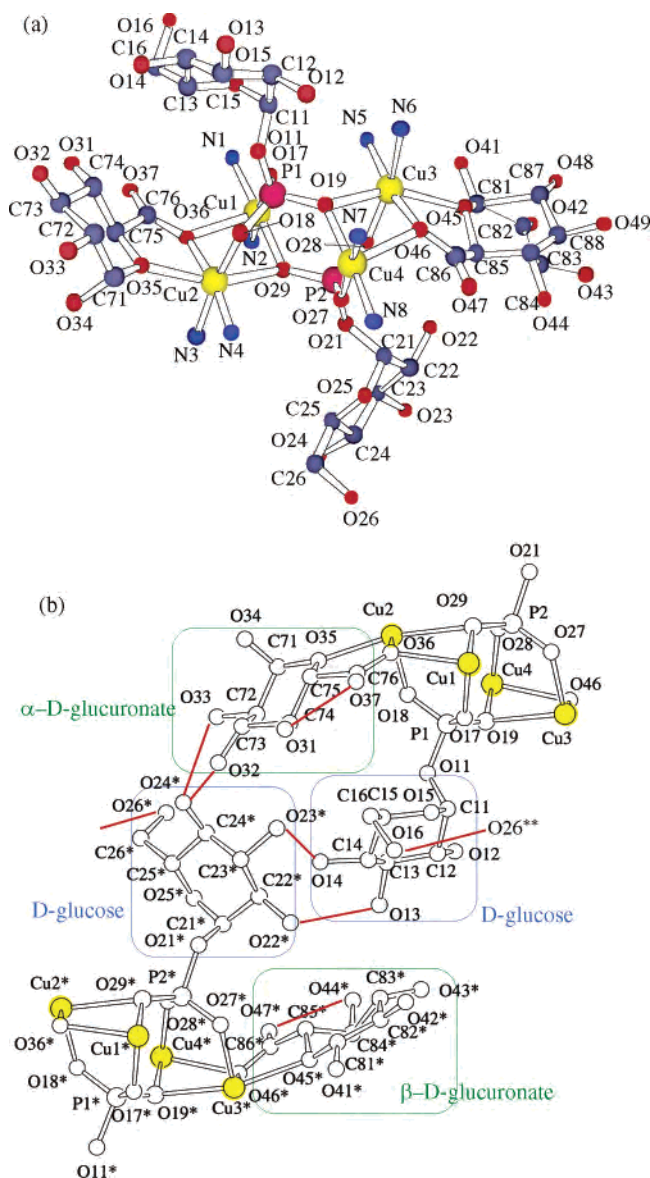
Figure 7. ORTEP plots for (a) the complex cation of **6**, with the C atoms of the bpy ligands omitted for clarity, and for (b) the structure showing intermolecular sugar–sugar H bonds as indicated by red lines. The atoms with * and ** are generated by the symmetry operators of $(x, y - 1, z)$ and $(x, y - 1, z - 1)$, respectively.

MeOH solution of **7** exhibited the dicationic peaks corresponding to {Cu$_4$(α-D-Glc-1P)$_2$(D-glucuronate)$_2$(bpy)$_4$}$^{2+}$ at $m/z = 889.24$ (calcd m/z 889.05), suggesting conservation of the tetranuclear structure as elucidated in the crystallographic analysis. The metal binding of the pyranoid cyclic O atom of D-glucuronate may accelerate interconversion between the α and β anomers through an intervening open-chain form in solution. Among the H bonds existing in the lattice packing, notable intermolecular sugar–sugar interactions are indicated in Figure 8b. A pincer pair of α-D-glucopyranosyl and α-D-glucuronopyranose pendants on the Cu$_4$ cluster recognizes a trans,trans sequence of the three OH groups at the C-2, C-3, and C-4 positions of the D-Glc-1P tethered on the neighboring Cu$_4$ complex generated by a symmetry operation of $(x, y + 1, z)$: O13···O22* = 2.78-

(1) Å, O14···O23* = 2.68(2) Å, O32···O24* = 2.93(4) Å, O33···O24* = 2.77(3) Å, and O16···O26** = 2.77(2) Å [the atoms with * and ** are generated by the symmetry operators of $(x, y + 1, z)$ and $(x + 1, y + 1, z)$, respectively].

One-Dimensional Chiral Coordination Polymers Containing Sugar Phosphate Bridged Tetracopper(II) Units Connected by D-Glucarate and D-Lactobionate. On the basis of analytical and spectroscopic measurements, complex **8a** with two D-glucarateH ligands was assumed to have a structure similar to that of complex **6**, and however, the detailed binding structures of the two D-glucarateH ligands, concerning combinations of C-1/C-1, C-1/C-6, and C-6/C-6 bridging carboxylate groups, are not clear. When complex **1a** was reacted with an equivalent amount of potassium D-glucarate, a polymeric compound formulated as {[Cu$_4${μ-

Figure 8. (a) Perspective plot for the complex cation of **7**, with the C atoms of the bpy ligands omitted for clarity. Color code: Cu, yellow; P, violet; O, red; N, blue; C, gray. (b) ORTEP plot for the structure showing intra- and intermolecular sugar–sugar H bonds as indicated by red lines. The atoms with * and ** are generated by the symmetry operators of (x, y + 1, z) and (x + 1, y + 1, z), respectively.

(α-D-Glc-1P)}$_2$(μ-D-glucarate)(bpy)$_4$](NO$_3$)$_2$}$_n$ (**8b**) was obtained in 34% yield (Chart 5). An ORTEP plot for the cationic unit of the polymer **8b** is illustrated in Figure 9a, and a packing diagram for the polymer chains is given in Figure 9b. The structural parameters are listed in Table S6 in the Supporting Information. The D-glucarate dianions take a stretched chain form and connect the tetracopper(II) units {Cu$_4${μ-(α-D-Glc-1P)}$_2$(bpy)$_4$}$^{4+}$, to result in an infinite chiral chain along the *a* axis with head-to-tail-type repeating units of {Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-D-glucarate)(bpy)$_4$}$^{2+}$ (unit length = 14.15 Å). The structure of the rectangular Cu$_4$ unit essentially resembles that of **6** [Cu1···Cu2 = 3.4379(8) Å, Cu3···Cu4 = 3.3083(8) Å, Cu1···Cu3 = 4.1944(8) Å, and Cu2···Cu4 = 3.9720(9) Å]. The Cu1 and Cu2 ions are bridged by the C-6 carboxylate group of the D-glucarate

