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Homonuclear Copper(II) Complexes with Multidentate Amino Alcohol Ligands. Synthesis and Characterization of a Hexanuclear Copper Compound with a Propeller Structure: Cu$^{II}_{6}$(bdmap)$_{3}$Cl$_{6}$(O)(OH) (bdmap = 1,3-Bis(dimethylamino)-2-propanolato)

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A new hexanuclear copper(II) complex with the formula Cu$^{II}_{6}$(bdmap)$_{3}$Cl$_{6}$(O)(OH) (**1**; bdmap = 1,3-bis(dimethylamino)-2-propanolato) has been synthesized and characterized structurally. Compound **1** has a propeller structure with an approximate C_3 symmetry. There are two possible diastereomers for this compound, and only one of them has been identified structurally, regardless the synthetic routes. The core structure of **1** consisting of six copper(II) ions and five oxygen atoms resembles that of cryptand. A proton is trapped inside this inorganic "cryptand". Crystal data for **1**, $C_{21}H_{52}Cu_6Cl_6O_5N_6$: monoclinic, space group $P2_1/n$, a = 12.691(7) Å, b = 16.31(1) Å, c = 20.45(2) Å, β = 107.07(5)°, V = 4047(5) Å^3, Z = 4. Magnetic susceptibility measurements at variable temperatures and an ^{1}H NMR study in solution established that compound **1** has an antiferromagnetically coupled ground state.

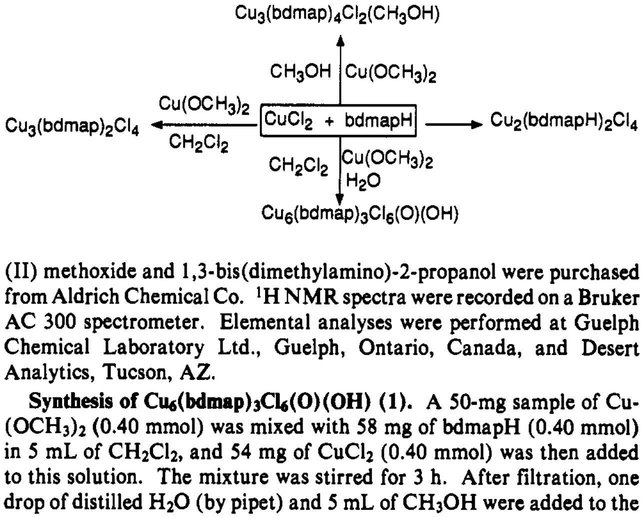
Introduction

We have been interested in the study of polynuclear copper(II) complexes involving amino alcohol ligands due to the fact that these ligands have been successfully used as cross-linking reagents in superconductor precursor systems.[1] Copper(II) complexes with the general formula $[Cu_2(L)_2X_2]_2$, where L = dialkylamino alcoholate and X = halide or pseudohalide, have been extensively studied previously.[2] We have been investigating copper(II) complexes involving the tridentate 1,3-bis(dimethylamino)-2-propanolato (bdmap) ligand. Two classes of polynuclear copper(II) complexes with the bdmap ligand have been synthesized by our group. Class I has the general composition Cu-bdmap-RCO_2^-, while class II has the general composition Cu-bdmap-Cl. Tetranuclear copper(II) complexes of class I with rectangular and chain structures have been reported recently.[1] Three members of class II, a dinuclear complex Cu_2(bdmapH)$_2$Cl$_4$ and[3a] two trinuclear complexes Cu_3(bdmap)$_2$Cl$_4$ and[3b] Cu_3(bdmap)$_4$Cl$_2$(CH$_3$OH), have also been synthesized by our group. The class II compounds were obtained by using $CuCl_2$ and bdmapH as the starting materials with or without the presence of $Cu(OCH_3)_2$. Reaction conditions have been found to play an important role in the formation of the class II compounds, as shown in Scheme I. We report here the structure and characterization of a new member of class II compounds, Cu$^{II}_{6}$(bdmap)$_{3}$Cl$_{6}$(O)(OH) (**1**), a hexanuclear copper(II) compound with an unprecedented propeller structure, obtained from the reaction of $Cu(OCH_3)_2$ and $CuCl_2$ with the bdmapH ligand in the presence of water.

