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The Assembly of Dinuclear Alkoxido-Bridged Cu^{II} Halide Complexes of Pyridine Alcohols To Form Tetranuclear and Polynuclear Compounds: Synthesis, Structure, and Magnetic Properties

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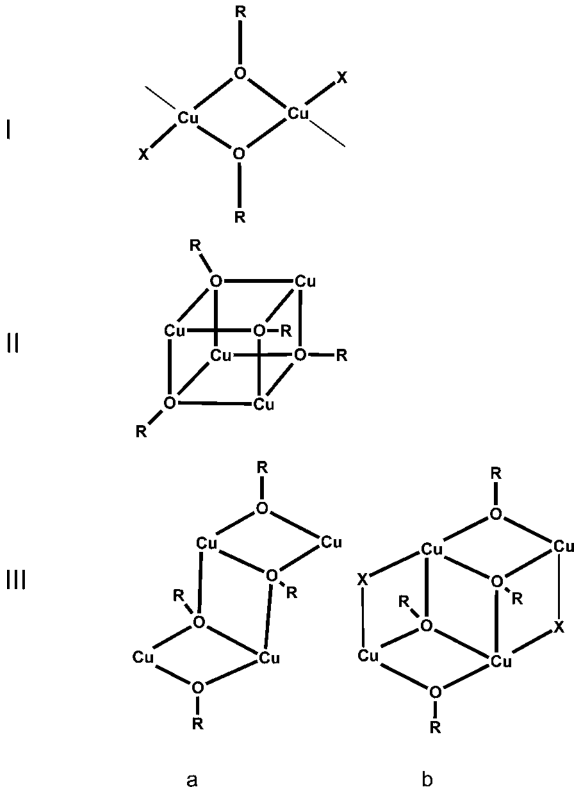
Reaction of CuX_2 (X = Cl, Br) with pyridine alcohol ligands [2-(hydroxymethyl)pyridine = Hhmp, 2-(hydroxyethyl)pyridine = Hhep and 2-(hydroxypropyl)pyridine = Hhpp] affords a series of new Cu^{II} alkoxide complexes with a similar Cu_2O_2 structural motif: a dinuclear complex, $[Cu_2(hpp)_2Br_2]$ (**1**), two tetranuclear compounds, $[Cu_4(hpp)_4Br_4]$ (**2**) and $[Cu_4(hpp)_4Cl_4]$ (**3**), and polynuclear chains, $[Cu_2(hep)_2Cl_2]_n$ (**4**) and $[Cu_2(Hhmp)_2Cl_4]_n$ (**5**). The dinuclear complex **1** represents the basic building unit of the four other materials. In this family of compounds, the pyridine alcohol type ligands (Hhmp, Hhep, or Hhpp) provide the two alkoxido functions that bridge the Cu^{II} centers. The tetranuclear analogues exhibit an unusual structure of the defect dicubane-like type with two missing vertices. The one-dimensional polymers **4** and **5** are composed of Cu_2O_2 dinuclear units interlinked through bridging chlorido ligands to form infinite chains. The analysis of the magnetic susceptibility measurements indicates the presence of strong antiferromagnetic coupling between the $S = 1/2$ Cu^{II} metal ions through the bis(alkoxido) bridge.

Introduction

The aggregation of small well-defined coordination building blocks to form larger architectures is one of the major trends of research in coordination chemistry.[1–4] Cu^{II} complexes are particularly popular since the metal ion is paramagnetic and affords easy formation of polynuclear clusters. Dinuclear Cu^{II} complexes have often been used as models to study the magnetic-exchange interactions and as building blocks for the construction of polynuclear compounds with interesting magnetic properties.[5] Among them, Cu^{II} carboxylates with a paddle-wheel structure and doubly bridged dinuclear complexes containing hydroxido alkoxido or halide bridging ligands have drawn considerable interest.[6] Our quest has been the preparation of new complexes based on the dinuclear $[Cu_2(OR)_2X_2]$ core. This motif consists of two copper atoms bridged by two alkoxido oxygen atoms from alkoxypyridine-type ligands. Moreover, each of the Cu^{II} metal ions displays a pseudo-square-planar coordination geometry completed by two halogen anions in *trans* positions (Scheme 1, I) and by the pyridine function of the chosen ligand. The tendency of copper ions to accept



Scheme 1. The $[Cu_2(OR)_2X_2]$ structural core (I) and the tetranuclear species of cubane type (II), stepped-cubane type (IIIa) and “defect dicubane type” (IIIb).

