



# Amino Alcohol Ligands

# Systematic Synthesis of Di-, Tri-, and Tetranuclear Homo- and Heterometal Complexes Using a Mononuclear Copper Synthon with a Tetradentate Amino Alcohol Ligand

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Abstract: The reaction of  $Cu(NO_3)_2 \cdot 3H_2O$  with an  $N_2O_2$  tetraamino alcohol, N,N-dibenzyl-N',N'-bis(2-hydroxydentate ethyl)ethylenediamine (H<sub>2</sub>L), afforded the mononuclear copper complex [Cu(H<sub>2</sub>L)(NO<sub>3</sub>)](NO<sub>3</sub>) (1), which has been used to construct a series of di-, tri-, and tetranuclear homo- and heterometallic complexes. Complex 1 dimerized in the presence of NEt<sub>3</sub> to form the  $Cu_2$  complex  $[Cu_2(HL)_2](NO_3)_2$  (2) by the deprotonation of one of the two hydroxy groups in the H<sub>2</sub>L ligand. The reaction of 1 with Cu(OCOH)<sub>2</sub> in the presence of NEt<sub>3</sub> afforded the  $Cu_3$  complex  $[Cu_3(HL)_2(OCOH)_2](NO_3)_2$  (5). The metalloligand  $\{Cu(HL)\}^+$  derived from 1 reacted with  $M(OAc)_2$  (M = Cu, Co, Zn, Ni) in the absence of NEt<sub>3</sub> to form the asymmetric CuM dinuclear complexes [CuM(HL)(OAc)(NO<sub>3</sub>)<sub>2</sub>] [M = Cu (**3a**), Co (3b), Zn (3c), Ni (3d)], whereas in the presence of NEt<sub>3</sub> a unit of M(OAc) was captured by two metalloligands to give the bent CuMCu trinuclear complexes  $[Cu_2M(HL)_2(OAc)_2(NO_3)](NO_3)$  [M =

## Introduction

The rationally designed synthesis of polynuclear transitionmetal complexes with intriguing topological structures is of substantial importance in inorganic chemistry because of their diverse applications as catalysts and in electronic, photochemical, and magnetic devices as well as in biological systems.<sup>[1]</sup> There are several strategies for synthesizing polynuclear metal complexes, including an approach involving the use of the socalled "metalloligands" as inorganic synthons, in other words, a method in which a complex of the M ion with a rationally designed multidentate ligand is bound to another metal ion M' by virtue of the bridging ability of the ligand.<sup>[2]</sup> In particular, the method is valuable for the synthesis of heterometal complexes, because one-pot syntheses based on self-assembly do not always afford the desired heterometal MM' complexes select-

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ively.<sup>[3]</sup> There are many examples of metal complexes with N<sub>2</sub>O<sub>2</sub> tetradentate Schiff-base and N<sub>2</sub>S<sub>2</sub> aminothiolate ligands that have been used as metalloligands to synthesize heterometal complexes.<sup>[4]</sup> However, amino alcohol based metalloligands are limited to a few examples incorporating *N*-glycosyl polyamines and aminophenol ligands,<sup>[5]</sup> in spite of the fact that *N*-alkylated diethanolamine ligands (Scheme 1, a) are widely used for the synthesis of polynuclear metal complexes by one-pot self-assembly methods.<sup>[6–9]</sup> The two alkoxide units formed in N-alkylated diethanolamine ligands by the deprotonation of the hydroxy groups under basic reaction conditions are able to bridge two or three metal ions to construct polynuclear complexes. In this regard, when mononuclear complexes supported by N-alkylated diethanolamine ligands in the diprotonated form are stabilized, they must be feasible metalloligands for the synthesis of heterometallic complexes due to the preserved bridging ability through deprotonation of two hydroxy groups. With the aim of exploring new metalloligands, we have synthesized a new N<sub>2</sub>O<sub>2</sub> tetradentate amino alcohol, N,N-dibenzyl-N',N'-bis(2hydroxyethyl)ethylenediamine (H<sub>2</sub>L; Scheme 1, b), to stabilize divalent mononuclear complexes with the  $\{M(H_2L)\}^{2+}$  synthon by introducing an extra nitrogen donor into the N-alkylated diethanolamine.

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Scheme 1. Structures of (a) *N*-alkylated diethanolamine and (b) H<sub>2</sub>L.

In this study, a mononuclear copper(II) complex with the H<sub>2</sub>L ligand was prepared and characterized as  $[Cu(H_2L)(NO_3)](NO_3)$ (1) containing two hydroxy groups. Complex 1 was found to be an effective metalloligand for the construction of a variety of di-, tri-, and tetranuclear homo- and heterometal complexes 2– 8 with the assistance of auxiliary bridging ligands:  $[Cu_2(HL)_2](NO_3)_2$  (2),  $[CuM(HL)(OAc)(NO_3)_2]$  (3: M = Cu, Co, Zn, Ni),  $[Cu_2M(HL)_2(OAc)_2(NO_3)](NO_3)$  (4: M = Cu, Co, Mn),  $[Cu_3(HL)_2(OCOH)_2](NO_3)_2$  (5),  $[Cu_2M(HL)_2\{(PhO)_2PO_2\}_2(MeOH)_n]$ -(NO<sub>3</sub>)<sub>2</sub> (7: n = 0, M = Cu; n = 2, M = Co, Mn), and  $[Cu_2M_2(HL)_2\{(PhO)PO_3\}_2(NO_3)_2]$  (8: M = Co, Zn). Their systematic synthesis and characterization are described with a focus on the flexible mononuclear synthon  $\{Cu(HL)\}^+$  as a new metalloligand.

### **Results and Discussion**

#### Synthesis of [Cu(H<sub>2</sub>L)(NO<sub>3</sub>)](NO<sub>3</sub>) (1) and Its Transformation into Cu<sub>2</sub> and Cu<sub>3</sub> Complexes

The N<sub>2</sub>O<sub>2</sub> tetradentate ligand H<sub>2</sub>L (Scheme 1, b) was synthesized in good yield by the reaction of *N*,*N*-dibenzyl-2-chloroethanamine hydrochloride with 2,2'-iminodiethanolamine in the presence of Na<sub>2</sub>CO<sub>3</sub> at reflux in acetonitrile.