Chart 5
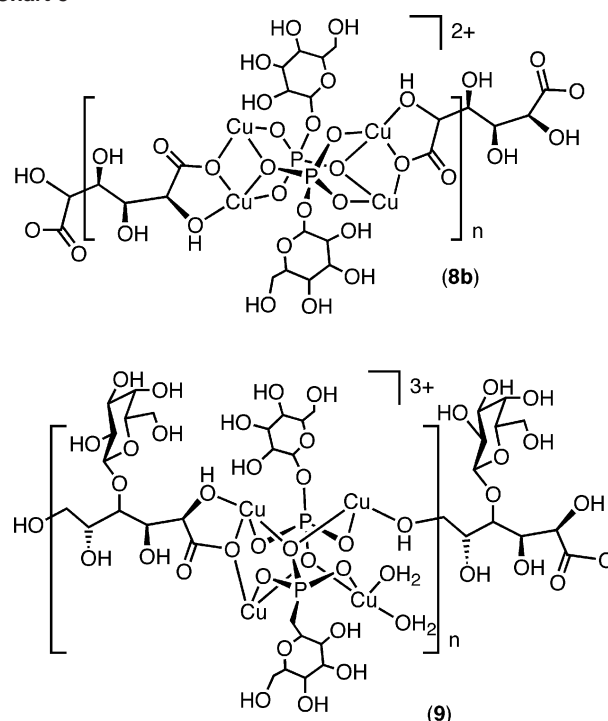
ligand in a 1,1-O monatomic fashion [Cu1−O30 = 2.347-(3) Å, Cu2−O30 = 1.990(3) Å, and Cu1−O30−Cu2 = 104.6(2)°], and the Cu3 and Cu4 ions are bridged by the C-1 carboxylate O atom of another D-glucarate unit [Cu3−O37* = 1.991(4) Å, Cu4−O37* = 2.284(3) Å, and Cu3−O37*−Cu4 = 101.2(2)°; the atoms with * are generated by the symmetry operation of (x − 1, y, z)]. The C-5 and C-2 hydroxy groups of the D-glucarate ligands, O32 and O35*, are axially bound to Cu2 and Cu3, respectively, to complete the considerably distorted octahedral structures [Cu2−O32 = 2.354(3) Å, Cu2−O29 = 2.627(3) Å, and O29−Cu2−O32 = 146.5(1)°; Cu3−O35* = 2.400(3) Å, Cu3−O19 = 2.420(3) Å, and O19−Cu3−O35* = 144.0(1)°]. In the crystal packing (Figure 9b), the polymer chains that are arranged parallel along the *a* axis further interact with each other by interchain sugar–sugar H bonds between the α-D-Glc-1P pendants [O13···O22* = 2.878(6) Å; O14···O23* = 2.722(6) Å], and the assembly results in the two-dimensional lattice framework (*a* × *c*) with hydrophilic spaces in which nitrate anions and solvent molecules are accommodated.

The sugar acid linked chiral coordination polymer with different types of tetracopper(II) units (**9**) was prepared by reacting **1a** with D-lactobionic acid (4-*O*-β-D-galacto-pyranosyl-D-gluconic acid; Chart 5). The structure of **9**, {[Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-D-lactobionate)(bpy)$_4$-(H$_2$O)$_2$](NO$_3$)$_3$·2CH$_3$OH·2H$_2$O}$_n$, was characterized by an X-ray crystallographic analysis; ORTEP diagrams for the tetracopper(II) polymer unit and the crystal packing viewed along the *b* axis are illustrated in Figure 10a,b, and some selected bond lengths and angles are listed in Table S7 (in the Supporting Information). The polymeric structure of **9** involves considerably distorted, asymmetric tetracopper units bridged by two α-D-Glc-1P ligands [Cu1···Cu2 = 3.572(1)

(a)

(b)
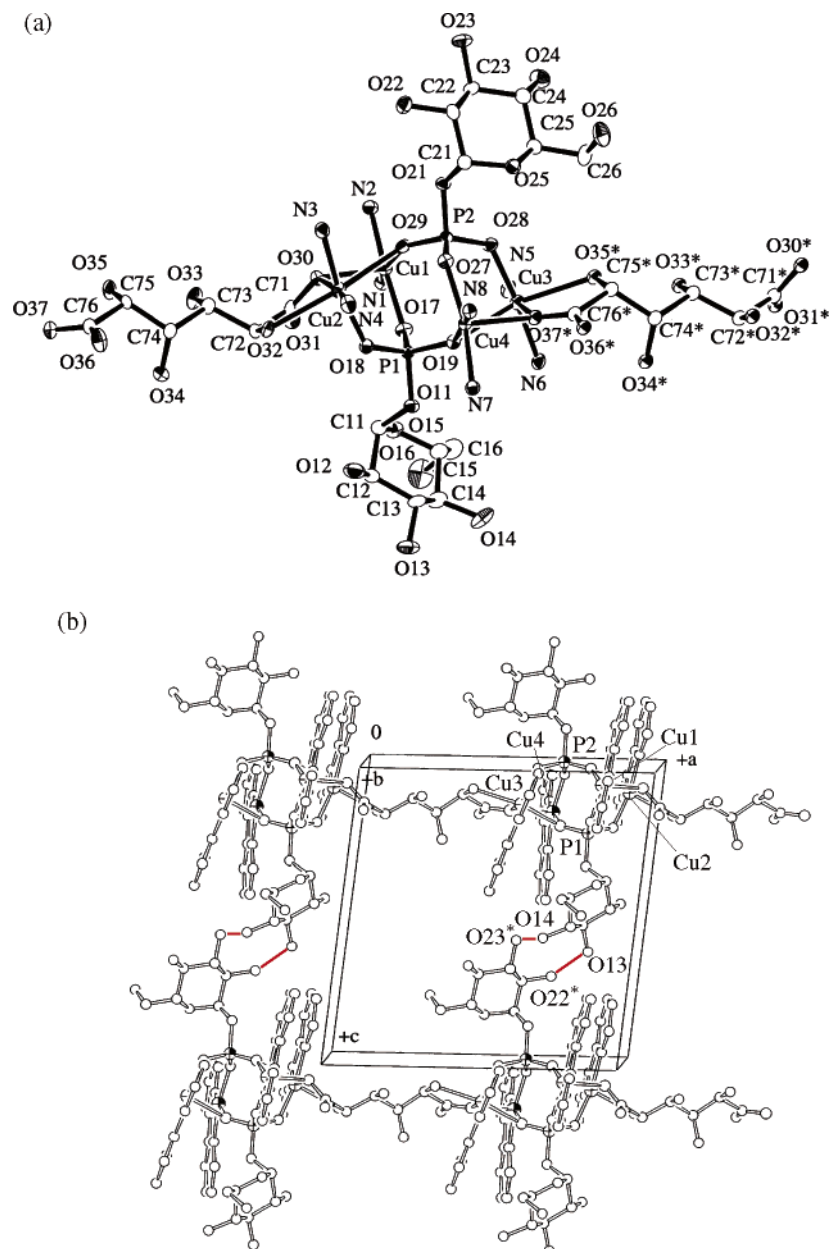
Figure 9. (a) ORTEP plot for the tetracopper(II) cationic unit of **8b**, with the C atoms of the bpy ligands omitted for clarity, and (b) the crystal packing diagram viewed along the *b* axis showing intermolecular sugar−sugar H bonds as indicated by red lines. The atoms with * are generated by the symmetry operator of (*x* − 1, *y*, *z*).