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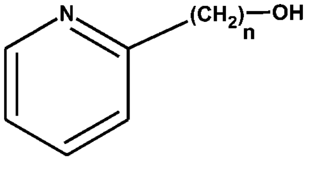
a fifth ligand at the axial coordination site and the ability of alkoxido ligands to participate in bridging allow for the possibility of associating these dinuclear units into discrete oligonuclear and polynuclear compounds. The assembly of two dinuclear units leads to two types of tetranuclear aggregates: the cubane type (Scheme 1, II) and the so-called stepped-cubane type (Scheme 1, IIIa). Both types are known in Cu^{II} alkoxide chemistry. While abundant structural data on cubane-type complexes is available in the literature,[7] the stepped cubanes appear much less frequently,[8] particularly, compounds that contain a halide ligand as one of the equatorial ligands of the copper centers in the dinuclear core. Upon association of the type I dinuclear units (Scheme 1), one of the two terminal halogenide ligands of each dimeric unit bridges neighboring $Cu_2(OR)_2$ building blocks to give rise to an unusual structural type (Scheme 1, IIIb). The resulting complex may be envisioned as an arrangement of two fused cubes, each missing one apex. It is worth noting that as far as we know, only one structurally characterized $[Cu_4(OR)_4X_4]$ species of this type has been reported in the literature.[9]

Although a considerable amount of research is currently focused on the rational design of premeditated architectures and complexes, it is often difficult, if not impossible, to answer the question why one complex is obtained rather than another. Progress in understanding self-assembly processes is likely to be developed by studying the aggregation of relatively simple and small building units. Herein we report on the preparation and structural characterization of copper(II) complexes that have the $Cu_2(OR)_2X_2$ core with three simple chelating pyridine-based alkoxido ligands (Scheme 2): 2-(hydroxymethyl)pyridine (Hhmp), 2-(hydroxyethyl)pyridine (Hhep), and 2-(hydroxypropyl)pyridine (Hhpp). Five new compounds are presented, spanning diverse architectures from dinuclear $[Cu_2(hpp)_2Br_2]$ to two tetranuclear complexes with a dicubane-type structure, ($[Cu_4(hpp)_4Br_4]$ and $[Cu_4(hpp)_4Cl_4]$), and two polymeric chain compounds with the composition $[Cu_2(hep)_2Cl_2]_n$ and $[Cu_2(Hhmp)_2Cl_4]_n$. In addition to the synthesis and the structural characterization, the magnetic properties of the $Cu_2(OR)_2X_2$ core will be discussed.



n = 1; 2-(hydroxymethyl) pyridine (Hhmp)
n = 2; 2-(hydroxyethyl) pyridine (Hhep)
n = 3; 2-(hydroxypropyl) pyridine (Hhpp)

Scheme 2. Pyridine alcohol ligands discussed in this work.

Results and Discussion

Simple pyridine-based alcohols such as 2-(hydroxymethyl)- (Hhmp), 2-(hydroxyethyl)- (Hhep) and 2-(hydroxypropyl)pyridine (Hhpp) have the ability to act as chelating and/or bridging ligands in their neutral and ionic forms, where the OH groups are deprotonated. Surprisingly, these simple commercially available substances have not been employed widely as ligands in coordination chemistry. Only in recent years, the simplest one from the above homologue series, Hhmp, has been used in manganese chemistry to obtain new single-molecule magnets (SMMs) or extended networks of SMMs.[10] Among the structurally characterized Cu^{II} complexes based on the ligands listed above, the compounds with (hydroxymethyl)pyridine (Hhmp) prevail. The search through the Cambridge Structural Database (CSD) revealed six structures containing Hhmp and Cu^{II} metal ions.[11] All of these examples are mononuclear species with six-coordinate Cu^{II} centers to which Hhmp binds as a chelating ligand. In addition, it is worth noting that there is only one report on a structure with the anionic hmp ligand that adopts a chelating-bridging mode, which results in a tetranuclear complex $[Cu_4(hmp)_4(CH_3COO)_4]$ of a cubane type.[12] Structures with Hhep/hep and Hhpp/hpp appear even less frequently. Two Cu^{II} mononuclear complexes with Hhep have been found in the CSD, while no example seems to exist with the ligand in its deprotonated form.[13] Only one mononuclear compound with Hhpp and one dinuclear example with the ligand in its deprotonated form (hpp) have been reported so far on the basis of a CSD search.[14]

We have carried out the syntheses by using simple bromide and chloride copper(II) salts (CuX_2 with X = Br, Cl) with Hhmp, Hhep, and Hhpp in methanol, ethanol, or a mixture of both alcohols. While the reactions with Hhep and Hhpp lead to the deprotonation of the ligand and thus alkoxido-bridged complexes (**1**–**4**), the Hhmp ligands stay protonated in **5**. The origin of this difference and the mechanism that assists the deprotonation of the coordinated alcohol in the case of the Hhep and Hhpp ligands is not clear. We have no explanation for the formation of alkoxido-bridged rather than hydroxido-bridged complexes, since the metal salts were not dried and water was not excluded from the reaction mixture. Analogically, the deprotonation of Hhmp under similar reaction conditions was expected even if the chelating mode of Hhmp coordination is apparently favored over the bridging mode. Indeed, this tendency to form five-membered chelating rings for the Hhmp ligand is also reflected in the CSD and in the occurrence of structures containing Hhmp.