The reaction of  $H_2L$  with 1 equiv. of  $Cu(NO_3)_2 \cdot 3H_2O$  in MeOH at room temperature afforded blue crystals formulated as  $[Cu(H_2L)(NO_3)](NO_3)$  (1) in 86 % yield. The structure of 1 was determined by X-ray crystallography (Figure 1 and Table S7 in the Supporting Information). The geometry around the copper ion is distorted square-pyramidal (trigonal-bipyramidal distortion parameter,  $\tau = 0.37$ )<sup>[10a]</sup> with the O2 hydroxy oxygen occupying the apical site and the hydroxy O1, the amino nitrogen N1 and N2 atoms of H<sub>2</sub>L, and a nitrate oxygen atom O3 forming the basal plane. According to the classification of the coordination mode of the nitrate ion utilizing two parameters, the difference between the two M–O<sub>nitrate</sub> bond lengths ( $\Delta d$ ) and the M–O–N bond angles  $(\Delta \theta)$ ,<sup>[10b]</sup> the nitrate coordinates to the Cu ion through the O3 oxygen atom [Cu-O3 1.852(2) Å, Cu-O5 2.762(4) Å] in monodentate mode ( $\Delta d = 0.910$  Å,  $\Delta \theta = 45.6^{\circ}$ ). The N<sub>2</sub>O<sub>2</sub> ligand surrounds the copper center in a tetradentate coordination mode in the diprotonated form H<sub>2</sub>L: Cu-N1 1.880(3) Å, Cu-O2 2.097(2) Å, Cu-N2 2.187(2) Å, and Cu-O1 2.232(3) Å. The O1 and O2 hydroxy groups are involved in two hydrogen bonds to the NO<sub>3</sub><sup>-</sup> counter ion [O1...O7 2.741(4), O2···O6\* 2.846(4) Å] to form a 1D network chain (see Figure S1 in the Supporting Information). It should be noted that the diprotonated form observed in 1 is relatively rare in the case of Nsubstituted diethanolamine ligands,<sup>[9g,11]</sup> and consequently the

mononuclear  $\{Cu(H_2L)\}^{2+}$  synthon seems to be a useful metalloligand for constructing multinuclear complexes through the deprotonation of the two hydroxy groups, as evidenced by its transformation into di- and trinuclear copper(II) complexes (see below).



Figure 1. ORTEP diagram of the complex cation of **1** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C-H hydrogen atoms have been omitted for clarity.

When complex **1** was treated with 1.5 equiv. of  $NEt_{3}$ , the dinuclear copper complex [Cu<sub>2</sub>(HL)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (2) was obtained in 80 % yield (Scheme 2). The structure of 2 (Figure 2 and Table S8 in the Supporting Information) has a crystallographically imposed inversion center and is comprised of a [Cu<sub>2</sub>O<sub>2</sub>] rhombic core supported by two HL- ligands. The copper ions exhibit a slightly distorted square-pyramidal geometry ( $\tau = 0.10$ ) with the O2 oxygen atom occupying the apical site. The Cu-O and Cu-N distances involved in the basal plane range from 1.917(1) to 2.049(1) Å, whereas the axial Cu-O2 bond is elongated [2.310(2) Å]. The N<sub>2</sub>O<sub>2</sub> ligand exists in the mono-deprotonated form HL<sup>-</sup> with the alkoxo O1 atom bridging two copper ions [Cu---Cu 2.991(1) Å, Cu-O1 1.953(1) Å, Cu\*-O1 1.917(1) Å, Cu-O1–Cu\* 101.22(5)°, O1–Cu–O1\* 78.78(5)°] to form the  $[Cu_2O_2]$ plane, which is usually observed in dinuclear complexes supported by N-alkylated diethanolamine ligands.<sup>[6h,7c,12]</sup> The axial



Scheme 2. Structure of 1 and its transformation into  $[Cu_2(HL)_2](NO_3)_2$  (2) and  $[Cu_3(HL)_2(OCHO)_2](NO_3)_2$  (5).





O2 hydroxy group is involved in a hydrogen bond to a  $NO_3^-$  counter ion [O2...O3 2.715(2) Å].



Figure 2. ORTEP diagram of **2** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C–H hydrogen atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines (O2–O3 and O2\*–O3\*).

The reaction of 1 with 1 equiv. of Cu(OCHO)<sub>2</sub>·4H<sub>2</sub>O in the presence of NEt<sub>3</sub> resulted in the formation of the linear Cu<sub>3</sub> complex [Cu<sub>3</sub>(HL)<sub>2</sub>(OCHO)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (5) in 90 % yield (Scheme 2). The structure of 5 was revealed by X-ray crystallography (Figure 3 and Table S11 in the Supporting Information) to possess a crystallographically imposed inversion center at the Cu2 atom. The Cu2 center adopts an axially elongated octahedral geometry with the µ-alkoxide O1 (O1\*) and bridging formate O4 (O4\*) atoms located in the equatorial plane [Cu2-O1 1.932(1), Cu2-O4 1.965(2) Å]. The axial positions are weakly occupied by the O7 (O7\*) atoms of nitrate anions [Cu2···O7 2.732(2) Å], which are also involved in hydrogen bonding with the hydroxy O2 (O2\*) oxygen atoms of HL<sup>-</sup> [O2···O7 2.692(2) Å]. The Cu1 ion exhibits square-pyramidal geometry ( $\tau = 0.19$ ) with the protonated O2 atom in the axial position. The apical Cu1-O2 bond length of 2.280(2) Å is longer than those to the basal donor atoms [Cu-O1 = 1.948(1) Å, Cu-O3 1.949(2) Å, Cu-N1 2.004(2) Å, Cu-N2 2.078(1) Å]. The HL<sup>-</sup> ligand coordinates to two copper ions similarly to **2**. The core structure of  $Cu_3(\mu-alkoxo)_2(\eta^1,\eta^1,\mu_2$ formate)<sub>2</sub> has been observed in  $[Cu_3(OCOH)_4(TEAH_2)_2]$  (TEAH<sub>3</sub> =



Figure 3. ORTEP diagram of **5** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C–H hydrogen atoms and phenyl rings have been omitted for clarity. Hydrogen bonds are shown as dashed lines (O2–O7 and O2\*–O7\*).

triethanolamine),<sup>[13]</sup> and related linear tricopper complexes with the Cu<sub>3</sub>(µ-alkoxo)<sub>2</sub>(η<sup>1</sup>,η<sup>1</sup>,µ<sub>2</sub>-acetate)<sub>2</sub> core have also been reported.<sup>[13,14]</sup> It should be noted that similar reactions with other metal salts such as M(OCHO)<sub>2</sub> (M = Co, Mn, Ni) did not afford the corresponding mixed-metal trinuclear complexes.