Experimental Section

General Procedures. All reactions were carried out under nitrogen atmosphere in an inert-atmosphere drybox or by using standard Schlenk line techniques. All solvents were freshly distilled prior to use. Copper(II) methoxide and 1,3-bis(dimethylamino)-2-propanol were purchased from Aldrich Chemical Co. ^{1}H NMR spectra were recorded on a Bruker AC 300 spectrometer. Elemental analyses were performed at Guelph Chemical Laboratory Ltd., Guelph, Ontario, Canada, and Desert Analytics, Tucson, AZ.

Scheme I



Synthesis of Cu$_6$(bdmap)$_3$Cl$_6$(O)(OH) (1). A 50-mg sample of $Cu(OCH_3)_2$ (0.40 mmol) was mixed with 58 mg of bdmapH (0.40 mmol) in 5 mL of CH_2Cl_2, and 54 mg of $CuCl_2$ (0.40 mmol) was then added to this solution. The mixture was stirred for 3 h. After filtration, one drop of distilled H_2O (by pipet) and 5 mL of CH_3OH were added to the solution. The solution was kept standing at 23 °C for 6 h. Diethyl ether was then added. After a few days, the initial light green precipitates were filtered off. Dark green crystals were obtained from the subsequently concentrated mother liquid (yield 40%). Mp: 178 °C. Anal. Calcd for $C_{21}H_{52}Cu_6Cl_6O_5N_6$: C, 23.72; H, 4.90; N, 7.91. Found: C, 23.73; H, 5.06; N, 7.70.

Synthesis of [Cu$_6$(bdmap)$_3$Cl$_6$(O)(OH)][Cu$_2$(bdmapH)$_2$Cl$_4$](H$_2$O) (2a). A 200-mg sample of Cu_2(bdmapH)$_2$Cl$_4$ (0.36 mmol) and 45 mg of $Cu(OCH_3)_2$ (0.36 mmol) were mixed in 10 mL of CH_2Cl_2. The solution was stirred overnight. A clear dark green solution was obtained. The solution was concentrated to about 5 mL in vacuum, and 5 mL of diethyl ether was added. Yield: 120 mg of dark green crystals (0.074 mmol, 41%). Mp: 150 °C. Anal. Calcd for $C_{35}H_{90}Cu_8Cl_{10}O_8N_{10}$: C, 25.65; H, 5.48; N, 8.53. Found: C, 25.50; H, 5.11; N, 8.32.

Synthesis of [Cu$_6$(bdmap)$_3$Cl$_6$(O)(OH)][Cu$_2$(bdmapH)$_2$Cl$_4$](H$_2$O)$_2$ (2b). A 200-mg sample of bdmapH (1.37 mmol) was placed in 15 mL of THF, and 50 mg (1.28 mmol) of potassium metal was added. The solution was stirred until the potassium metal reacted completely. A 250-mg quantity of $CuCl_2$ (1.86 mmol) was then added. After the mixture was stirred for a few hours, a dark green solution with green precipitation was obtained. The solid was collected by filtration and extracted with CH_2Cl_2. Diethyl ether was added to crystallize the product. After a few days, 95 mg of dark green crystals was obtained (0.059 mmol, yield 19%).

Magnetic Susceptibility Measurements. The magnetic susceptibilities at 0.49 kG in the temperature range 5–300 K for **1** were measured on

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Table I. Crystallographic Data for **1** and **2**