Å, Cu3···Cu4 = 4.510(1) Å, Cu1···Cu3 = 3.8026(8) Å, and Cu2···Cu4 = 3.3966(8) Å]. Each phosphate group connects three Cu^{II} ions with 1,3-OPO′ equatorial coordination and, in addition, is weakly bound to the fourth metal center as apical semicoordination [Cu1−O28 = 2.819(4) Å; Cu4−O18 = 2.532(4) Å], resulting in a significantly distorted 1,1-O monoatom bridge at the O18 and O28 atoms over the Cu2/Cu4 and Cu1/Cu3 pairs, respectively. The Cu1 and Cu2 atoms are further bridged by the C-1 carboxylate O atoms (O31) of the D-lactobionate moiety [Cu1−O31 = 1.967(6) Å; Cu2−O31 = 2.224(5) Å], and the C-2 hydroxy group of the sugar axially attaches to the Cu1 center [Cu1−O33 = 2.226(4) Å]. These bridging structures provide a [N$_2$O$_4$] octahedral environment around the Cu1 atom with a Jahn−Teller distortion along the O28−Cu1−O33 axis and a [N$_2$O$_3$]

square-pyramidal one for the Cu2 atom. On the other hand, the Cu3 and Cu4 ions are not bridged by the D-lactobionate residue. The terminal C-6 hydroxy group of the neighboring D-lactobionate (O36*) is bound to the Cu3 center at its apical site [Cu3−O36* = 2.423(4) Å] to complete the [N$_2$O$_3$] square-pyramidal geometry. The Cu4 ion adopts a distorted [N$_2$O$_4$] octahedral structure with two additional water molecules [Cu4−O51 = 2.379(5) Å; Cu4−O52 = 1.972(5) Å]. The D-gluconate part acts as a linear linker connecting the Cu$_4$ units with the C-1 carboxylate and the C-6 hydroxy group, which may further be supported by weak H-bonding interaction observed in O36*···O52 [3.024(8) Å] and O35*···O51 [3.06(1) Å]; the atoms with * are generated by the symmetry operation of (*x* − 1, *y*, *z* − 1). The directions of β-D-galactopyranosyl and α-D-glucopyranosyl
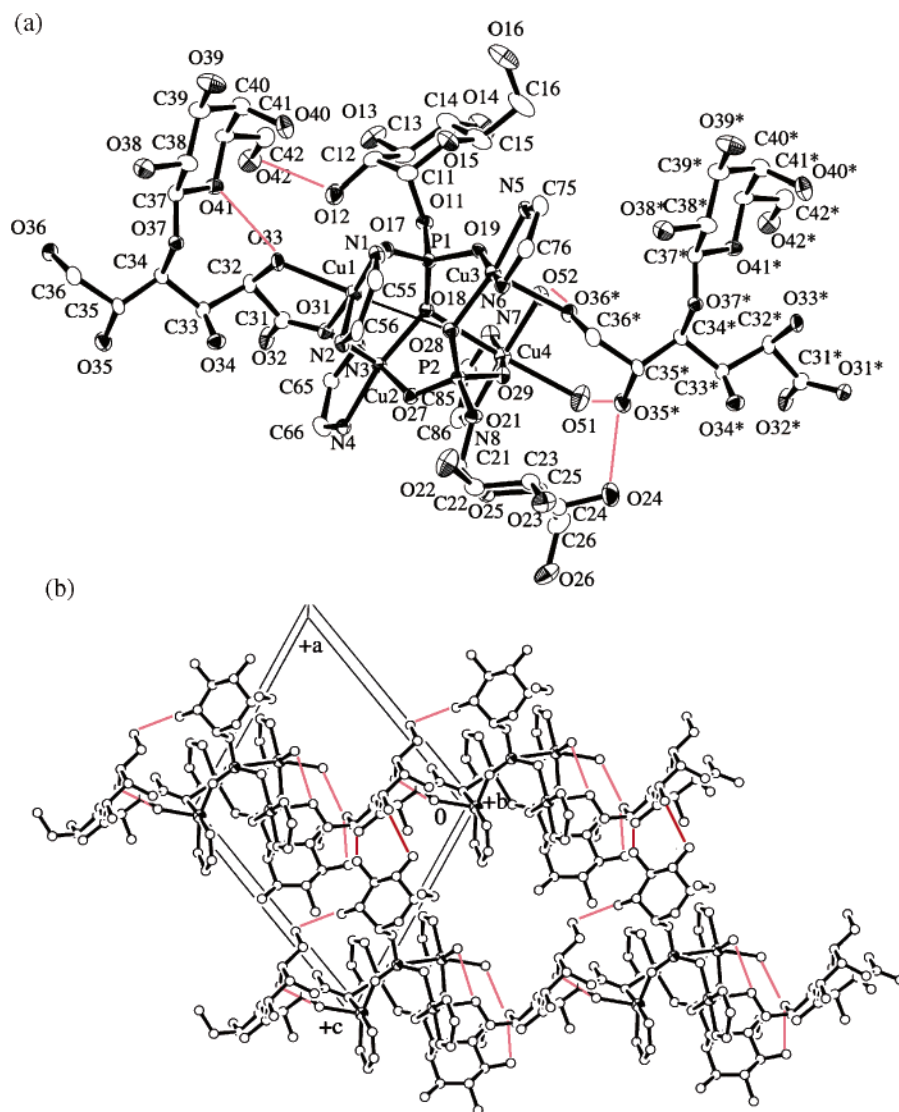
Figure 10. (a) ORTEP plot for the tetracopper(II) cationic unit of **9**, with the C atoms of the bpy ligands omitted for clarity, and (b) the crystal packing diagram viewed along the *b* axis. The intra- and interpolymer sugar−sugar H bonds as indicated by red dotted and true lines, respectively. The atoms with * are generated by the symmetry operator of $(x - 1, y, z - 1)$.

pendants of the sugar acid and phosphate moieties are also fixed by H-bonding networks, as indicated in Figure 10a,b [O33···O41 = 2.715(5) Å, O12···O42 = 2.751(7) Å, and O24···O35* = 2.949(7) Å]. The parallel-oriented one-dimensional chiral polymers in the lattice mutually interact through a pair of H bonds between the α-D-glucopyranosyl and β-D-galactopyranosyl sugar pendants for each unit: O13···O38* = 2.69(1) Å and O14···O39* = 2.78(1) Å (indicated by red true lines in Figure 10b). The sugar−sugar interaction between the one-dimensional chiral polymers results in the two-dimensional lattice framework, which provides the different types of hydrophilic space compared to that in the crystal structure of **8b**.

Oxidative Degradation of D-Glucuronate in Complex 7 via C−C Bond Cleavage. During some attempts to examine the reactivities of the sugar pendants tethered onto the tetracopper(II) unit, novel oxidative degradation of D-glucuronate was found by isolating mononuclear copper-(II) complexes with 2-dihydroxymalonate and oxalate. When

Chart 6
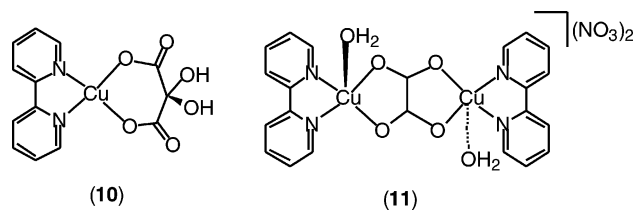
an aqueous solution of complex **7** was heated at reflux for 3 h, blue crystals of [Cu(O₂CC(OH)₂CO₂)(bpy)] (**10**) and [Cu₂-(μ-C₂O₄)(bpy)₂(H₂O)₂](NO₃)₂ (**11**)[32] were separately obtained, although their yields were not satisfactory, 14% (**10**) and 10% (**11**) vs sugar acid (Chart 6). The structure of **10** was characterized by X-ray crystallography to consist of a square-planar Cu^{II} ion ligated by bpy and 2-dihydroxyma-