# Synthesis of the CuM and CuMCu Homo- and Heterometal Complexes $[CuM(HL)(OAc)(NO_3)_2]$ (3: M = Cu, Co, Zn, Ni) and $[Cu_2M(HL)_2(OAc)_2](NO_3)_2$ (4: M = Cu, Co, Mn) from 1

The treatment of **1** with 1 equiv. of  $M(OAc)_2$  (M = Cu, Co, Zn, Ni) in the absence of NEt<sub>3</sub> in MeOH at room temperature afforded the dinuclear complexes  $[CuM(HL)(OAc)(NO_3)_2]$  [M = Cu (3a), Co (3b), Zn (3c), Ni (3d)] in yields of 67-90 % (Scheme 3). The crystal structures of 3a-3d are isomorphous and consist of a CuM heterodimetallic core supported by a mono-deprotonated HL<sup>-</sup> ligand, one acetate, and two NO<sub>3</sub><sup>-</sup> ions (see Figure 4 for **3b** and Figures S2–S4 in the Supporting Information for **3a**, 3c, and 3d). The geometry around the Cu1 atom is distorted square-pyramidal ( $\tau = 0.29$  for **3a–3c**, 0.30 for **3d**) with the hydroxy O2 atom in the axial position [Cu1-O2 2.282(2) Å (3a), 2.290(2) Å (3b), 2.294(2) Å (3c), 2.319(3) Å (3d)]. The distances to the basal donors (O1, O3, N1, N2) fall in the normal range of 1.928(2)-2.051(2) Å (3a), 1.918(2)-2.059(2) Å (3b), 1.915(2)-2.053(2) Å (3c), and 1.912(2)-2.059(2) Å (3d). The M2 centers adopt a highly distorted octahedral geometry with six M2-O distances of 1.887(1)-2.503(2) Å (**3a**), 1.938(1)-2.252(2) Å (**3b**), 1.925(2)–2.369(3) Å (**3c**), and 1.941(2)–2.113(4) Å (**3d**). Two nitrate anions chelate the M2 ion asymmetrically, with each having one short and one long bond. The two nitrate ions in **3a**  $[(\Delta d, \Delta \theta) = (0.492 - 0.526 \text{ Å}, 22.1 - 23.7^{\circ})]^{[10b]}$  are anisodentate due to a Jahn-Teller effect at the Cu2 center, whereas those in **3b–3d**  $[(\Delta d, \Delta \theta) = (0.001 - 0.298 \text{ Å}, 0.3 - 13.0^{\circ})]$  are bidentate.<sup>[10b]</sup> The mono-deprotonated HL<sup>-</sup> ligand bridges the two metal centers in a structure similar to that in 2. The Cu1 and M2 ions are bridged by the alkoxo O1 atom of the HL<sup>-</sup> ligand and an acetate in  $\eta^1, \eta^1, \mu_2$  mode and span 3.3713(4) Å (**3a**), 3.3850(4) Å (**3b**), 3.353(1) Å (3c), and 3.398(1) Å (3d) with Cu1-O1-M2 = 124.17(8)° (3a), 122.76(7)° (3b), 121.71(8)° (3c), and 123.7(1)° (3d). Several examples of related asymmetric dinuclear copper complexes with the  $Cu_2(\mu-alkoxo)(\eta^1,\eta^1,\mu_2-carboxylate)$  unit have been reported.<sup>[15]</sup> However, mixed-metal dinuclear complexes CuM (M = Co, Zn, Ni) are limited to a few examples, and in all cases the two metal centers are triply bridged by (µalkoxo)<sub>2</sub>( $\eta^1$ , $\eta^1$ , $\mu_2$ -carboxylate) or ( $\mu$ -alkoxo)( $\eta^1$ , $\eta^1$ , $\mu_2$ -carboxylate)<sub>2</sub> units.<sup>[16]</sup>

When **1** was treated with 1 equiv. of  $M(OAc)_2$  (M = Cu, Co, Mn) in the presence of NEt<sub>3</sub> in MeOH at room temperature, the CuMCu trinuclear complexes  $[Cu_2M(HL)_2(OAc)_2](NO_3)_2$  [M = Cu (**4a**), Co (**4b**), Mn (**4c**)] were obtained selectively in yields of 90, 80, and 93 % (with respect to **1**), respectively. When the ratio of  $M(OAc)_2$  (M = Cu, Co, Mn) was reduced to 0.5 equiv., **4a**-**c** were isolated in lower yields although the reasons for this are not yet clear.

The crystal structures of 4a-4c are isomorphous and comprised of a trinuclear Cu<sub>2</sub>M core supported by two mono-de-







Scheme 3. Preparation of  $[CuM(HL)(OAc)(NO_3)_2]$  (3: M = Cu, Co, Zn, Ni) and  $[Cu_2M(HL)_2(OAc)_2](NO_3)_2$  (4: M = Cu, Co, Mn) from 1.



Figure 4. ORTEP diagram of  $[CuCo(HL)(OAc)(NO_3)_2]$  (**3b**) with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C–H hydrogen atoms have been omitted for clarity.

protonated HL<sup>-</sup> ligands and two acetate and two nitrate anions (see Figure 5 for 4c and Figures S5 and 6 in the Supporting Information for 4a,b). The structures were refined with a disorder model in which the M(OAc)<sub>2</sub>(NO<sub>3</sub>) unit and the hydrogenbonded  $NO_3^-$  anion occupy two sites, each related by  $C_i$  symmetry with 0.5 occupancy (one set of disordered structures is illustrated for clarity). Complexes 4a-4c are apparently derived from the substitution of one of the two nitrate ions in 3a-3c by the {Cu(OAc)(HL)} fragment. Owing to the presence of two hydrogen bonds between the O10\* atom of the nitrate ion and the hydroxy O2\* and O3 atoms of HL<sup>-</sup> [O10\*...O2\* 2.6786(2) Å (4a), 2.625(1) Å (4b), 2.6635(8) Å (4c); O10\*--O3 2.6786(2) Å (4a), 2.625(1) Å (4b), 2.6635(8) Å (4c)], the three metal ions of CuMCu are arranged in a bent structure [Cu1...M2 3.525(1) Å (4a), 3.523(2) Å (4b), 3.569(1) Å (4c); Cu1\*---M2 3.3085(8) Å (4a), 3.352(2) Å (4b), 3.455(1) Å (4c); Cu1...Cu1\* 6.0710(6) Å (4a), 6.107(2) Å (4b), 6.219(2) Å (4c); Cu1-M2-Cu1\* 125.31(3)° (4a),

125.32(2)° (**4b**), 124.60(3)° (**4c**)]. The Cu1····M2 distances [3.523(2)–3.569(1) Å] are significantly longer than those of Cu1\*···M2 [3.3085(8)–3.455(1) Å], which is related to the larger angles of O4–C21–O6 [122.7(4)–124.0(3)°] and Cu1–O1–M2 [120.3(5)–124.1(3)°] compared with those of O4–C21–O5 [120.8(5)–122.4(4)°] and Cu1\*–O3\*–M2 [108.3(1)–110.0(1)°].



Figure 5. ORTEP diagram of 4c with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C–H hydrogen atoms and phenyl rings have been omitted for clarity. Hydrogen bonds are shown as dashed lines (O3–O10\* and O2\*–O10\*).