	1	**2a**	**2b**
formula	$C_{21}H_{52}Cu_6Cl_6O_5N_6$	$C_{35}H_{88}Cu_8Cl_{10}O_7N_{10}\cdot H_2O$	$C_{35}H_{88}Cu_8Cl_{10}O_7N_{10}(H_2O)_2\cdot CH_2Cl_2$
fw	1062.02	1624.01	
space group	$P2_1/n$	$C2/c$	$P2_1/a$
a, Å	12.691(7)	19.66(1)	19.811(6)
b, Å	16.31(1)	19.958(7)	14.919(4)
c, Å	20.45(2)	19.383(8)	24.860(7)
β, deg	107.07(5)	118.12(3)	95.15(4)
V, Å^3	4047(5)	6707(6)	7318(3)
Z	4	4	4
d_{calc}, g cm^{-3}	1.74	1.626	1.580
μ(Mo, Kα), cm^{-1}	35.4	29.43	27.75
λ, Å	0.710 69	0.710 69	0.710 69
T, °C	22		
R^a	0.100	0.072	0.069
$R_w{}^b$	0.102	0.074	0.081

[a] $R = \sum_{i=1}^{n}(|F_o|_i - |F_c|_i)/\sum_{i=1}^{n}|F_o|_i$. [b] $R_w = (\sum_{i=1}^{n}(w_i(|F_o|_i - |F_c|_i)^2/\sum_{i=1}^{n}(w_i|F_o|_i^2))^{1/2}$; $w = 1/\sigma^2(F_o)$.

a SQUID device (SHE variable-temperature susceptometer) at Michigan State University. The sample was quenched to 5 K at zero applied field. The field was cycled to minimize the residual field. The sample was loaded into a nitrogen-filled glovebag and run in an Al–Si alloy bucket.

X-ray Diffraction Analysis. Single crystals of **1**, **2a**, and **2b** were obtained by the slow diffusion of diethyl ether into the CH_2Cl_2 or CH_2Cl_2/CH_3OH solutions at 23 °C. All crystals were mounted on glass fibers and sealed with epoxy glue. Data were collected over the ranges $2 < 2\theta < 45°$ for compound **1** and $2 < 2\theta < 48°$ for compounds **2a** and **2b** at 23 °C on a Rigaku four-circle AFC6-S diffractometer using graphite-monochromated Mo Kα radiation and operating at 50 kV and 35 mA. The initial orientation matrix for **1** was obtained from 20 reflections ($9 < 2\theta < 15°$) located by the SEARCH routine. High-angle cell refinement was not performed for **1**. The initial orientation matrixes were obtained from 20 reflections ($12 < 2\theta < 16°$) for **2a** and from 20 reflections ($6 < 2\theta < 13°$) for **2b**. High-angle cell refinements were not performed for both crystals. Three standard reflections were measured every 147 reflections. All data processing was performed on a VAX 3520 workstation using the TEXSAN crystallographic package (Version 5.0, obtained from the Molecular Structure Corp., The Woodlands, TX). Data were corrected for Lorentz–polarization effects and absorptions.

All crystals belong to the monoclinic crystal system. The space groups $P2_1/n$ for **1** and $P2_1/a$ for **2b** were uniquely determined by the systematic absences. The systematic absences of **2a** agree with both Cc and $C2/c$. The centric $C2/c$ was chosen. The correctness of this choice was confirmed by the successful solution and refinement of the structure. The positions of metal atoms in all compounds were determined by direct methods (MITHRIL). All non-hydrogen atoms were located by the subsequent difference Fourier synthesis. The positions of hydrogen atoms except those of the disordered ligand were calculated. Their temperature factors were tried to the temperature factor of the carbon atoms to which they are bonded (multiplied by 1.10). Their contributions in structure factor calculations were included. The molecule of **2a** possesses a crystallographic 2-fold rotation axis with the C8 and O2 atoms of a bdmap ligand lying on the axis. As a consequence, this bdmap ligand displays a 2-fold rotation disorder. Two sets of CH_2 groups with 50% occupancy were located and refined successfully. The crystal of **1** was small and had significant twinning problems, which could have resulted in the high R factors. Due to the low ratio of data versus variables, only metal atoms and chlorine atoms in all crystals were refined anisotropically. One H_2O molecule was located in the crystal lattice of **2a**, while two H_2O molecules were found in the crystal lattice of **2b**. Two CH_2Cl_2 solvent molecules were also located in the crystal lattice of **2b**. One of the CH_2Cl_2 molecules was refined successfully with a 50% occupancy factor. The refinement of the other CH_2Cl_2 molecule was not satisfactory due to the disorder of this molecule. The high R factors of structures **2a** and **2b** can be attributed to the disorders of molecules in the crystal lattice and the limited number of data. The data of the X-ray diffraction analyses are given in Table I.