Structural Descriptions

Dinuclear Complex $[Cu_2(hpp)_2Br_2]$ (1)

Compound **1** represents the smallest complex in terms of nuclearity in this study (Figure 1). It consists of two copper atoms doubly bridged by chelating μ-hpp ligands. The remaining sites of the distorted square-planar environment around the copper centers are occupied by two bromido ligands that are arranged in a *trans* fashion. The two copper atoms are symmetry related by an inversion center and are separated by 3.0642(5) Å. The μ-O bridge is asymmetrical with Cu–O distances of 1.9179(13) and 1.9489(13) Å and a Cu–O–Cu angle of 104.8°. Basic geometric parameters, relevant to the Cu coordination sphere, are summarized in Table 1. There are no covalent interactions between the dimeric units.

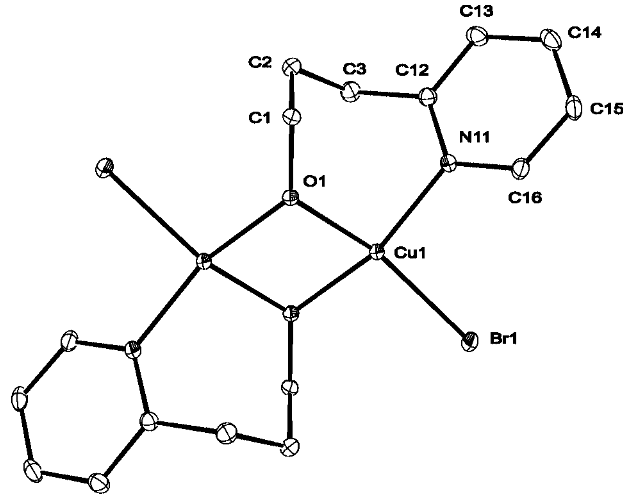


Figure 1. View of a centrosymmetric dinuclear unit in **1** (30% probability thermal ellipsoids). Only the atoms of the asymmetric unit are labeled.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.[a]

Cu1–O1	1.9489(13)
Cu1–N11	2.0011(16)
Cu1–Br1	2.3753(3)
Cu1–O1^i	1.9179(13)
Cu1–Cu1^i	3.0642(5)
Cu1–O1–Cu1^i	104.82(6)

[a] Symmetry code: (i) $-x+2$, $-y+1$, $-z+1$.

Tetramers [$Cu_4(hpp)_4Br_4$] (2) and [$Cu_4(hpp)_4Cl_4$] (3)

The basic molecular motif of these two materials is similar and is composed of four copper centers arranged to form a planar "rhombic" geometry (Scheme 1, IIIb). These tetranuclear complexes can be described as two [$Cu_2(hpp)_2X_2$] (with X: Br or Cl) dinuclear units, one lying on top of the other and slipped with respect to each other. One of the two bridging hpp oxygen atoms of each dinuclear unit is triply bridging and connects the two [$Cu_2(hpp)_2X_2$] moieties to form a stepped-cubane-type geometry. The tetranuclear aggregate is further stabilized by two halogen bridges inducing the "defect dicubane type" geometry: a pair of uncompleted cubes connected by a common Cu_2O_2 face. The bromido complex **2** crystallizes in a noncentrosymmetric space group $P2_1$ with the whole tetranuclear molecule as the asymmetric unit (Figure 2). The geometry of the two dinuclear moieties is essentially the same as can be seen from bond lengths and angles given in Table 2. The copper centers, which are doubly bridged by alkoxido oxygen atoms, are separated by 3.0421(9) and 3.0464(9) Å, while the distances between the copper atoms belonging to different dinuclear units are longer. Those involving μ_3-O- and μ-Br-bridged Cu atoms are 3.6003(9) and 3.6113(9) Å for the Cu1–Cu3 and Cu4–Cu2 pairs, respectively. The (μ_3-O)$_2$-bridged pair of copper atoms (Cu1 and Cu2) is separated by 3.3555(8) Å. The chloride analogue **3** crystallizes in the space group $P2_1/n$ with an inversion center located in the center of the $Cu_2(\mu_3\text{-}O)_2$ plane (Figure 3). Thus, the asymmetric unit here is composed only of a dimeric half of the tetranuclear complex [$Cu_2(hpp)_2X_2$]. The geometry of this dinuclear unit (Table 2) is similar to that of the bromido analogue. Again, the bridging alkoxido group from one [$Cu_2(hpp)_2X_2$] motif coordinates to the copper ions of the other moiety, thereby becoming a μ_3 ligand. Additionally, two chlorido bridges consolidate the tetranuclear core to form a centrosymmetric complex with a IIIb topology (Scheme 1), as presented in Figure 3. In these aggregates, two types of Cu^{II} ions with a square-pyramidal coordination sphere can be distinguished: (i) Cu1 and Cu2 in **2** or Cu2 in **3** possess a $CuXNO_3$ environment with a basal plane occupied by a triply bridging hmp oxygen atom, a halogen ion, a pyridine-type nitrogen atom, and μ-O atom from a chelating hmp. The apical site is occupied by a μ_3-O atom from the neighboring dinuclear unit. The remaining