The environment around the Cu1 center is similar to those observed in **3a**–**3c**, but it has a distorted trigonal-bipyramidal geometry [ $\tau$  = 0.61 (**4a**), 0.65 (**4b**), 0.68 (**4c**)] with the O4 and N1 atoms occupying the axial sites. The bond lengths involving the Cu1 atom are in the normal range of 1.913(3)–2.120(4) Å (**4a**), 1.921(3)–2.117(3) Å (**4b**), and 1.916(2)–2.119(2) Å (**4c**). The M2 ions exhibit slightly distorted octahedral structures with six M2–O bond lengths of 1.906(6)–2.406(7) Å (**4a**), 1.967(5)–2.337(5) Å (**4b**), and 1.973(11)–2.363(5) Å (**4c**), and they are connected to the two Cu ions through two  $\eta^1, \eta^1, \mu^2$ -acetate and two alkoxides of HL<sup>-</sup>. The O7 and O8 atoms of a nitrate are bound to the M2 ion in bidentate fashion [( $\Delta d$ ,  $\Delta \theta$ ) = (0.010–0.170 Å, 2.5–7.8°)].<sup>[10b]</sup>

Although several examples of bent trinuclear copper complexes with Cu<sub>3</sub>(µ-alkoxo)<sub>2</sub>(η<sup>1</sup>,η<sup>1</sup>,µ<sub>2</sub>-carboxylate)<sub>2</sub> moieties have been reported,<sup>[17]</sup> bent mixed-metal complexes with Cu<sub>2</sub>M(µ-alkoxo)<sub>2</sub> cores (M = Co,<sup>[18]</sup> Mn<sup>[19]</sup>) are limited to a few examples and, furthermore, no angular mixed-metal trinuclear complex with a Cu<sub>2</sub>M(µ-alkoxo)<sub>2</sub>(η<sup>1</sup>,η<sup>1</sup>,µ<sub>2</sub>-carboxylate)<sub>2</sub> core has been reported, based on a CSD analysis.

# Phosphate-Bridged $Cu_2M$ (M = Cu, Co, Mn) and $Cu_2M_2$ (M = Co, Zn) Complexes by Using the {Cu(HL)}<sup>+</sup> Synthon

In the light of the significant influence of carboxylate ligands on the trinuclear metal alignment, the phosphate anion  $(PhO)_2PO_2^-$  was introduced in place of the carboxylate ligand. The reaction of **1** with 1 equiv. of  $(PhO)_2PO(OH)$  in the presence



of NEt<sub>3</sub> in MeOH at room temperature resulted in the formation of the mononuclear complex  $[Cu(H_2L){(PhO)_2PO_2}](NO_3)$  (6) in 85 % yield (Scheme 4), with the coordinated nitrate anion of **1** replaced by the phosphate anion  $(PhO)_2PO_2^{-}$  (Figure 6 and Table S12 in the Supporting Information). The copper ion adopts a distorted trigonal-bipyramidal geometry ( $\tau = 0.52$ ) with the axial sites occupied by the O3 oxygen atom of the diphenyl phosphate and the N1 amino nitrogen atom [O3-Cu-N1 178.79(10)°]. The P1–O4 distance [1.470(2) Å] is marginally shorter than the P1-O3 distance [1.497(3) Å], with the two P-O<sub>Ph</sub> distances being considerably longer [1.599(2), 1.607(3) Å]. The O1 hydroxy group is involved in a hydrogen bond with an oxygen atom of the counter nitrate ion [O1...O7 2.716(3) Å], and two stronger hydrogen bonds are established between adjacent mononuclear units through the O2 hydroxy group and the P–O oxygen of O4 [O2····O4\* 2.659(3) Å] to form a dimeric structure (see Figure S7).



Scheme 4. Preparation of [Cu(HL){(PhO)<sub>2</sub>PO<sub>2</sub>}]NO<sub>3</sub> (6), [Cu<sub>2</sub>M(HL)<sub>2</sub>- $\{(PhO)_2PO_2\}_2](NO_3)_2$  (7: M = Cu, Mn, Co), and  $[Cu_2M_2(HL)_2\{(PhO)PO_3\}_2(NO_3)_2]$ (8: M = Co, Zn).

The mononuclear complex **6** is also a useful precursor of Cu<sub>2</sub>M heterotrinuclear complexes and reacted with 0.5 equiv. of  $M(NO_3)_2$  (M = Cu, Co, Mn) in the presence of NEt<sub>3</sub> in MeOH at room temperature to afford the linear homo- and heterometallic trinuclear complexes [Cu<sub>3</sub>(HL)<sub>2</sub>{(PhO)<sub>2</sub>PO<sub>2</sub>}<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (7a) and  $[Cu_2M(HL)_2{(PhO)_2PO_2}_2(MeOH)_2](NO_3)_2$  [M = Co (7b), Mn (7c)] in yields of 87, 67, and 14 %, respectively (Scheme 4). Complexes 7a-c were also synthesized from the reactions of 4a-c with 2 equiv. of (PhO)<sub>2</sub>PO(OH) in MeOH in yields of 76, 84, and 82 %, respectively.

Complexes 7a-c are composed of linear CuMCu metal ions (M = Cu, Co, Mn) bridged by two  $\eta^1, \eta^1$ -(diphenyl phosphate) ligands and two mono-deprotonated HL<sup>-</sup> ligands (see Figures 7 and 8 for 7a,b, respectively, and Figure S8 in the Supporting Information for 7c). The structures clearly indicate that the auxiliary bridging ligands are crucial to determine the CuMCu trinuclear structures; the linear structures of **7a-c** with bridging phosphates can be contrasted with the bent structures of 4a-





Figure 6. ORTEP diagram of the complex cation of **6** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level. and the C-H hydrogen atoms have been omitted for clarity.

c bridged by acetate ligands. The Cu1---Cu2 distance [3.304(1) Å] in **7a** is significantly shorter than the corresponding distances in **7b**,c [3.6051(4) Å (**7b**), 3.6544(8) Å (**7c**)] because of the absence of axial MeOH ligands at the central Cu2 ion. In the Cu<sub>3</sub> complex 7a, the central Cu<sub>2</sub> center adopts a squareplanar geometry ligated by pairs of phosphate and alkoxo oxygen atoms (O1, O1\*, O4, and O4\*) in a trans configuration [Cu2-O1 1.941(4) Å, Cu2–O4 1.946(4) Å]. The terminal Cu ions are pentacoordinated by the N<sub>2</sub>O<sub>2</sub> donors of HL<sup>-</sup> and one oxygen atom of the phosphate bridge with  $\tau = 0.33$ . The protonated O2 oxygen atom of HL<sup>-</sup> is involved in a hydrogen bond with an oxygen atom of the outer nitrate ion [O2...O7 2.704(5) Å]. The nitrate ion is located far from the axial positions of the Cu2 center, although a weak axial interaction is observed in 5; the structural difference between 7a and 5 may be ascribed to the steric bulkiness of the diphenyl phosphate in comparison with formate. Instead of the nitrate ion in 5, the O2 atom is located at the axial position of Cu2 with a long distance of Cu2...O2 [2.997(3) Å]. As a result of the weak interaction between the Cu2 and O2 atoms, the Cu1-O1-Cu2 angle of 116.0(2)° in 7a is meaningfully smaller than that in 5 [124.56(8)°]. These structural differences may lead to the Cu1---Cu2 distance of 3.304(1) Å being appreciably shorter than that of 5 [3.4342(6) Å].