Results and Discussion

Synthesis and Crystal Structure of 1. Compound **1** was synthesized by the reaction of $Cu(OCH_3)_2$, $CuCl_2$, and bdmapH in 1:1:1 ratio in the presence of water. Single-crystal X-ray diffraction and elemental analysis established that compound **1** is a hexanuclear complex with the formula $Cu^{II}{}_6(bdmap)_3Cl_6(O)(OH)$. Two trinuclear compounds, $Cu_3(bdmap)_2Cl_4$ and $Cu_3(bdmap)_4Cl_2(HOCH_3)$, were synthesized previously by using the same starting materials as those for compound **1**, but under different reaction conditions, as shown in Scheme I. The successful synthesis of these compounds demonstrates that copper(II) complexes with the bdmap and halide ligands have versatile compositions and structures, depending on the stoichiometry of the starting materials and the reaction conditions. In contrast, copper(II) complexes with 2-(dialkylamino)ethanolato and halide ligands are limited to the tetranuclear compound $[Cu_2L_2X_2]_2$, only, where L = 2-(dialkylamino)ethanolato.[2]

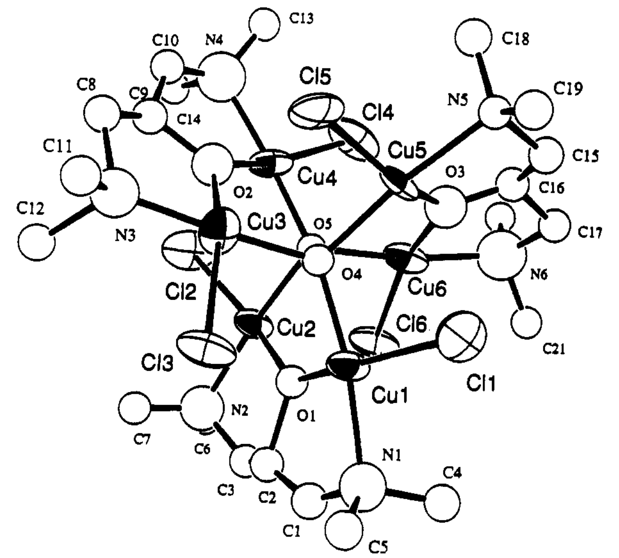

Figure 1. Molecular structure of **1** with labeling scheme and 50% thermal ellipsoids.

The molecular structure of **1** is shown in Figure 1. Selected bond distances and angles are listed in Table II. The structure of **1** can be viewed as two tricopper units bridged by three bdmap ligands through the oxygen atoms. In each tricopper unit, the three copper atoms are bridged by an oxygen atom with nearly equal Cu–O distances. The two triply bridging oxygen atoms have an approximate pyramidal geometry. O4 is 0.356 Å above the Cu1–Cu3–Cu5 plane, while O5 is 0.452 Å above the Cu2–Cu4–Cu6 plane. Similar tricopper units with a pyramidal bridging oxygen atom have been reported previously.[4,5] The Cu–Cu

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Table II. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Distances