(32) (a) Castillo, O.; Muga, I.; Luque, A.; Zorrilla, J. M. G.; Sertucha, J.; Vitoria, P.; Roman, P. *Polyhedron* **1999**, *18*, 1235. (b) Tang, J.; Gao, E.; Bu, W.; Liao, D.; Yan, S.; Jiang, Z.; Wang, G. *J. Mol. Struct.* **2000**, *525*, 271.
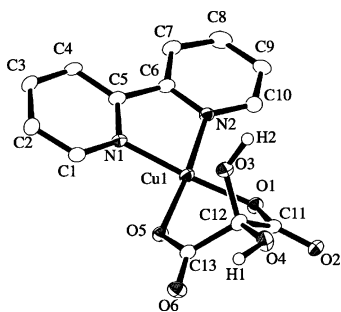
Figure 11. ORTEP plot of **10**. Selected bond lengths (Å) and angles (deg) are as follows: Cu1−O1 = 1.943(3), Cu1−O5 = 1.971(3), Cu1−N1 = 1.987(4), Cu1−N2 = 1.986(4), O1−C11 = 1.274(4), O2−C11 = 1.238-(5), O3−C12 = 1.435(4), O4−C12 = 1.380(4), O5−C13 = 1.281(4), O6−C13 = 1.225(6), C11−C12 = 1.559(8), C12−C13 = 1.552(8), O1−Cu1−O5 = 91.4(1), N1−Cu1−N2 = 81.5(2), Cu1−O1−C11 = 119.2(3), Cu1−O5−C13 = 118.8(4), O1−C11−C12 = 115.2(4), O5−C13−C12 = 114.9(4), C11−C12−C13 = 108.8(4).

lonate ligands (Figure 11). Notably, this is the first example of characterized transition-metal complexes containing 2-dihydroxymalonate dianions on the basis of CCDC analysis, except the zinc(II) complex recently reported.[33] Complex **10** was also obtained in low yield by the reaction of **1a** with D-glucuronic acid in refluxing water. When complex **1a** or other sugar acid complexes **6** and **8a** were heated in water, no complex with sugar-degraded fragments was obtained, which demonstrated that the D-glucuronate moieties in **7** underwent the oxidative degradation and the C-1 aldehyde group should be indispensable to the degradation. It is well-known that aldoses are able to reduce Cu^{II} ions into Cu^{I} species, and the resultant Cu^{I} centers activate molecular oxygen to generate peroxo and/or hydroxy radical species. These reactions could further be coupled with oxidative degradation of aldoses through C−C bond cleavage to yield carboxylic acid fragments, usually under basic conditions primarily producing formic acid via a 1,2-ene-diol intermediate.[34] Whereas the detailed mechanism is not clear, the present reaction proceeded under a slight acidic condition and formation of the C3 fragment, 2-dihydroxymalonate, as a major product should be unprecedented, which might be of potential importance concerning industrial utilization of carbohydrates as biomass resources.

Conclusion

In the present study, novel tetranuclear copper(II) complexes with a (μ-hydroxo)bis(μ-sugar phosphate) bridging system, [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(L)$_4$(H$_2$O)$_2$]$^{3+}$ [L = bpy (**1**), phen (**2**); α-D-Glc-1P = α-D-glucose-1-phosphate], were successfully synthesized and characterized by X-ray crystallography (**2**) as the first example of a transition-metal complex containing a sugar phosphate monoester. The structure of **2** demonstrated an interesting C_2 chiral switch of the cluster core {Cu$_4$(μ-OH)(μ-PO$_4$)$_2$(phen)$_4$(H$_2$O)$_2$},

(33) Shi, J.-M.; Zhu, S.-C.; Wu, C.-J. *Chin. J. Struct. Chem.* **2004**, *23*, 1027.
(34) (a) Arts, S. J. H. F.; Mombarg, E. J. M.; van Bekkum, H.; Sheldon, R. A. *Synthesis* **1997**, 597. (b) Ródio, R. T.; Pereira, E. M.; Tavares, M. F. M.; Ferreira, A. M. C. *Carbohydr. Res.* **1999**, *315*, 319 and references cited therein.

depending on the direction of α-D-glucopyranosyl pendants. Complex **1a**, [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(bpy)$_4$(H$_2$O)$_2$]-(NO$_3$)$_3$, was revealed to incorporate a series of sugar acids through the Cu$_4$ core structural changes, resulting in the sugar-coated rectangular Cu$_4$ clusters [Cu$_4${μ-(α-D-Glc-1P)}$_2$-(μ-SA)$_2$(bpy)$_4$]$^{2+}$ [SA = D-gluconate (**6**), D-glucuronate (**7**), D-glucarateH (**8a**)]. The sugar moieties tethered onto the Cu$_4$ core, α-D-glucopyranosyl pendant of the sugar phosphate, and the open-chain D-gluconate or the pyranoid rings of D-glucuronate exhibited various types of intermolecular sugar−sugar interactions. The similar reactions with D-glucarate and D-lactobionate were applied to construct linearly ordered chiral coordination polymers, in which the sugar phosphate bridged Cu$_4$ units are connected by the linear D-glucarate (**8b**) or D-gluconate part of lactobionate (**9**). The linear chiral polymers are arranged in parallel supported with interchain sugar−sugar H-bonding interactions to provide different types of hydrophilic spaces depending on the sugar acid linkers. The present results could provide molecular-based information and methodology in relation to the development of bioactive materials by accumulation of carbohydrates on metal cluster compounds.

Experimental Section

Materials. All reagents were of the best commercial grade and were used as received. α-D-Glucose-1-phosphate disodium salt was purchased from Wako Co. Ltd. The following abbreviation is used: α-D-glucose-1-phosphate disodium salt, Na$_2$[α-D-Glc-1P].

Measurements. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrometer and CD spectra on a Jasco J-720 spectropolarimeter. IR spectra were measured on KBr pellets with a Jasco FT/IR 410 spectrometer. ESI-MS spectra were recorded on an Applied Biosystems Mariner spectrometer in positive mode of detection. Variable-temperature magnetic susceptibility measurements were carried out with a MPMS-5S Quantum Design SQUID magnetometer over a range of 4.5−300 K, and the obtained magnetic susceptibility data were corrected for diamagnetism using Pascal's constants and were fitted by theoretical expressions for the molar magnetic susceptibility derived from the van Vleck equation (see the Supporting Information), in which the value of $N\alpha$ (temperature-independent paramagnetism) was estimated at 60 × 10^{-6} cm^3 mol^{-1} per Cu^{II} ion.