The structures of **7b,c** are isomorphous and similar to that of 7a except for the coordination of two methanol molecules to the central M2 ion, which results in an octahedral structure at this site with six normal M2-O bond lengths [2.018(1)-2.176(2) Å (7b), 2.120(2)–2.220(3) Å (7c); Figure 8]. The terminal copper ions adopt a distorted square-pyramidal geometry with  $\tau = 0.42$  (**7b**) and 0.43 (**7c**). The distances of Cu1–N [2.006(2)– 2.116(2) Å (7b), 1.987(3)-2.113(3) Å (7c)] and Cu1-O [1.942(2)-2.260(2) Å (**7b**), 1.934(2)–2.269(3) Å (**7c**)] are comparable to those in 7a. The two protonated O2 and O7 oxygen atoms are involved in hydrogen bonds with the O9 and O8 atoms of the nitrate ion [O2•••O9 2.765(2) Å (7b), 2.771(4) Å (7c); O7•••O8 2.729(2) Å (7b), 2.714(4) Å (7c)]. As a result of the presence of







Figure 7. ORTEP diagram of **7a** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C–H hydrogen atoms and phenyl rings have been omitted for clarity. Hydrogen bonds are shown as dashed lines (O2–O7 and O2\*–O7\*).

axial MeOH ligands at the M2 center, the Cu1--M2 distances [3.6051(4) (**7b**), 3.6544(8) (**7c**)] are significantly longer than those in **7a** [3.304(1) Å] and, as a result, the Cu1-O1-M2 angles of 130.59(7)° (**7b**) and 128.6(1)° (**7c**) are larger than those in**7a** [116.0(2)°]. There are several examples of homometallic trinuclear complexes bridged by phosphate or phosphonate ligands,<sup>[20]</sup> however, mixed-metal trinuclear complexes are limited to only a few examples with the metal combinations V<sub>2</sub>M (M = Mn, Co, Ni, Fe).<sup>[20a]</sup>



Figure 8. ORTEP diagram of **7b** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C-H hydrogen atoms and phenyl rings have been omitted for clarity. Hydrogen bonds are shown as dashed lines (O2–O9, O7–O8, O2\*–O9\*, and O7\*–O8\*).

With the aim of assembling more than three metal ions, the phosphate mono ester (PhO)PO(OH)<sub>2</sub> was utilized instead of (PhO)<sub>2</sub>PO(OH). The treatment of **1** with 1 equiv. of  $M(OAc)_2$  (M = Co, Zn) and (PhO)PO(OH)<sub>2</sub> in the presence of NEt<sub>3</sub> in MeOH

gave the Cu<sub>2</sub>M<sub>2</sub> mixed-metal tetranuclear complexes  $[Cu_2M_2(HL)_2\{(PhO)PO_3\}_2(NO_3)_2]$  [M = Co (8a), Zn (8b)] in yields of 87 and 4 %, respectively (Scheme 4). It should be noted that a similar reaction of 1 with Cu(OAc)<sub>2</sub> did not afford any analogous tetranuclear copper complexes. Complexes 8a,b consist of Cu<sub>2</sub>M<sub>2</sub> ions supported by two HL<sup>-</sup> ligands, two phenyl phosphates, and two nitrate ions, possessing a crystallographically imposed inversion center (Figure 9 and Figure S9 in the Supporting Information). The core structures are composed of three fused macrocyclic rings containing a central [M2O4P2] eightmembered ring flanked at each side by two outer [CuMO<sub>3</sub>P] six-membered rings. The central  $[M_2O_4P_2]$  ring is formed by two tetracoordinate M ions and two PhOPO<sub>3</sub><sup>2-</sup> ligands, and the two outer [CuMO<sub>3</sub>P] rings are formed by two {Cu(HL)}<sup>-</sup> synthons, which are approximately perpendicular to the central ring and lie in opposite directions, resulting in a staircase-like core structure. Although a similar core structure has been observed in  $[Cu_4Cl_2(bpy)_4(PCh^-)_2](ClO_4)_4$  [PCh<sup>-</sup> = 2-(trimethylammonio)ethyl phosphate],<sup>[23]</sup> mixed-metal tetranuclear complexes bridged by phosphate ligands in  $\eta^1, \eta^1, \eta^1, \mu_3$  mode are limited to a few examples containing  $V_2M_2$  (M = Mn, Co, Cu, Zn) ions.<sup>[24]</sup> Hence, 8 is the first  $Cu_2M_2$  (M = Co, Zn) mixed-metal structure with  $\eta^1, \eta^1, \eta^1, \mu_3$ -phosphate bridges. The geometry around the M2 ions is tetrahedral with  $\tau_4$  values of 0.93 (8a) and 0.93 (8b),<sup>[21]</sup> and that around the Cu1 ions is distorted square-pyramidal [ $\tau$  = 0.18 (8a), 0.18 (8b)] with the hydroxy O2 atom of HL- at the apical site as observed in 2-5. The protonated O2 atom is involved in an intramolecular hydrogen bond with the phosphate O4\* atom [O2•••O4\* 2.765(2) Å (8a), 2.771(4) Å (8b)]. The phenyl phosphate (PhO)PO32- bridges one Cu ion and two M ions in a  $\eta^1, \eta^1, \eta^1, \mu_3$  fashion. The P–O distances [av. 1.516 Å (**8a**), 1.516 Å (8b)] for the metal bound oxygens are shorter than the P-O<sub>Ph</sub> bonds [1.616(2) Å (8a), 1.632(3) Å (8b)], which has been observed in related metal complexes bridged by phosphate or phosphonate ligands in the  $\eta^1, \eta^1, \eta^1, \mu_3$  form.<sup>[22]</sup>



Figure 9. ORTEP diagram of **8a** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40 % probability level, and the C–H hydrogen atoms and phenyl rings have been omitted for clarity. Hydrogen bonds are shown as dashed lines ( $O2-O4^*$  and  $O4-O2^*$ ).







Figure 10. Systematic preparation of di-, tri-, and tetranuclear homo- and heterometal complexes with Cu<sub>2</sub> (**2**), CuM (**3**: M = Cu, Co, Zn, Ni), Cu<sub>3</sub> (**5**), *bent*-CuMCu (**4**: M = Cu, Co, Mn), *linear*-CuMCu (**7**: M = Cu, Co, Mn), and Cu<sub>2</sub>M<sub>2</sub> (**8**: M = Co, Zn) cores utilizing the mononuclear {Cu(HL)}<sup>-</sup> synthon as a metalloligand.