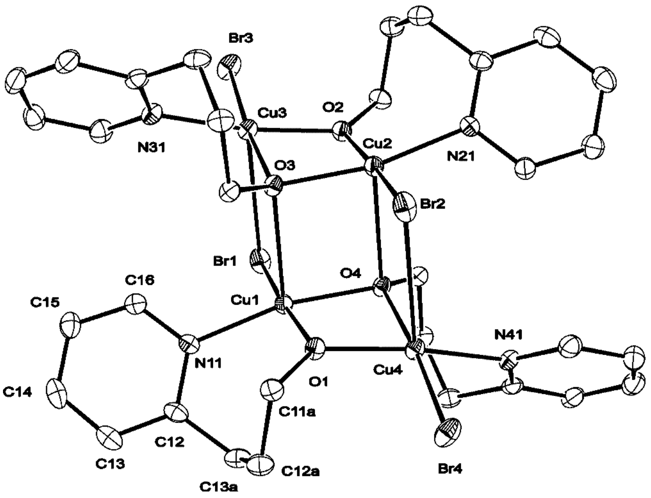


Figure 2. Structural representation of **2** (30% probability thermal ellipsoids).

Table 2. Selected bond lengths [Å] and angles [°] for the tetranuclear compounds **2** and **3**.[a]

2				**3**	
Cu2–Cu3	3.0421(9)	Cu1–Cu4	3.0464(9)	Cu1–Cu2	3.0438(3)
Cu2–O2	1.934(4)	Cu1–O1	1.941(4)	Cu1–O1b	1.9071(12)
Cu2–O3	1.979(4)	Cu1–O4	1.972(4)	Cu1–O1a	1.9791(12)
Cu2–Br2	2.4023(10)	Cu1–Br1	2.4105(9)	Cu1–Cl1	2.2474(5)
Cu2–N21	2.022(5)	Cu1–N11	2.021(5)	Cu1–N11	2.0093(15)
Cu3–O2	1.896(4)	Cu4–O1	1.907(4)	Cu2–O1a	1.9293(12)
Cu3–O3	2.003(4)	Cu4–O4	1.984(4)	Cu2–O1b	1.9891(12)
Cu3–Br3	2.4087(9)	Cu4–Br4	2.4105(9)	Cu2–Cl2	2.2553(5)
Cu3–N31	2.002(5)	Cu4–N41	2.004(5)	Cu2–N21	2.0227(15)
Cu2–O4	2.536(4)	Cu1–O3	2.512(4)	Cu1–Cl2^i	3.0035(6)
Cu3–Br1	3.1102(10)	Cu4–Br2	3.1667(10)		
Cu3–O2–Cu2	105.2(2)	Cu1–O1–Cu4	104.7(2)	Cu1–O1a–Cu2	100.18(5)
Cu3–O3–Cu2	99.63(17)	Cu1–O4–Cu4	100.72(18)	Cu1–O1b–Cu2	105.01(6)

[a] Symmetry code: (i) $-x$, $-y$, $-z$.

two copper centers, Cu3 and Cu4 in **2** or Cu1 in **3**, possess a CuX_2NO_2 geometry. The equatorial plane is formed by a μ-O atom from a bridging hmp ligand, a halogen ion, a pyridine-type nitrogen atom, and a μ_3-O atom from a chelating hmp. The axial site is occupied by a halogen ion from the adjacent dinuclear unit. It is worth noting that the assembly of two alkoxido-bridged dicopper units usually results in a compact cube-like complex, particularly when the dinuclear unit contains halide ligands. To the best of our knowledge, there is only one structure known, $[Cu_4(M3)_2(\mu_3\text{-}OMe)_2(\mu\text{-}Cl)_2Cl_2]$, that contains the $[Cu_4(\mu\text{-}OR)_2(\mu_3\text{-}OR)_2(\mu\text{-}X)_2X_2]$ tetranuclear defect dicubane core.[9] However, the arrangement of the bridging and terminal halogenide ligands in the present tetranuclear complexes differ from that observed in the reported structure. In **2** and **3**, the basic dinuclear moiety contains halogen ions located in a *trans* fashion, whereas in the aforementioned complex, the Cl ions are coordinated to the Cu^{II} centers in *cis* positions. The $[Cu_4(M3)_2(\mu_3\text{-}OMe)_2(\mu\text{-}Cl)_2Cl_2]$ complex contains two different alkoxido ligands: μ_3-bridging methoxy groups and a tridentate macrocyclic ligand (M3) that offers a μ-bridging phenoxo group and occupies, by its two nitrogen atoms, the two (*cis*) equatorial positions of each of the copper metal ions. This peculiar macrocyclic ligand geometry thus prevents the chlorido ligands from adopting *trans* positions.