Preparation of [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(bpy)$_4$(H$_2$O)$_2$]X$_3$ [X = NO$_3$ (1a), Cl (1b), Br (1c)]. To an aqueous solution (2 mL) of Na$_2$[α-D-Glc-1P] (163 mg, 0.535 mmol) were added portions of Cu(NO$_3$)$_2$·3H$_2$O (129 mg, 0.535 mmol) and bpy (84 mg, 0.54 mmol). The reaction solution was stirred for 1 h at room temperature, then concentrated under reduced pressure, and allowed to stand for slow evaporation. Over about 1−2 days, block-shaped blue crystals of [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(bpy)$_4$(H$_2$O)$_2$](NO$_3$)$_3$·10H$_2$O (**1a**·10H$_2$O) were deposited from the concentrated solution. The crystals were filtered, washed with ethanol and diethyl ether, and dried under vacuum (153 mg, 63% based on Cu). Anal. Calcd for C$_{52}$H$_{79}$O$_{40}$N$_{11}$P$_2$Cu$_4$: C, 34.42; H, 4.39; N, 8.49. Found: C, 34.47; H, 4.16; N, 8.45. IR (KBr, cm^{-1}): 3407 (br), 1602 (m), 1384 (s), 1108 (m), 1055 (w), 1032 (w), 942 (m). UV−vis (CH$_3$-OH): λ_{max} 667 nm (ϵ = 1.72 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 647 nm ($\Delta\epsilon$ = 3.70 × 10^{-1} M^{-1} cm^{-1}). MS (ESI): m/z 694.97 [calcd 695.00 for {Cu$_4$(α-D-Glc-1-P)$_2$(bpy)$_4$ − 2H}$^{2+}$ (z = 2)]. A procedure similar to that described for **1a**, but using CuCl$_2$·2H$_2$O or CuBr$_2$, afforded dark-blue crystals of [Cu$_4$(μ-OH){μ-(α-D-Glc-

1P)}$_2$(bpy)$_4$(H$_2$O)$_2$]X$_3 \cdot n$H$_2$O [X = Cl, n = 14 (**1b**); X = Br, n = 10 (**1c**)]. For **1b**·14H$_2$O, yield 35% vs Cu. Anal. Calcd for C$_{52}$H$_{87}$O$_{35}$N$_8$P$_2$Cl$_3$Cu$_4$: C, 34.57; H, 4.85; N, 6.20. Found: C, 34.90; H, 4.53; N, 6.35. IR (KBr, cm^{-1}): 3400 (br), 1602 (s), 1447 (s), 1141 (br), 1057 (w), 1031 (m), 943 (m), 773 (s). UV−vis (CH$_3$-OH): λ_{max} 679 nm (ϵ = 1.63 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 647 nm ($\Delta\epsilon$ = 2.82 × 10^{-1} M^{-1} cm^{-1}). MS (ESI): m/z 695.00 [calcd 695.00 for {Cu$_4$(α-D-Glc-1-P)$_2$(bpy)$_4$ − 2H}$^{2+}$ (z = 2)]. For **1c**·10H$_2$O, yield 45% vs Cu. Anal. Calcd for C$_{52}$H$_{79}$O$_{31}$N$_8$P$_2$Br$_3$-Cu$_4$: C, 33.43; H, 4.26; N, 6.00. Found: C, 33.54; H, 4.04; N, 6.11. IR (KBr, cm^{-1}): 3343 (br), 1601 (s), 1445 (s), 1135 (s), 1059 (w), 1032 (m), 938 (s), 775 (s). UV−vis (CH$_3$OH): λ_{max} 695 nm (ϵ = 2.07 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 647 nm ($\Delta\epsilon$ = 3.37 × 10^{-1} M^{-1} cm^{-1}). MS (ESI): m/z 695.00 [calcd 695.00 for {Cu$_4$(α-D-Glc-1-P)$_2$(bpy)$_4$ − 2H}$^{2+}$ (z = 2)].

Preparation of [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(phen)$_4$(H$_2$O)$_2$]-(NO$_3$)$_3$ (2). A procedure similar to that described for **1a**·10H$_2$O, but using phen instead of bpy, gave dark-blue crystals of [Cu$_4$(μ-OH){μ-(α-D-Glc-1P)}$_2$(phen)$_4$(H$_2$O)$_2$](NO$_3$)$_3$·6H$_2$O (**2**·6H$_2$O) in 11% yield (vs Cu). Anal. Calcd for C$_{60}$H$_{71}$O$_{36}$N$_{11}$P$_2$Cu$_4$: C, 39.20; H, 3.89; N, 8.38. Found: C, 39.10; H, 3.85; N, 8.49. IR (KBr, cm^{-1}): 3394 (br), 1629 (w), 1385 (s), 1141 (m), 941 (w), 722 (m). UV−vis (CH$_3$OH): λ_{max} 673 nm (ϵ = 2.05 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 651 nm ($\Delta\epsilon$ = 2.33 × 10^{-1} M^{-1} cm^{-1}). MS (ESI): m/z 743.23 [calcd 743.00 for {Cu$_4$(α-D-Glc-1-P)$_2$(phen)$_4$ − 2H}$^{2+}$ (z = 2)].

Preparation of [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-CH$_3$COO)$_2$(bpy)$_4$]-(NO$_3$)$_2$ (3). To a solution containing **1a**·10H$_2$O (57 mg, 0.031 mmol) in DMF (2 mL) was added an excess of acetic acid (ca. 1.8 mmol). The mixture was stirred for 12 h, and the solvent was removed under reduced pressure. The residue was extracted with methanol. Blue crystals of complex **3**·4H$_2$O were obtained from a methanol/diethyl ether mixed solvent (12 mg, 23% based on Cu). Anal. Calcd for C$_{56}$H$_{68}$O$_{32}$N$_{10}$Cu$_4$P$_2$: C, 39.35; H, 4.01; N, 8.19. Found: C, 39.12; H, 3.89; N, 8.24. IR (KBr, cm^{-1}): 3403 (br), 1603 (s), 1576 (m), 1385 (s), 1132 (s), 1107 (s), 1032 (s), 941 (m), 773 (w). UV−vis (CH$_3$OH): λ_{max} 657 nm (ϵ = 2.25 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 640 nm ($\Delta\epsilon$ = 2.87 × 10^{-1} M^{-1} cm^{-1}). MS (ESI): m/z 695.08 [calcd 695.00 for {Cu$_4$(α-D-Glc-1-P)$_2$(bpy)$_4$ − 2H}$^{2+}$ (z = 2)].

Preparation of [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-o-C$_6$H$_4$(COO)(COOH))$_2$(bpy)$_4$](NO$_3$)$_2$ (4). A procedure similar to that described for **3**, but using o-pthalic acid instead of acetic acid, afforded [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-o-C$_6$H$_4$(COO)(COOH))$_2$(bpy)$_4$](NO$_3$)$_2$·5H$_2$O (**4**·5H$_2$O) in 43% yield (vs Cu). Anal. Calcd for C$_{68}$H$_{74}$O$_{37}$N$_{10}$-Cu$_4$P$_2$: C, 42.11; H, 3.85; N, 7.22. Found: C, 42.30; H, 3.76; N, 7.20. IR (KBr, cm^{-1}): 3389 (br), 1713 (w), 1603 (m), 1575 (w), 1448 (m), 1384 (s), 1131 (br), 1033 (w), 944 (m), 768 (m). UV−vis (CH$_3$OH): λ_{max} 660 nm (ϵ = 2.11 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 652 nm ($\Delta\epsilon$ = 5.33 × 10^{-2} M^{-1} cm^{-1}).