### Conclusions

We have synthesized a new N2O2 amino alcohol, N,N-dibenzyl-N', N'-bis(2-hydroxyethyl)ethylenediamine (H<sub>2</sub>L), which acts as a flexible tetradentate ligand with two intact hydroxy groups and forms the mononuclear copper complex [Cu(H<sub>2</sub>L)(NO<sub>3</sub>)](NO<sub>3</sub>) (1). Deprotonation of 1 generated the mononuclear {Cu(HL)}synthon, which has proven an effective metalloligand for the systematic and selective synthesis of novel di-, tri-, and tetranuclear homo- and heterometal complexes with various combinations of metal ions to form  $Cu_2$  (2), CuM (3: M = Cu, Co, Zn, Ni),  $Cu_3$  (5), bent- $Cu_2M$  (4: M = Cu, Co, Mn), linear- $Cu_2M$  (7: M = Cu, Co, Mn), and  $Cu_2M_2$  (8: M = Co, Zn) cores (Figure 10). The pentacoordinated copper metalloligand in 2-8 exhibits a variety of geometrical structures from square-pyramidal to distorted trigonal-bipyramidal with  $\tau$  values of 0.10–0.68, ascribable to the flexible nature of the  $N_2O_2$  ligand. In the various structures of 2-8, auxiliary bridging ligands, such as acetate, formate, and mono- and diphenyl phosphate ligands, have a significant influence on the metal alignments. The present results will be very useful for developing the systematic expansion of homo- and heterometallic multinuclear complexes by utilizing so-called "metalloligands". We are now attempting to further deprotonate the {Cu(HL)}<sup>-</sup> synthon to create larger heterometal architectures by finely designed techniques.

### **Experimental Section**

**General:** All chemicals were purchased and used without further purification.  ${}^{1}$ H and  ${}^{13}$ C NMR spectra were recorded with a JEOL

JMN-AL400 spectrometer at 400 and 100 MHz, respectively. IR spectra were recorded as KBr pellets with a Jsaco FT/IR-410 spectrometer.

*N,N*-Dibenzyl-*N',N'*-bis(2-hydroxyethyl)ethylenediamine (H<sub>2</sub>L): A mixture of *N*,*N*-dibenzyl-2-chloroethanamine hydrochloride (22.3 g, 75 mmol), 2,2'-iminodiethanolamine (11.8 g, 113 mmol), and Na<sub>2</sub>CO<sub>3</sub> (22.3 g, 211 mmol) in CH<sub>3</sub>CN (150 mL) was heated at reflux for 13 d. The resultant solution was filtered and dried in vacuo. The residue was extracted with CHCl<sub>3</sub> and washed with H<sub>2</sub>O. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> to afford the product in 93 % yield (23.9 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.26–7.13 (m, 5 H), 3.48 (s, 4 H), 3.39 (t, *J* = 5 Hz, 4 H), 2.57 (t, *J* = 6 Hz, 2 H), 2.46 (t, *J* = 5 Hz, 4 H), 2.43 (t, *J* = 6 Hz, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.0, 129.2, 128.3, 127.1, 59.6, 58.9, 56.9, 52.4, 51.9 ppm.

[**Cu<sub>2</sub>(HL)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (2):** A solution of **1** (515 mg, 1.0 mmol) and NEt<sub>3</sub> (156 mg, 1.5 mmol) was stirred at room temperature for 1 h. The resulting green precipitate was filtered off and crystallized from MeOH and diethyl ether mixed solvent to afford green crystals of **2** (401 mg, 89 %). Complex **2** was also obtained in 80 % yield by the reaction of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.0 mmol), H<sub>2</sub>L (1.0 mmol), and NEt<sub>3</sub> (1.5 mmol) in MeOH (5 mL). IR (KBr):  $\tilde{v} = 1384$  (s), 1342 (m), 1299 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 658 (228), 264 nm





 $(6.43\times\,10^3~{\rm M}^{-1}~{\rm cm}^{-1}).~C_{40}H_{54}Cu_2N_6O_{10}$  (905.99): calcd. C 53.03, H 6.01, N 9.28; found C 52.63, H 5.77, N 9.20.

**[Cu<sub>2</sub>(HL)(OAc)(NO<sub>3</sub>)<sub>2</sub>] (3a):** Cu(OAc)<sub>2</sub> (36.4 mg, 0.2 mmol) was added to a solution of **1** (104 mg, 0.20 mmol) in MeOH (5 mL). The resulting solution was stirred at room temperature for 1 h. Addition of diethyl ether (45 mL) afforded blue crystals of **3a** (116 mg, 90 %). IR (KBr):  $\tilde{v} = 1558$  (s), 1484 (s), 1471 (s), 1384 (s), 1288 (s), 1062 (m), 1016 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 731 (2.30 × 10<sup>2</sup>), 266 nm (6.40 × 10<sup>3</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>22</sub>H<sub>30</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>10</sub> (637.59): calcd. C 41.44, H 4.74, N 8.79; found C 41.29, H 4.77, N 8.73.

**[CuZn(HL)(OAc)(NO<sub>3</sub>)<sub>2</sub>] (3c):** A procedure similar to that for **3a**, using **1** (104 mg, 0.20 mmol) and Zn(OAc)<sub>2</sub> (36.5 mg, 0.20 mmol), afforded blue crystals of **3c** (110 mg, 85 %). IR (KBr):  $\tilde{v} = 1560$  (s), 1492 (s), 1473 (m), 1444 (s), 1384 (s), 1301 (s), 1288 (m) cm<sup>-1</sup>. UV/ Vis (MeOH):  $\lambda_{max}$  (ε) = 726 (1.60 × 10<sup>2</sup>), 283 nm (4.50 × 10<sup>3</sup> м<sup>-1</sup> cm<sup>-1</sup>). C<sub>22</sub>H<sub>30</sub>CuN<sub>4</sub>O<sub>10</sub>Zn (639.43): calcd. C 41.32, H 4.73, N 8.76; found C 41.45, H 4.78, N 8.82.

**[CuNi(HL)(OAc)(NO<sub>3</sub>)<sub>2</sub>] (3d):** A procedure similar to that for **3a**, using **1** (104 mg, 0.20 mmol) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (49.5 mg, 0.20 mmol), afforded blue crystals of **3d** (84.7 mg, 67 %). IR (KBr):  $\tilde{v} = 1561$  (s), 1507 (s), 1475 (s), 1445 (s), 1384 (s), 1286 (m) cm<sup>-1</sup>. A small amount of inorganic impurity prevented satisfactory elemental analysis results from being obtained. The chemical formula of **3d** was determined by X-ray analysis.

**[Cu<sub>3</sub>(HL)<sub>2</sub>(OAc)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (4a):** Cu(OAc)<sub>2</sub> (36.4 mg, 0.2 mmol) and NEt<sub>3</sub> (20.1 mg, 0.20 mmol) were added to a solution of **1** (104 mg, 0.20 mmol) in MeOH (5 mL). The resulting solution was stirred at room temperature for 4 h. Addition of diethyl ether (45 mL) afforded greenish blue crystals of **4a** (98.9 mg, 90 %). IR (KBr):  $\tilde{v} = 1577$  (s), 1425 (s), 1384 (s), 1303 (s), 1070 (s), 1025 (m), 946 (w), 931 (w), 917 (w), 894 (w) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 712 (371), 266 nm (1.00 × 10<sup>4</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>44</sub>H<sub>60</sub>Cu<sub>3</sub>N<sub>6</sub>O<sub>14</sub> (1087.63): calcd. C 48.59, H 5.56, N 7.73; found C 48.30, H 5.75, N 7.78.