Cu–Cl1	2.29(2)	Cu5–O3	1.92(4)	N3–C11	1.43(7)
Cu1–O1	1.89(3)	Cu5–O4	1.95(3)	N3–C12	1.7(1)
Cu1–O4	1.89(3)	Cu5–N5	1.98(4)	N4–C10	1.37(9)
Cu1–N1	2.08(5)	Cu6–Cl6	2.31(2)	N4–C13	1.39(8)
Cu2–Cl2	2.31(2)	Cu6–O3	2.08(4)	N4–C14	1.6(1)
Cu2–O1	1.99(3)	Cu6–O5	1.95(3)	N5–C15	1.50(7)
Cu2–O5	1.92(3)	Cu6–N6	1.97(6)	N5–C18	1.37(8)
Cu2–N2	2.03(6)	O1–C2	1.60(7)	N5–C19	1.4(1)
Cu3–Cl3	2.29(2)	O2–C9	1.41(7)	N6–C17	1.52(9)
Cu3–O2	2.08(4)	O3–C16	1.34(6)	N6–C20	1.51(8)
Cu3–O4	1.82(3)	N1–C1	1.22(9)	N6–C21	1.48(8)
Cu3–N3	1.88(5)	N1–C4	1.42(9)	C1–C2	1.35(9)
Cu4–Cl4	2.31(2)	N1–C5	1.51(9)	C2–C3	1.3(1)
Cu4–O2	1.89(4)	N2–C3	1.43(9)	C8–C9	1.39(8)
Cu4–O5	1.85(3)	N2–C6	1.43(8)	C9–C10	1.35(9)
Cu4–N4	1.92(6)	N2–C7	1.33(9)	C15–C16	1.46(8)
Cu5–Cl5	2.25(2)	N3–C8	1.54(7)	C16–C17	1.45(9)

Angles

Cl1–Cu1–O1	159(1)	O3–Cu6–N6	83(2)	C11–N3–C12	99(5)
Cl1–Cu1–O4	92(1)	O5–Cu6–N6	171(2)	Cu4–N4–C10	112(5)
Cl1–Cu1–N1	98(2)	Cu1–O1–Cu2	138(2)	Cu4–N4–C13	111(5)
O1–Cu1–O4	89(1)	Cu1–O1–C2	115(3)	Cu4–N4–C14	108(5)
O1–Cu1–N1	82(2)	Cu2–O1–C2	107(3)	C10–N4–C13	122(7)
O4–Cu1–N1	169(2)	Cu3–O2–Cu4	130(2)	C10–N4–C14	95(6)
Cl2–Cu2–O1	159(1)	Cu3–O2–C9	108(4)	C13–N4–C14	107(6)
Cl2–Cu2–O5	90(1)	Cu4–O2–C9	122(4)	Cu5–N5–C15	101(4)
Cl2–Cu2–N2	96(2)	Cu5–O3–Cu6	131(2)	Cu5–N5–C18	109(4)
O1–Cu2–O5	88(1)	Cu5–O3–C16	124(4)	Cu5–N5–C19	112(5)
O1–Cu2–N2	87(2)	Cu6–O3–C16	105(4)	C15–N5–C18	117(6)
O5–Cu2–N2	174(2)	Cu1–O4–Cu3	119(2)	C15–N5–C19	109(6)
Cl3–Cu3–O2	158(1)	Cu1–O4–Cu5	115(2)	C18–N5–C19	109(7)
Cl3–Cu3–O4	88(1)	Cu3–O4–Cu5	115(2)	Cu6–N6–C17	115(6)
Cl3–Cu3–N3	96(2)	Cu2–O5–Cu4	113(2)	Cu6–N6–C20	107(5)
O2–Cu3–O4	93(1)	Cu2–O5–Cu6	114(2)	Cu6–N6–C21	112(5)
O2–Cu3–N3	83(2)	Cu4–O5–Cu6	116(2)	C17–N6–C20	111(6)
O4–Cu3–N3	176(2)	Cu1–N1–C1	102(6)	C17–N6–C21	105(6)
Cl4–Cu4–O2	161(1)	Cu1–N1–C4	109(5)	C20–N6–C21	106(6)
Cl4–Cu4–O5	92(1)	Cu1–N1–C5	106(5)	N1–C1–C2	139(9)
Cl4–Cu4–N4	98(2)	C1–N1–C4	129(8)	O1–C2–C1	97(6)
O2–Cu4–O5	91(2)	C1–N1–C5	106(7)	O1–C2–C3	106(7)
O2–Cu4–N4	78(2)	C4–N1–C5	103(6)	C1–C2–C3	148(9)
O5–Cu4–N4	169(2)	Cu2–N2–C3	99(5)	N2–C3–C2	122(9)
Cl5–Cu5–O3	157(1)	Cu2–N2–C6	116(4)	N3–C8–C9	108(6)
Cl5–Cu5–O4	89(1)	Cu2–N2–C7	115(5)	O2–C9–C8	120(6)
Cl5–Cu5–N5	96(1)	C3–N2–C6	103(7)	O2–C9–C10	102(7)
O3–Cu5–O4	94(2)	C3–N2–C7	121(7)	C8–C9–C10	133(8)
O3–Cu5–N5	82(2)	C6–N2–C7	103(7)	N4–C10–C9	123(8)
O4–Cu5–N5	173(2)	Cu3–N3–C8	112(4)	N5–C15–C16	119(6)
Cl6–Cu6–O3	159(1)	Cu3–N3–C11	119(4)	O3–C16–C15	101(5)
Cl6–Cu6–O5	91(1)	Cu3–N3–C12	121(5)	O3–C16–C17	123(6)
Cl6–Cu6–N6	98(2)	C8–N3–C11	103(5)	C15–C16–C17	119(7)
O3–Cu6–O5	89(2)	C8–N3–C12	100(5)	N6–C17–C16	103(7)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