Preparation of [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-m-C$_6$H$_4$(CH$_2$COO)(CH$_2$COOH))$_2$(bpy)$_4$](NO$_3$)$_2$ (5a) and {[Cu$_4${μ-(α-D-Glc-1P)}$_2$-(μ-m-C$_6$H$_4$(CH$_2$COO)$_2$)(bpy)$_4$](NO$_3$)$_2$}$_n$ (5b). Complex **1a**·10H$_2$O (254 mg, 0.140 mmol) was reacted with m-phenylenediacetic acid (54 mg, 0.28 mmol) in DMF (3 mL) for 12 h, and then the solvent was removed under reduced pressure. The residue was extracted with methanol (5 mL), and slow evaporation of the solvent at room temperature afforded blue crystals of [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-m-C$_6$H$_4$(CH$_2$COO)(CH$_2$COOH))$_2$(bpy)$_4$](NO$_3$)$_2$·11H$_2$O (**5a**·11H$_2$O) in 10% yield (30 mg). Anal. Calcd for C$_{72}$H$_{94}$O$_{43}$N$_{10}$Cu$_4$P$_2$: C, 41.11; H, 4.50; N, 6.66. Found: C, 40.67; H, 4.16; N, 7.13. IR (KBr, cm^{-1}): 3393 (br), 1712 (m), 1603 (s), 1574 (m), 1384 (s), 1125 (s), 1033 (m), 938 (m). UV−vis (CH$_3$OH): λ_{max} 657 nm (ϵ = 2.44

× 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 642 nm ($\Delta\epsilon$ = 4.91 × 10^{-2} M^{-1} cm^{-1}). Treatment of **1a**·10H$_2$O (58 mg, 0.032 mmol) similar to that described for **5a**, but using a portion of m-phenylenediacetic acid (7.4 mg, 0.038 mmol), gave {[Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-m-C$_6$H$_4$(CH$_2$COO)$_2$)(bpy)$_4$](NO$_3$)$_2$·2H$_2$O}$_n$ (**5b**·2H$_2$O) in 32% yield (18 mg). Anal. Calcd for C$_{62}$H$_{66}$O$_{30}$N$_{10}$Cu$_4$P$_2$: C, 42.62; H, 3.81; N, 8.02. Found: C, 42.56; H, 3.85; N, 7.99. IR (KBr, cm^{-1}): 3405 (br), 1603 (s), 1564 (m), 1384 (s), 1133 (s), 1105 (s), 1031 (s), 939 (m), 772 (w). UV−vis (CH$_3$OH): λ_{max} 657 nm (ϵ = 2.02 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 647 nm ($\Delta\epsilon$ = 1.34 × 10^{-1} M^{-1} cm^{-1}).

Preparation of [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-SA)$_2$(bpy)$_4$](NO$_3$)$_2$ [SA = D-Gluconate (6), D-Glucuronate (7)]. To a solution of **1a**·10H$_2$O (103 mg, 0.057 mmol) in DMF (10 mL) was added D-gluconic acid anhydrous (δ-D-gluconolactone) (21 mg, 0.12 mmol) in water (4 mL). The reaction mixture was stirred at room temperature for 12 h. The solvent was then evaporated under reduced pressure, and the residue was crystallized from a methanol/diethyl ether mixed solvent. Block-shaped blue crystals of [Cu$_4$-{μ-(α-D-Glc-1P)}$_2$(μ-D-gluconate)$_2$(bpy)$_4$](NO$_3$)$_2$ (**6**·2H$_2$O) formed after 2 days and were collected, washed with diethyl ether, and dried under vacuum (26 mg, 23%). Anal. Calcd for C$_{64}$H$_{80}$O$_{40}$N$_{10}$-Cu$_4$P$_2$: C, 39.51; H, 4.14; N, 7.20. Found: C, 39.63; H, 4.51; N, 7.49. IR (KBr, cm^{-1}): 3391 (br), 1657 (s), 1603 (m), 1448 (m), 1385 (s), 1354 (s), 1144 (s), 1057 (w), 1031 (m), 1020 (w), 974 (w), 939 (m), 774 (m), 732 (w). UV−vis (CH$_3$OH): λ_{max} 669 nm (ϵ = 1.80 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 630 nm ($\Delta\epsilon$ = 8.84 × 10^{-2} M^{-1} cm^{-1}), 786 nm (−3.03 × 10^{-2} M^{-1} cm^{-1}).

A procedure similar to that described for **6**, but using D-glucuronic acid, gave blue microcrystals of [Cu$_4${μ-(α-D-Glc-1P)}$_2$-(μ-D-glucuronate)$_2$(bpy)$_4$](NO$_3$)$_2$·6H$_2$O (**7**·6H$_2$O) in 49% yield. Anal. Calcd for C$_{64}$H$_{84}$O$_{44}$N$_{10}$Cu$_4$P$_2$: C, 38.18; H, 4.20; N, 6.96. Found: C, 38.16; H, 4.13; N, 7.04. IR (KBr, cm^{-1}): 3382 (br), 1774 (w), 1630 (m), 1610 (s), 1448 (m), 1385 (s), 1129 (s), 1033 (s), 939 (m), 773 (w). UV−vis (CH$_3$OH): λ_{max} 669 nm (ϵ = 2.11 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 683 nm ($\Delta\epsilon$ = 2.30 × 10^{-1} M^{-1} cm^{-1}). MS (ESI): m/z 889.24 [M^{2+}, calcd 889.05 for {Cu$_4$-(α-D-Glc-1P)$_2$(D-glucuronate)$_2$(bpy)$_4$}$^{2+}$ (z = 2)].

Preparation of [Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-D-glucarateH)$_2$(bpy)$_4$]-(NO$_3$)$_2$ (8a) {[Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-D-glucarate)(bpy)$_4$](NO$_3$)$_2$}$_n$ (8b). To a solution of **1a**·10H$_2$O (102 mg, 0.0560 mmol) in DMF (9 mL) was added D-glucarate potassium salt (28 mg, 0.11 mmol) in water (2 mL). The reaction mixture was stirred for 5 min. The solvent was then evaporated under reduced pressure, and the residue was crystallized from methanol (5 mL) at room temperature. Over several days of slow evaporation, block-shaped blue crystals of [Cu$_4$-{μ-(α-D-Glc-1P)}$_2$(μ-D-glucarateH)$_2$(bpy)$_4$](NO$_3$)$_2$·7H$_2$O (**8a**·7H$_2$O) were deposited and then were collected, washed with diethyl ether, and dried under vacuum (57 mg, 49%). Anal. Calcd for C$_{64}$H$_{86}$O$_{47}$-N$_{10}$P$_2$Cu$_4$: C, 37.25; H, 4.20; N, 6.79. Found: C, 37.23; H, 4.20; N, 6.71. IR (KBr, cm^{-1}): 3382 (br), 1735 (w), 1609 (s), 1448 (s), 1384 (s), 1138 (s), 1058 (m), 1033 (m), 773 (s), 732 (m). UV−vis (CH$_3$OH): λ_{max} 664 nm (ϵ = 2.01 × 10^2 M^{-1} cm^{-1}). CD (CH$_3$-OH): λ_{max} 475 nm ($\Delta\epsilon$ = 3.57 × 10^{-2} M^{-1} cm^{-1}), 626 nm (1.04 × 10^{-1} M^{-1} cm^{-1}), 743 nm (4.99 × 10^{-2} M^{-1} cm^{-1}).