**[Cu<sub>2</sub>Co(HL)<sub>2</sub>(OAc)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (4b):** A procedure similar to that for **4a**, using **1** (104 mg, 0.20 mmol), Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (49.4 mg, 0.20 mmol), and NEt<sub>3</sub> (80.8 mg, 0.80 mmol), afforded purple crystals of **4b** (86.5 mg, 80 %). IR (KBr):  $\tilde{v} = 1577$  (s), 1428 (s), 1384 (s), 1303 (s), 1070 (s), 1027 (s), 946 (w), 931 (w), 917 (w), 892 (w) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 709 (339), 278 nm (1.00 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>). C<sub>44</sub>H<sub>60</sub>CoCu<sub>2</sub>N<sub>6</sub>O<sub>14</sub> (1083.02): calcd. C 48.80, H 5.58, N 7.76; found C 48.51, H 5.65, N 7.73.

[**Cu<sub>2</sub>Mn(HL)<sub>2</sub>(OAc)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (4c):** A procedure similar to that for **4a**, using **1** (104 mg, 0.20 mmol), Mn(OAc)<sub>2</sub> (34.4 mg, 0.20 mmol), and NEt<sub>3</sub> (19.5 mg, 0.20 mmol), afforded greenish blue crystals of **4c** (100 mg, 93 %). IR (KBr):  $\tilde{v} = 1577$  (s), 1419 (s), 1384 (s), 1307 (m), 1072 (m), 946 (w), 931 (w), 917 (w), 892 (w) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 717 (441), 277 nm (1.46 × 10<sup>4</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>44</sub>H<sub>60</sub>Cu<sub>2</sub>MnN<sub>6</sub>O<sub>14</sub> (1079.02): calcd. C 48.98, H 5.60, N 7.79; found C 48.74, H 5.76, N 7.85.

 $[Cu_3(HL)_2(OCOH)_2](NO_3)_2$  (5):  $Cu(OCHO)_2 + 4H_2O$  (44.4 mg, 0.20 mmol) and NEt<sub>3</sub> (40.9 mg, 0.40 mmol) were added to a solution of 1 (100 mg, 0.19 mmol) in MeOH (5 mL). After stirring the solution at room temperature for 2 h, the addition of diethyl ether (45 mL)

afforded blue crystals of **5**·H<sub>2</sub>O (92.8 mg, 90 %). Complex **5**·H<sub>2</sub>O was also obtained in 65 % yield by the reaction of Cu(HCO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.50 mmol), H<sub>2</sub>L (0.50 mmol), and NEt<sub>3</sub> (1.0 mmol) in MeOH (5 mL). IR (KBr):  $\tilde{v} = 1608$  (s), 1384 (s), 1371 (s), 1291 (s) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 722 (196), 267 nm (5.98 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>). C<sub>42</sub>H<sub>58</sub>Co-Cu<sub>3</sub>N<sub>6</sub>O<sub>15</sub> (1136.52): calcd. C 46.18, H 5.43, N 7.80; found C 46.87, H 5.05, N 7.72.

$$\label{eq:constraint} \begin{split} & [\text{Cu(H}_2\text{L}){(PhO)}_2\text{PO}_2]{(NO}_3) \quad \textbf{(6):} \quad (\text{PhO)}_2\text{PO(OH)} \quad (\text{63.7 mg}, \\ & 0.25 \text{ mmol)} \text{ and NEt}_3 (27.5 mg, 0.27 \text{ mmol)} \text{ were added to a solution} \\ & \text{of 1} (129 \text{ mg}, 0.25 \text{ mmol)} \text{ in MeOH} (5 \text{ mL}). \\ & \text{After stirring at room} \\ & \text{temperature for 1.5 h, diethyl ether (45 mL)} \text{ was added to afford} \\ & \text{greenish blue crystals of 6} (149 \text{ mg}, 85 \%). \\ & \text{IR} (\text{KBr}): \tilde{\nu} = 1594 \text{ (s)}, \\ & 1492 \text{ (m)}, 1454 \text{ (m)}, 1376 \text{ (s)}, 1251 \text{ (m)}, 1205 \text{ (m)} \text{ cm}^{-1}. \\ & \text{C}_{32}\text{H}_{38}\text{CuN}_3\text{O}_9\text{P} (703.19): \\ & \text{calcd. C 54.66, H 5.45, N 5.98; found C 54.59, H 5.67, N 6.11.} \end{split}$$

#### $[Cu_{3}(HL)_{2}\{(PhO)_{2}PO_{2}\}_{2}](NO_{3})_{2}$ (7a)

**Method A:**  $(PhO)_2PO(OH)$  (47.2 mg, 0.20 mmol) was added to a solution of **4a** (104 mg, 0.10 mmol) in MeOH (5 mL), and the solution was stirred at room temperature for 2.5 h. The addition of diethyl ether (45 mL) afforded blue crystals of **7a** (107 mg, 76 %).

**Method B:**  $Cu(NO_3)_2$ ·3H<sub>2</sub>O (30.1 mg, 0.12 mmol) and NEt<sub>3</sub> (26.7 mg, 0.26 mmol) were added to a solution of **6** (175 mg, 0.25 mmol) in MeOH (5 mL). After stirring the solution at room temperature for 2.5 h, the addition of diethyl ether (45 mL) afforded blue crystals of **7a** (160 mg, 87 %).

**Method C:** Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (29.6 mg, 0.12 mmol), (PhO)<sub>2</sub>PO(OH) (63.9 mg, 0.26 mmol), and NEt<sub>3</sub> (51.0 mg, 0.50 mmol) were added to a solution of **1** (129 mg, 0.25 mmol) in MeOH (5 mL). After stirring at room temperature for 1.5 h, the addition of diethyl ether (45 mL) afforded blue crystals of **7a** (160 mg, 87 %). IR (KBr):  $\tilde{v} = 1589$  (m), 1490 (m), 1455 (m), 1392 (s), 1376 (m), 1305 (m), 1201 (s), 1099 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\epsilon$ ) = 734 (294), 295 (7.50 × 10<sup>3</sup>), 264 nm (9.83 × 10<sup>3</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>64</sub>H<sub>74</sub>Cu<sub>3</sub>N<sub>6</sub>O<sub>18</sub>P<sub>2</sub> (1467.90): calcd. C 52.37, H 5.08, N 5.73; found C 52.76, H 5.23, N 5.79.