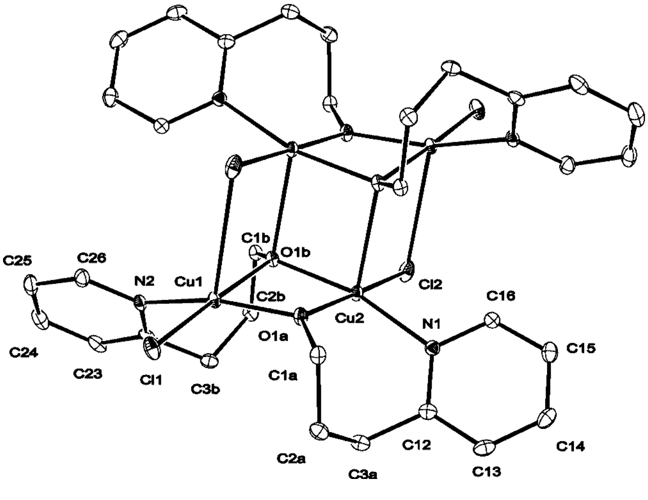


Figure 3. Structural representation of a centrosymmetric tetranuclear core of **3** (30% probability thermal ellipsoids).

Polymer $[Cu_2(hep)_2Cl_2]_n$ (4)

In **4**, the centrosymmetric dimeric units (Figure 4, Table 3) assemble through weak interactions arising from two bridging chlorido ligands to form a linear chain shown in Figure 5. The distance between the copper centers within the alkoxido dimer is 3.0833(4) Å, whereas the distance between the copper centers that are doubly bridged by μ-Cl is longer: 3.8080(5) Å. The consecutive bridging planes (Cu_2O_2 and Cu_2Cl_2) are twisted with respect to each other and the dihedral angle is 77.93(5)°. The overall structure may be compared to the one observed in the complex $[Cu(nhep)Cl]_2$ containing 1-(2-hydroxyethyl)pyrazole (nhep) as the alkoxido bridging ligand.[15] In this compound, the basic dinuclear unit has no center of symmetry but connects through weak inter-dimer interactions arising from two bridging chlorido ligands to form polynuclear chains with di-μ-O and di-μ-Cl bridges, as described here.

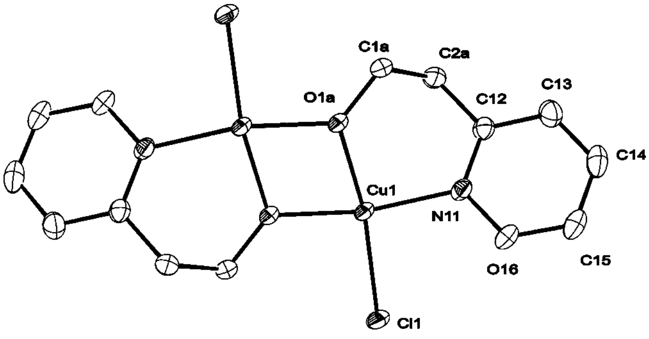


Figure 4. Structural representation of a centrosymmetric dinuclear core in **4** (30% probability thermal ellipsoids).

Table 3. Selected bond lengths [Å] and angles [°] for polynuclear compounds **4** and **5**.[a]

4		5	
Cu1–O1a	1.9349(14)	Cu1–Cl2	2.2418(5)
Cu1–O1a^{i}	1.9434(14)	Cu1–Cl2^{iii}	2.9415(6)
Cu1–N11	2.0211(18)	Cu1–N11	1.9957(17)
Cu1–Cl1	2.2597(6)	Cu1–O1	1.9959(16)
Cu1–Cl1^{ii}	2.9413(7)	Cu1–Cl1	2.2607(6)
		Cu1–O1^{iv}	2.9073(16)
Cu1–Cu1^{i}	3.0833(4)	Cu1–Cu1^{iii}	3.8641(5)
Cu1–Cu1^{ii}	3.8080(5)	Cu1–Cu1^{iv}	3.9191(5)
Cu1–O1a–Cu1^{i}	105.31(7)		

[a] Symmetry codes: (i) $-x+1$, $-y$, $-z+1$, (ii) $-x+2$, $-y$, $-z+1$, (iii) $-x$, $-y$. $-z+2$, (iv) $-x+1$, $-y$, $-z+2$.

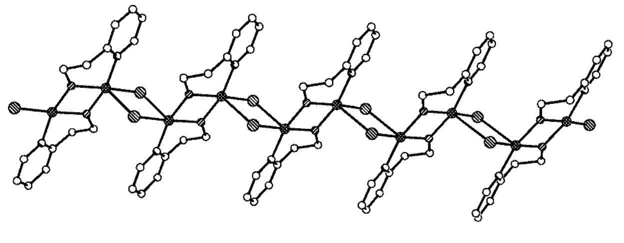


Figure 5. The one-dimensional chain structure of **4**.