To a solution of **1a**·10H$_2$O (64 mg, 0.035 mmol) in DMF (3 mL) was added D-glucarate potassium salt (8.8 mg, 0.035 mmol). The reaction mixture was stirred for 5 min. The solvent was then evaporated under reduced pressure, and the residue was crystallized from methanol (5 mL) at room temperature. Over several days of slow evaporation, block-shaped blue crystals of {[Cu$_4${μ-(α-D-Glc-1P)}$_2$(μ-D-glucarate)(bpy)$_4$](NO$_3$)$_2$·8H$_2$O}$_n$ (**8b**·8H$_2$O) were deposited and then were collected, washed with diethyl ether, and dried

Table 1. Crystal Structure and Refinement Data for **2**·15H$_2$O, **3**·2CH$_3$OH·0.5H$_2$O, **4**·6CH$_3$OH·H$_2$O, and **5b**·CH$_3$OH

	2·15H$_2$O	**3**·2CH$_3$OH·0.5H$_2$O	**4**·6CH$_3$OH·H$_2$O	**5b**·CH$_3$OH
formula	C$_{60}$H$_{89}$N$_{11}$O$_{45}$P$_2$Cu$_4$	C$_{58}$H$_{69}$N$_{10}$O$_{30.5}$P$_2$Cu$_4$	C$_{74}$H$_{90}$N$_{10}$O$_{39}$P$_2$Cu$_4$	C$_{63}$H$_{66}$N$_{10}$O$_{29}$P$_2$Cu$_4$
fw	2000.52	1710.36	2059.70	1743.40
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1$ (No. 4)	$P1$ (No. 1)	$P1$ (No. 1)	$P1$ (No. 1)
a, Å	15.454(1)	11.6421(2)	11.1536(1)	11.5923(2)
b, Å	31.618(2)	12.9269(1)	14.5022(1)	12.8139(2)
c, Å	16.698(1)	13.2228(1)	16.3328(4)	13.0141(2)
α, deg		64.151(6)	60.075(5)	64.790(13)
β, deg	101.660(3)	82.562(9)	68.681(8)	79.938(15)
γ, deg		73.240(8)	79.736(9)	74.286(15)
V, Å^3	7990.5(9)	1714.8(1)	2132.95(6)	1679.74(5)
Z	4	1	1	1
T, °C	−120.0	−120	−120.0	−120
μ(Mo Kα), cm^{-1}	12.0	13.67	11.21	13.96
ρ_{calc}, g cm^{-3}	1.663	1.656	1.603	1.723
2θ range, deg	$6 < 2\theta < 55$	$6 < 2\theta < 51$	$6 < 2\theta < 55$	$6 < 2\theta < 55$
no. of obsd reflns	31 336 [$I > 2\sigma(I)$]	5037 [$I > 2\sigma(I)$]	13 094 [$I > 2\sigma(I)$]	11 581 [$I > 2\sigma(I)$]
no. of variables	2199	642	1148	975
R1^a	0.052	0.050	0.046	0.044
wR2^b	0.136	0.144	0.120	0.113
GOF	1.02	0.99	1.06	0.98

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $[\Sigma(w(F_o{}^2 - F_c{}^2)^2)/\Sigma w(F_o{}^2)^2]^{1/2}$.

under vacuum (23 mg, 34%). Anal. Calcd for C$_{58}$H$_{78}$O$_{40}$N$_{10}$P$_2$Cu$_2$: C, 37.22; H, 4.20; N, 7.48. Found: C, 37.12; H, 4.06; N, 7.46. IR (KBr, cm^{-1}): 3390 (br), 1604 (s), 1575 (m), 1448 (m), 1384 (s), 1139 (s), 1058 (m), 1033 (m), 975 (w), 936 (m), 774 (m), 732 (w). UV−vis (CH$_3$OH): λ_{max} 662 nm ($\epsilon = 1.87 \times 10^2$ M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 612 nm ($\Delta\epsilon = 1.34 \times 10^{-1}$ M^{-1} cm^{-1}).

Preparation of {[Cu$_4${μ-(α-D-Glc-1P)}]$_2$(μ-D-lactobionate)-(bpy)$_4$(H$_2$O)$_2$](NO$_3$)$_3$}$_n$ (9). To a solution of **1a**·10H$_2$O (107 mg, 0.0590 mmol) in DMF (6 mL) was added D-lactobionic acid (44 mg, 0.12 mmol). The reaction mixture was stirred overnight. The solvent was then evaporated under reduced pressure, and the residue was extracted with methanol (6 mL). Over several days of slow evaporation of the solvent at room temperature, block-shaped blue crystals of {[Cu$_4${μ-(α-D-Glc-1P)}]$_2$(μ-D-lactobionate)(bpy)$_4$(H$_2$O)$_2$]-(NO$_3$)$_3$·5H$_2$O}$_n$ (**9**·5H$_2$O) were obtained in 29% yield (35 mg). Anal. Calcd for C$_{64}$H$_{89}$O$_{46}$N$_{11}$Cu$_4$P$_2$: C, 37.23; H, 4.35; N, 7.46. Found: C, 37.56; H, 4.25; N, 7.40. IR (KBr, cm^{-1}): 3377 (br), 1639 (s), 1611 (s), 1603 (s), 1576 (m), 1568 (m), 1474 (m), 1359 (s), 1140 (s), 1086 (s), 1053 (m), 1034 (m), 1020 (m), 942 (m), 772 (m). UV−vis (CH$_3$OH): λ_{max} 670 nm ($\epsilon = 2.04 \times 10^2$ M^{-1} cm^{-1}). CD (CH$_3$OH): λ_{max} 629 nm ($\Delta\epsilon = -2.57 \times 10^{-2}$ M^{-1} cm^{-1}), 778 nm (-6.05×10^{-2} M^{-1} cm^{-1}).

Preparation of [Cu(O$_2$CC(OH)$_2$CO$_2$)(bpy)] (10). Complex **7**·6H$_2$O (55 mg, 0.027 mmol) was dissolved in water (5 mL). The solution was heated at reflux for 3 h, and the reaction mixture was cooled to room temperature. The solution was allowed to stand for several days to gave blue crystals of [Cu(O$_2$CC(OH)$_2$CO$_2$)(bpy)] (**10**), which were collected, washed with Et$_2$O, and dried in vacuo (2.8 mg, 7% vs Cu; 14% vs sugar acid). Anal. Calcd for C$_{13}$H$_{10}$O$_6$N$_2$Cu: C, 44.14; H, 2.85; N, 7.92. Found: C, 43.92; H, 2.88; N, 7.91. IR (KBr, cm^{-1}): 1662 (s), 1641 (s), 1615 (s), 1453 (w), 1398 (m), 1294 (w), 1181 (s), 1049 (w), 1034 (w), 782 (s). From the mother liquor, blue crystals of [Cu$_2$(μ-C$_2$O$_4$)(bpy)$_2$(H$_2$O)$_2$]-(NO$_3$)$_2$ (**11**)^{32} were obtained (3.8 mg, 10% vs Cu and sugar acid) and were characterized by UV−vis and IR spectra and an X-ray crystallographic analysis.