separations within the tricopper unit are similar: Cu1–Cu3 = 3.19(1), Cu1–Cu5 = 3.24(1), Cu3–Cu5 = 3.18(1), Cu2–Cu4 = 3.14(1), Cu2–Cu6 = 3.25(1), Cu4–Cu6 = 3.23(1) Å. These distances are comparable to those of previously reported trinuclear copper(II) complexes with a triply bridging hydroxo or oxo ligand.[4,5] Each copper(II) center is similarly coordinated by one nitrogen atom, one chlorine atom, and two oxygen atoms with an approximate square-planar geometry and normal bond distances. In the tricopper unit, the dihedral angles between the three planar Cu(II) units range from 65.6 to 72.2°. The chlorine atom on each copper center is weakly coordinated to the second copper center in the same trimer unit as the fifth ligand, as evidenced by the long Cu–Cl distances: Cu1–Cl3 = 2.81(2), Cu2–Cl6 = 2.90(2), Cu3–Cl5 = 2.83(2), Cu4–Cl2 = 2.75(2), Cu5–Cl1 = 2.93(2), Cu6–Cl4 = 2.91(2) Å. The geometry of each copper center can be, therefore, best described as an approximate square pyramid.

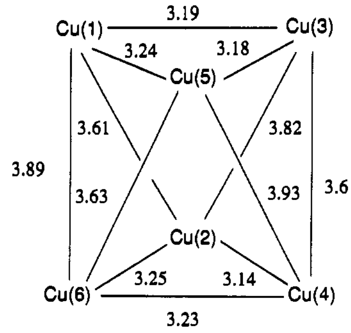

Figure 2. Diagram showing the arrangement of copper atoms in **1**.

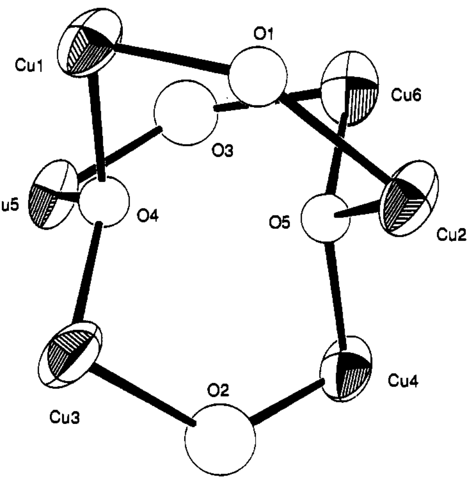

Figure 3. Diagram showing the core structure of **1**.

The structure of 1 can also be viewed as three Cu_2(bdmap)Cl_2 dimers linked together through two oxygen atoms. In each dimer, the two copper atoms are bridged by the oxygen atom of the bdmap ligand. The Cu–Cu separations, Cu1–Cu2 = 3.61(1), Cu3–Cu4 = 3.61(1), and Cu5–Cu6 = 3.63(1) Å, within the dimers, are similar to the Cu–Cu separations with the similar single bdmap bridge found in other previously reported polynuclear copper(II) complexes.[1a,3] All other copper–copper separations are more than 3.80 Å. The geometry of the hexacopper cluster can be best described as a distorted trigonal antiprism, as shown in Figure 2. The two CuO_2NCl units in each dimer are approximately coplanar. The dihedral angles between Cu1 and Cu2 planes, Cu3 and Cu4 planes, and Cu5 and Cu6 planes are 17.4, 16.2, and 13.1°, respectively.