Polymer $[Cu_2(Hhmp)_2Cl_4]_n \cdot 2nCH_3OH$ (5)

Complex **5** contains 2-(hydroxymethyl)pyridine (Hhmp) in its protonated form. The polymeric chain is built up from centrosymmetric dinuclear $[Cu_2Hhmp_2Cl_4]$ units presented in Figure 6. The two Cu atoms, separated by 3.8641(5) Å, are doubly bridged by two chlorido ligands. The bridge is far from symmetrical with Cu1–Cl2 and Cu1–Cl2* (with *: $-x$, $-y$ $-z+2$) distances of 2.2418(5) and 2.9415(6) Å, respectively, and a Cu1–Cl2–Cu1* bridging angle of 95.45°. The Hhmp ligand binds to a single Cu metal ion within the dimer in a chelating manner [Cu1–N11: 1.9957(17) Å and Cu1–O1: 1.9959(16) Å]. The fifth coordination site is occupied by a terminal chlorido ligand at a distance of 2.2607(6) Å. Additionally, copper ions show rather weak interactions with the Hhmp oxygen atom from a neighboring dimer with a distance between Cu1 and O1* (with *: $-x+1$, $-y$ $-z+2$) of 2.9073(16) Å. As a result of this weak interaction, infinite chains are formed in which [$Cu_2Hhmp_2Cl_4$] dimers are further doubly bridged by Hhmp oxygen atoms as illustrated by Figure 7. The interdimer Cu–Cu separation is 3.9191(5) Å. The consecutive bridging planes Cu_2Cl_2 and Cu_2O_2 are almost perpendicular to each other [dihedral angle of 88.34(5)°]. Topologically, the chain structure of compound **5** is related to that of **4**. Its formation may as well be described as [$Cu_2Hhmp_2Cl_2$] dimers connected into chains through μ-Cl ligands. Because Hhmp exists in **5** in the neutral form, such a chain would bear a positive charge. Thus, an additional terminal chlorido ligand is bound to each copper atom to compensate for the charge and complete the six-coordinate geometry of the Cu centers. The compound crystallizes as methanol solvate with two solvate molecules per dimeric unit. Both alcohols, Hhmp and methanol, are involved in hydrogen-bond interactions [O1–O2* with *: $-x+1$, $-y$, $-z+2$ = 2.583(2) Å; O2–Cl1* with *: $x+1$, y, z = 3.090(2) Å].

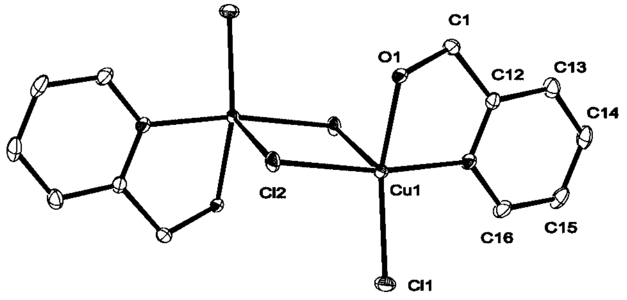


Figure 6. Structural representation of the centrosymmetric dinuclear unit in **5** (30% probability thermal ellipsoids).

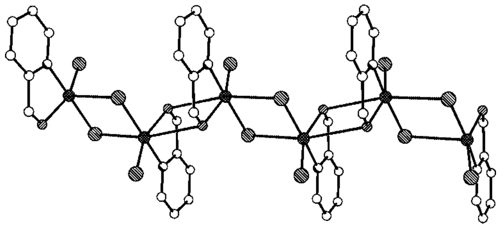


Figure 7. The one-dimensional chain structure of **5**.

Magnetic Behavior

The variable temperature magnetic susceptibility measurements for compound **1** are shown in Figure 8 as an χT vs. T plot. By lowering the temperature, the χT product that reaches 0.06 $cm^3\,K\,mol^{-1}$ at room temperature continuously decreases down to 130 K. Below 130 K, the compound displays a diamagnetic ground state. This magnetic behavior is typically observed for dinuclear Cu^{II} complexes that possess a strong intracomplex antiferromagnetic interaction. A simple dinuclear Heisenberg $S = 1/2$ model[16] has been used to fit the magnetic susceptibility (Figure 8) by considering the following spin Hamiltonian: $H = -2J\ \{S_{Cu1}\cdot S_{Cu2}\}$ (where S_{Cu1} and S_{Cu2} are the spin operators with $S_{Cu1} = S_{Cu2} = 1/2$). The best set of parameters obtained for **1** by using the above model is: $J/k_B = -580(20)$ K, $g = 2.1(1)$ and $\rho = 0.002$ [this ρ parameter has been added to the model in order to take into account a residual paramagnetic Curie component as $\chi = (1-\rho)\ \chi_{dimer} + \rho C_{S=1/2}/T$]. From a magnetic point of view, all the other compounds, **2**, **3**, and **4**, can be described as CuO_2Cu dinuclear complexes by considering only the magnetic interactions through the bis(alkoxido) bridge. The assembly of these dinuclear units takes place through the axial sites of each copper ion and thus the bis(chlorido) bridge is likely to be much weaker. Therefore, the magnetic susceptibility of compounds **2**, **3**, and **4** can be modeled by using the above-described magnetic Heisenberg approach (Figure 8). The best set of parameters obtained by using this model is: $J/k_B = -586(20)$ K, $g = 2.3(1)$, $\rho = 0.026$ for **2**, $J/k_B = -641(25)$ K, $g = 2.2(1)$, $\rho = 0.021$ for **3**, and $J/k_b = -850(30)$ K, $g = 2.1(1)$, $\rho = 0.02$ for **4**. It is worth noting that similar magnetic behavior and antiferromagnetic interactions have been found for bis(alkoxido) dinuclear copper(II) complexes.[9,15] The present compounds thus possess a diamagnetic ground state that is the only thermally populated state above 130 K.