X-ray Crystallography. Slow evaporation of aqueous and methanolic solutions afforded X-ray-quality crystals of **2**·15H$_2$O, **3**·2CH$_3$OH·0.5H$_2$O, **4**·6CH$_3$OH·H$_2$O, **5b**·CH$_3$OH, **6**·4H$_2$O, **7**·2H$_2$O, **8b**·4.25CH$_3$OH·2H$_2$O, **9**·2CH$_3$OH·2H$_2$O, and **10**, which were quickly coated with Paraton N oil and mounted on top of a glass

fiber at low temperature. Crystal data and experimental conditions are summarized in Tables 1 and 2. All data were collected at −120 °C on a Rigaku AFC8R/Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation using a rotating-anode X-ray generator. A total of 1440 (**3** and **10**) and 2160 (**2**, **4**, **5b**, **6**, **7**, **8b**, and **9**) oscillation images, covering a whole sphere of $2\theta < 55°$, were corrected with exposure rates of 96 (**3**), 128 (**4**, **5b**, **6**, **7**, **8b**, **9**, and **10**), and 240 s/deg (**2**) by the ω−scan method [$-70° < \omega < 110°$ (**2**, **3**, and **10**) and $-62° < \omega < 118°$ (**4**, **5b**, **6**, **7**, **8b**, and **9**)] with $\Delta\omega$ of 0.25°. The crystal-to-detector (70 × 70 mm) distance was set to 60 mm. The data were processed using the *Crystal Clear 1.3.5* program (Rigaku/MSC)^{35} and corrected for Lorentz−polarization and absorption effects.

The structures of complexes **3**, **4**, **5b**, **6**, **7**, **8b**, **9**, and **10** were solved by direct methods (SIR-92 and -97)^{36} and refined on F^2 with full-matrix least-squares techniques with *SHELXL-93* and *-97*.^{37} The structure of complex **2** was solved by DIRDIF(patty)^{38} and was refined on F^2 with *SHELXL-97*. In the refinement of **2**, all non-H atoms were refined with anisotropic thermal parameters. The C-bound H atoms were placed at ideal positions and fixed in the refinement. The O−H hydrogen atoms were not determined. In the refinement of **3**, the Cu, P, O, and N atoms, except those of solvent molecules, were refined anisotropically and other non-H atoms were refined with isotropic temperature factors. The positions of C−H hydrogen atoms were calculated and were fixed in the refinement. The O−H hydrogen atoms were not determined. In the refinement of **4** and **5b**, all non-H atoms were refined anisotropically, and the calculated C−H hydrogen atoms were refined with a riding model.

(35) *Crystal Clear 1.3.5: Operating Software for the CCD Detector System*; Rigaku and Molecular Structure Corp.: Tokyo, Japan, 2003.
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Table 2. Crystal Structure and Refinement Data for **6**·4H$_2$O, **7**·2H$_2$O, **8b**·4.25CH$_3$OH·2H$_2$O, **9**·2CH$_3$OH·2H$_2$O, and **10**

	6·4H$_2$O	**7**·2H$_2$O	**8b**·4.25CH$_3$OH·2H$_2$O	**9**·2CH$_3$OH·2H$_2$O	**10**
formula	C$_{64}$H$_{84}$N$_{10}$O$_{42}$P$_2$Cu$_4$	C$_{64}$H$_{76}$N$_{10}$O$_{40}$P$_2$Cu$_4$	C$_{62.25}$H$_{83}$N$_{10}$O$_{38.25}$P$_2$Cu$_4$	C$_{66}$H$_{91}$N$_{11}$O$_{45}$P$_2$Cu$_4$	C$_{13}$H$_{10}$N$_2$O$_6$Cu
fw	1981.54	1941.48	1899.52	2074.62	353.78
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P1$ (No. 1)	$P1$ (No. 1)	$P2_1$ (No. 4)	$P1$ (No. 1)	$P\bar{1}$ (No. 2)
a, Å	11.988(1)	13.0090(2)	14.1488(5)	13.9873(5)	8.4583(5)
b, Å	13.148(1)	14.9517(1)	19.0043(5)	14.5454(5)	9.3130(4)
c, Å	13.471(1)	12.5086(1)	14.4367(5)	13.0262(7)	9.7735(3)
α, deg	108.734(3)	78.772(8)		114.86(1)	60.63(1)
β, deg	93.762(3)	110.062(7)	96.0380(5)	117.134(10)	68.80(1)
γ, deg	99.933(4)	113.420(6)		67.444(10)	87.68(2)
V, Å^3	1963.9(3)	2092.3(1)	3860.3(2)	2078.7(3)	616.6(1)
Z	1	1	2	1	2
T, °C	−120.0	−120	−120	−120	−120.0
μ(Mo Kα), cm^{-1}	12.16	11.38	12.30	11.56	18.07
ρ_{calc}, g cm^{-3}	1.675	1.541	1.534	1.657	1.905
2θ range, deg	$6 < 2\theta < 55$	$6 < 2\theta < 55$	$6 < 2\theta < 55$	$6 < 2\theta < 55$	$6 < 2\theta < 52$
no. of obsd reflns	6637 [$I > 2\sigma(I)$]	6031 [$I > 2\sigma(I)$]	15 652 [$I > 2\sigma(I)$]	13 104 [$I > 2\sigma(I)$]	1646 [$I > 2\sigma(I)$]
no. of variables	1100	758	1054	1154	200
R1^a	0.052	0.081	0.054	0.055	0.035
wR2^b	0.133	0.227	0.160	0.141	0.088
GOF	1.06	1.03	1.11	1.10	1.12

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $[\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

In the refinement of **6**, **9**, and **10**, all non-H atoms were refined with anisotropic thermal parameters. The C−H hydrogen atoms were placed at ideal positions, and the O−H hydrogen atoms were found in the difference Fourier maps. All H atoms were fixed in the refinement. In the structure refinement of **7**, the Cu, P, O, and N atoms, except those of solvent water molecules and the disordered glucuronate part, were refined anisotropically, and other non-H atoms were refined with isotropic temperature factors. The C-2 and C-3 positions of the β-D-glucuronate moiety are disordered and refined isotropically with a two-site model, each having 0.5 occupancy ([C82O42C83O43], [C87O48C88O49]). The C−H hydrogen atoms, except those for the disordered glucuronate part, were placed at ideal positions and the O−H hydrogen atoms were not included in the refinement. In the refinement of **8b**, all non-H atoms, except those of the disordered solvent methanol, were refined anisotropically; the disordered methanol was refined isotropically with 0.25 multiplicity. The C−H hydrogen atoms were calculated, and the O−H ones were determined from difference Fourier syntheses. All H atoms were refined with a riding model, and the H atoms of the solvent molecules were not included. The absolute configurations for the structures of **2**−**4**, **5b**, **6**, **7**, **8b**, and **9** were determined by using the chiral C centers of the sugar moieties, α-D-Glc-1P, as internal references, which was further confirmed by consistency with Flack parameters. All calculations were carried out on a Pentium PC with Crystal Structure package 3.6[39] and a Silicon Graphics O2 station with a teXsan crystallographic software package.[40]

Supporting Information Available: X-ray crystallographic files in CIF format, ORTEP plots of **2**−**4**, **5b**, **6**, **7**, **8b**, **9**, **10**, and **1c**, ESI MS spectra of **1a**−**c**, **2**, and **7**, CD spectra of **3**, **4**, **5a**,**b**, **6**, **7**, **8a**,**b**, and **9**, temperature-dependent magnetic data for **3** and **5b**, theoretical expressions for the magnetic susceptibility data, and tables for some selected bond distances and angles of **2**−**4**, **5b**, **6**, **7**, **8b**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) *Crystal Structure 3.6: Crystal Structure Analysis Package*; Rigaku and Molecular Structure Corp.: Tokyo, Japan, 2003.
(40) *teXsan: Crystal Structure Analysis Package*; Rigaku and Molecular Structure Corp.: Tokyo, Japan, 1999.