Most interestingly, the core structure of 1, consisting of six copper atoms and five oxygen atoms, resembles those of cryptands,[6] as illustrated by Figure 3. In fact, this molecule appeared to behave like a cryptand. If both O4 and O5 atoms are formulated as oxo ligands, the molecule, then, has a –1 charge. To neutralize this charge, a proton is required. We believe that this proton is trapped inside the cavity of the "cryptand" through hydrogen bonding. The separation between O4 and O5 atoms is 2.45(4) Å, much shorter than the sum of covalent radii of the O^{2-} anion (2.64 Å) and the sum of van der Waals radii of the oxygen atom (2.80 Å),[7] an indication of the presence of a strong hydrogen bond.[8] Although the distances from the three oxygen atoms of bdmap ligands to the O4 and O5 atoms are also quite short, O1–O4 = 2.64(5), O1–O5 = 2.70(5), O2–O4 = 2.70(5), O2–O5 = 2.67(5), O3–O4 = 2.83(5), and O3–O5 = 2.83(5) Å, the lone pairs of electrons of these bdmap oxygen atoms do not

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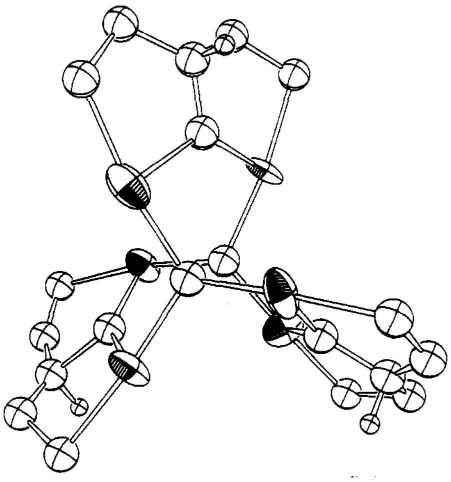
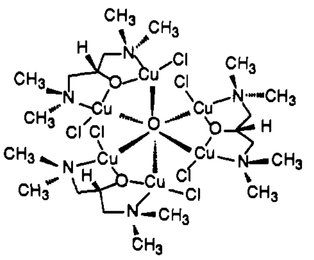


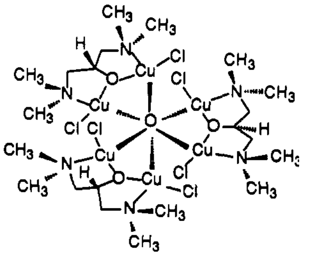
Figure 4. Diagram showing the conformation of **1**.

have the appropriate orientation for the formation of hydrogen bonds, as shown in Figures 1 and 3. In contrast, both O4 and O5 atoms have a pyramidal geometry, with the lone pair of electrons pointing to the center of the cavity, ideal for the hydrogen bonding. Therefore, the proton is mostly likely situated between the O4 and O5 atoms. We have not be able to unambiguously assign the vibrational stretching frequency in the IR spectrum for the proposed O···H···O bond. Nevertheless, we believe that it is most appropriate to formulate **1** as $Cu_6(bdmap)_3Cl_6(O)(OH)$ where the proton is shared between the oxo and the hydroxo ligands. The formation of oxo and hydroxo ligands in **1** was probably caused by the reaction of the methoxo group with H_2O. This is also supported by the fact that compound **1** could only be obtained in good yield with the addition of H_2O to the reaction mixture. Formation of oxo and hydroxo ligands in copper(II) complexes with the bdmap ligand has been observed previously.[1a]

Compound **1** is a chiral molecule with an unprecedented propeller structure. If the conformations of the five-membered rings are ignored, this molecule has an approximate C_3 symmetry. The Λ and Δ enantiomers coexist in the centric crystal lattice. A careful examination of the conformations of the five-membered rings and the orientation of the CH group leads to two possible diastereomers, **A** and **B**. In **A** all three CH groups of the bdmap ligands point in the same direction, while, in **B** two of them point in the same direction and the other point in the opposite direction. Compound **1** has the conformation **B**, as shown in Figure 4.