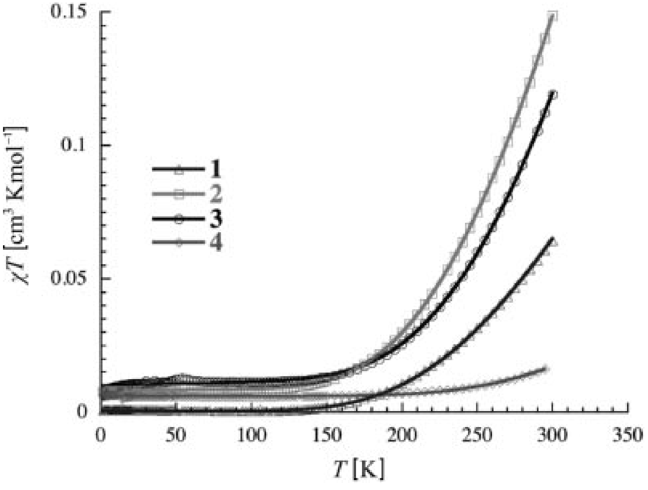


Figure 8. χT vs. T data (where $\chi = M/H$) for compound **1**, **2**, **3**, and **4** measured at 1000 Oe. The solid lines are the best fits obtained with the Heisenberg model described in the text.

Concluding Remarks

The reactions of copper(II) halides with three pyridine alcohol ligands afforded a series of new complexes based on a dinuclear $Cu_2(OR)_2X_2$ core. Among them, two tetranuclear compounds (**2**, **3**) exhibit a defect dicubane structure with two missing vertices, which is rarely observed in Cu^{II} alkoxide chemistry. As shown by the magnetic properties of **1**, this dinuclear $Cu_2(OR)_2X_2$ building block possesses a singlet ground state and thus induces all the resulting complexes based on this unit to also exhibit a diamagnetic ground state. The paramagnetic triplet state is thermally populated above 130 K for all the reported materials. The existence of neutral and deprotonated forms of the coordinated ligands warrants further investigation on the reaction conditions necessary for ligand deprotonation.

Experimental Section

General Procedures and Materials: All manipulations were carried out under ambient conditions by using commercial grade solvents. Chemicals were used as received (Aldrich) without further purification.

Synthesis

[Cu$_2$(hpp)$_2$Br$_2$] (1): CuBr$_2$ (0.11 g) was dissolved in a mixture of methanol (10.0 mL) and ethanol (10.0 mL). On adding the disodium salt of succinic acid (0.05 g), a blue product precipitated. After the addition of 2-(hydroxypropyl)pyridine (0.13 mL), the mixture was heated to boiling and then cooled to ambient temperature. The remaining blue product was filtered off. Slow cooling of the green filtrate to 5 °C gave bluish-green plate-like crystals of **1**. Yield: 0.023 g (16%). $C_{16}H_{20}Br_2Cu_2N_2O_2$ (559.24): calcd. C 34.36, H 3.60, N 5.01; found C 34.55, H 3.76, N 4.95.

[Cu$_4$(hpp)$_4$Br$_4$] (2): CuBr$_2$ (0.11 g) was dissolved in methanol (9.0 mL) and 2-(hydroxypropyl)pyridine (0.13 mL) was added. Slow cooling of the resulting olive-green solution to 5 °C gave grass-green rod-like crystals. Yield: 0.067 g (48%). $C_{32}H_{40}Br_4Cu_4N_4O_4$ (1118.48): calcd. C 34.36, H 3.60, N 5.01; found C 34.57, H 3.72, N 4.90.

[Cu$_4$(hpp)$_4$Cl$_4$] (3): CuCl$_2$·2H$_2$O (0.11 g) was dissolved in methanol (10 mL). 2-(Hydroxypropyl)pyridine (0.13 mL) was then added whilst stirring. Upon ligand addition, the color of the solution changed from light blue to olive green. Green crystals precipitated on standing overnight at ambient conditions. Yield: 0.073 g (62%). $C_{32}H_{40}Cl_4Cu_4N_4O_4$ (940.68): calcd. C 40.85, H 4.29, N 5.96; found C 40.89 H, 4.39, N 5.81.