**[Cu<sub>2</sub>Co(HL)<sub>2</sub>{(PhO)<sub>2</sub>PO<sub>2</sub>}<sub>2</sub>(MeOH)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (7b):** By a procedure similar to that for **7a**, **7b** was obtained as green crystals in yields of 84 (Method A), 67 (Method B), and 79 % (Method C), respectively. IR (KBr):  $\tilde{v} = 1594$  (m), 1488 (s), 1455 (m), 1384 (s), 1311 (m), 1257 (s), 1203 (m), 1101 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 710 (256), 291 (6.81 × 10<sup>3</sup>), 264 nm (8.54 × 10<sup>3</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>66</sub>H<sub>82</sub>CoCu<sub>2</sub>N<sub>6</sub>O<sub>20</sub>P<sub>2</sub> (1527.37): calcd. C 51.90, H 5.41, N 5.50; found C 51.61, H 5.63, N 5.63.

**[Cu<sub>2</sub>Mn(HL)<sub>2</sub>{(PhO)<sub>2</sub>PO<sub>2</sub>}<sub>2</sub>(MeOH)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (7c):** By a procedure similar to that for **7a**, **7c**-5H<sub>2</sub>O was obtained as green crystals in yields of 82 (Method A), 14 (Method B), and 20 % (Method C), respectively. IR (KBr):  $\tilde{v} = 1592$  (m), 1490 (s), 1455 (m), 1384 (s), 1311 (s), 1253 (s), 1203 (m), 1103 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 698 (256), 288 (8.55 × 10<sup>3</sup>), 264 nm (1.09 × 10<sup>3</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>66</sub>H<sub>92</sub>Cu<sub>2</sub>MnN<sub>6</sub>O<sub>25</sub>P<sub>2</sub> (1617.45): calcd. C 49.19, H 5.75, N 5.21; found C 49.00, H 5.36, N 5.34.

**[Cu<sub>2</sub>Co<sub>2</sub>(HL)<sub>2</sub>{(PhO)PO<sub>3</sub>}<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (8a):** Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (49.6 mg, 0.20 mmol), the phenyl monophosphate (PhO)PO(OH)<sub>2</sub> (34.9 mg, 0.20 mmol), and NEt<sub>3</sub> (20.9 mg, 0.21 mmol) were added to a solution of **1** (103 mg, 0.20 mmol) in MeOH (5 mL). After stirring the solution at room temperature for 1.5 h, the addition of diethyl ether (45 mL) afforded blue crystals of **8a**·4H<sub>2</sub>O (160 mg, 87 %). IR (KBr):  $\tilde{v} = 1488$  (s), 1384 (m), 1292 (m), 1231 (m), 1158 (m), 1109 (m), 1002 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 266 nm (1.14 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>). C<sub>52</sub>H<sub>72</sub>Co<sub>2</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>22</sub>P<sub>2</sub> (1440.07): calcd. C 43.37, H 5.04, N 5.84; found C 43.18, H 4.65, N 5.89.



**[Cu<sub>2</sub>Zn<sub>2</sub>(HL)<sub>2</sub>{(PhO)PO<sub>3</sub>}<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (8b):** By a procedure similar to that for **8a**, using **1** (104 mg, 0.20 mmol), Zn(OAc)<sub>2</sub> (36.6 mg, 0.20 mmol), (PhO)PO(OH)<sub>2</sub> (34.9 mg, 0.20 mmol), and NEt<sub>3</sub> (21.5 mg, 0.21 mmol), **8b**·H<sub>2</sub>O was obtained in 4 % yield as pale-blue crystals. IR (KBr):  $\tilde{v} = 1486$  (s), 1384 (w), 1297 (m), 1231 (m), 1166 (m), 1110 (m), 1004 (m) cm<sup>-1</sup>. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$ ) = 297 nm (1.50 × 10<sup>4</sup> m<sup>-1</sup> cm<sup>-1</sup>). C<sub>52</sub>H<sub>66</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>19</sub>P<sub>2</sub>Zn<sub>2</sub> (1398.92): calcd. C 44.65, H 4.76, N 6.01; found C 44.83, H 4.75, N 5.91.

X-ray Crystallographic Analysis: The crystals 1-8 were quickly coated with Paratone N oil and mounted on a loop fiber at room temperature. The crystal and experimental data are summarized in Tables S1-S6 in the Supporting Information. All data were collected at low temperature with a Rigaku VariMax Mo/Saturn CCD diffractometer equipped with graphite-monochromated confocal Mo- $K_{\alpha}$ radiation and a rotating-anode X-ray generator RA-Micro7 (50 kV, 24 mA for 8a, 8b) or a Rigaku AFC8R/Mercury CCD diffractometer equipped with graphite-monochromated Mo- $K_{\alpha}$  radiation and a rotating-anode X-ray generator (50 kV, 190 mA for 1; 50 kV, 180 mA for 2, 4a, 5; 50 kV, 100 mA for 7b). A total of 720 (3a, 3b, 4b, 4c, 6, 7a, 7c), 1080 (8a, 8b), 1800 (3c), and 2160 (1, 2, 4a, 5, 7b) oscillation images, covering a whole sphere of  $6^{\circ} < 2\theta < 55^{\circ}$  were corrected by the  $\omega$ -scan method [-62° <  $\omega$  < 118° (**1**, **2**, **4a**, **5**, **7b**), -65° <  $\omega$ < 115° (3c),  $-70^{\circ} < \omega < 110^{\circ}$  (3a, 3b, 4b, 4c, 7a, 7c, 8a, 8b)] with  $\Delta \omega$  of 0.25° (1, 2, 4a, 5, 7b), 0.30° (3c), and 0.5° (3a, 3b, 3d, 4b, 4c, 6, 7a, 7c, 8a, 8b). The crystal-to-detector distance was set at 45 mm (3a-d, 4b, 4c, 7a, 7c, 8a, 8b), 55 mm (3c), or 60 mm (1, 2, 4a, 5, 6, 7b). The data were processed by using Crystal Clear (version 1.3.5, Rigaku/MSC)<sup>[25]</sup> and corrected for Lorentzian-polarization and absorption effects.<sup>[26]</sup> The structures of the complexes were solved by SHELXL-97<sup>[27]</sup> (2, 4c, 5, 8a) and SIR-92<sup>[28]</sup> (1, 3a-d, 4a, 4b, 6, 7a-c, **8b**) and were refined on  $F^2$  with full-matrix least-squares techniques with SHELXL-97<sup>[27]</sup> using Crystal Structure 4.1 package.<sup>[29]</sup> All nonhydrogen atoms were refined with anisotropic thermal parameters and the C-H hydrogen atoms were calculated at ideal positions and refined with riding models. All calculations were carried out on a Pentium PC using the Crystal Structure 4.1 package.<sup>[29]</sup>

CCDC 1452436 (for 1), 1452437 (for 2), 1452438 (for 3a), 1452439 (for 3b), 1452440 (for 3c), 1452441 (for 3d), 1452442 (for 4a), 1452443 (for 4b), 1452444 (for 4c), 1452445 (for 5), 1452446 (for 6), 1452447 (for 7a), 1452448 (for 7b), 1452449 (for 7c), 1452450 (for 8a), and 1452451 (for 8b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): Structural parameters of 1–8 and ORTEP diagrams of 3a,c,d, 4a,b, 6b, 7c, and 8b.

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