[Cu$_2$(hep)$_2$Cl$_2$]$_n$ (4): CuCl$_2$·2H$_2$O (0.11 g) was dissolved in methanol (15 mL). 2-(Hydroxyethyl)pyridine (0.13 mL) was then added whilst stirring. Upon ligand addition, the color of the solution changed from light blue to grass green. Green crystals precipitated on standing overnight at room temperature. Yield: 0.078 g (27%). $C_{14}H_{16}Cl_2Cu_2N_2O_2$ (442.28): calcd. C 38.02, H 3.65, N 6.33; found C 38.16, H 3.74, N 6.21.

[Cu$_2$(Hhmp)$_2$Cl$_4$]$_n$·2nCH$_3$OH (5): CuCl$_2$·2H$_2$O (0.11 g) was dissolved in methanol (10 mL). 2-(Hydroxymethyl)pyridine (0.20 mL) was then added whilst stirring. Upon ligand addition, the color of the solution changed from light blue to grass green. On standing at room temperature, a green microcrystalline product precipitated, which was then filtered off. The mother liquor was cooled slowly to 5 °C, which resulted in the precipitation of grass-green elongated blocks, unstable in air.

Physical Measurements: Elemental analyses were measured at the Faculty of Chemistry and Chemical Technology, University of Ljubljana with a Perkin–Elmer 240 C, H, N analyzer. IR spectra were recorded with a Perkin–Elmer 2000 spectrometer. Spectra can be obtained from authors upon request. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID MPMS-XL magnetometer. Measurements were performed on finely ground crystalline samples: 25.13 mg (**1**), 13.48 mg (**2**), 32.14 mg (**3**), and 25.73 mg (**4**) over the temperature range 1.8–300 K. The magnetic data were corrected for the sample holder, and the diamagnetic contribution calculated from Pascal's constants.[17] The presence of ferromagnetic impurities has been systematically checked by measuring the magnetization as a function of the field at 100 K. No presence of ferromagnetic impurities was seen in **1**, **3**, and **4**. For **2**, the susceptibility obtained at 100 K from the M vs. H data has been used to correct the extrinsic ferromagnetic contribution. Physical characterizations of **5** have not been possible because of its high instability in air.

Crystallography: X-ray single-crystal data were collected with a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150 K for compounds **1**, **3**, and **5** and at 293 K for compounds **2** and **4**. The data were processed by using DENZO and SCALEPACK.[18] The structures were solved by direct methods implemented in the SHELX-97 package[19] and refined by a full-matrix least-squares method on F^2 against all reflections by using the same program. Hydrogen atoms were placed in geometrically calculated positions and were refined using a riding model, except those of the alcohol groups in compound **5**, which were found from a Fourier difference map and freely refined. Compound **2** crystallizes in the noncentrosymmetric space group $P2_1$. The value of the Flack parameter 0.495(12) indicates possible racemic twinning. Crystallographic data are listed in Table 4. CCDC-602082, -602083, -602084, -611672, and -611673 contain the supplementary crystallographic data for this paper. These data

Table 4. Crystallographic data for compounds **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{16}H_{20}Br_2Cu_2N_2O_2$	$C_{32}H_{40}Br_4Cu_4N_4O_4$	$C_{32}H_{40}Cl_4Cu_4N_4O_4$	$C_{14}H_{16}Cl_2Cu_2N_2O_2$	$C_{14}H_{18}Cl_4Cu_2NO_4$
Formula mass [g mol^{-1}]	559.24	1118.48	940.68	442.28	551.24
Space group	$P2_1/a$	$P2_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Z	2	2	2	1	2
T [K]	150	293	150	293	150
a [Å]	9.9878(2)	9.5570(10)	9.25380(10)	6.19550(10)	6.87280(10)
b [Å]	8.83220(10)	17.2949(2)	16.8305(2)	8.0167(2)	14.9500(2)
c [Å]	10.1894(2)	11.89280(10)	11.61430(10)	8.5418(2)	10.4520(2)
α [°]				89.7300(10)	
β [°]	95.2740(10)	104.658(2)	104.899(10)	79.2820(10)	104.7518(7)
γ [°]				70.0321(10)	
V [Å^3]	895.05(3)	1841.80(4)	1748.07(9)	390.994(15)	1038.53(3)
μ (Mo-K_α) [mm^{-1}]	6.851	6.659	2.750	3.067	2.584
$d_{calcd.}$ [g cm^{-3}]	2.075	2.017	1.787	1.878	1.763
R_1, wR_2 [$I > 2\sigma(I)$]	0.0200, 0.0486	0.0377, 0.0938	0.0231, 0.0587	0.0240, 0.0572	0.0263, 0.0596

can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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