A



B

Hexanuclear copper(II) complexes are scarce. Among the few known hexanuclear Cu(II) complexes are the $[Cu_3O(dpeo)_3(ClO_4)]_2$ complex,[5a] where dpeo = 1,2-diphenyl-2-(methylimino)ethanone 1-oxime and the two trinuclear $[Cu_3O(dpeo)_3]^+$ units are linked together through two intermolecular Cu–O bonds (2.33 Å), and the $Cu_6(\mu\text{-}OCMe_3)_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2$ complex,[9] where the six Cu(II) atoms are linked together by six alkoxo ligands to form a hexagon. Compound **1** is the first hexanuclear Cu(II) complex with a propeller structure.

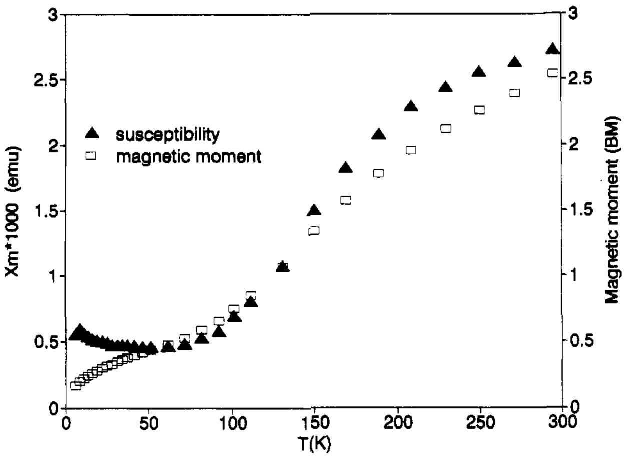


Figure 5. Plot of molar susceptibility and magnetic moment of **1** versus *T* at 0.49 kG.

Synthesis and Crystal Structure of $[Cu_6(bdmap)_3Cl_6O(OH)][Cu_2(bdmapH)_2Cl_4]$ (2). In an attempt to synthesize diastereomer A of compound **1**, alternative synthetic methods were used. From the reaction of $Cu_2(bdmapH)_2Cl_4$ with $Cu(OCH_3)_2$, we isolated a new Cu(II) complex formulated as $[Cu_6(bdmap)_3Cl_6O(OH)][Cu_2(bdmapH)_2Cl_4](H_2O)$ (**2a**). The structure of this compound was determined by single-crystal X-ray diffraction analysis. The crystal lattice contains two independent $Cu_6(bdmap)_3Cl_6O(OH)$ and $Cu_2(bdmapH)_2Cl_4$ units. The structure of the $Cu_2(bdmapH)_2Cl_4$ unit is essentially identical with that of the previously reported $Cu_2(bdmapH)_2Cl_4$ compound obtained from the reaction of $CuCl_2$ with bdmapH ligands.[3a] The structure of the $Cu_6(bdmap)_3Cl_6O(OH)$ portion in **2a** is very similar to that of **1** except that this molecule possesses a crystallographic 2-fold rotation axis and one of the bdmap ligands is disordered over the 2-fold axis. Again, the conformation of this molecule belongs to type **B**. A similar Cu(II) compound was also isolated from the reaction of K(bdmap) with $CuCl_2$. The crystals (**2b**) isolated from this reaction contain the CH_2Cl_2 solvent molecule and two H_2O molecules and belong to a space group different from that of **2a**. Althoug the structural refinement of **2b** was not very satisfactory, the data clearly revealed that the structure of the Cu_6 unit in **2b** is the same as that in **2a**, and no crystallographic disorder was observed. Although H_2O molecules were found in the crystals of both **2a** and **2b**, no intermolecular contacts or hydrogen bonds between the Cu_6 and the Cu_2 units in both crystal lattices were observed. The cocrystallization of these two compounds could be attributed to the packing forces of these molecules in the crystal lattice. It has not been understood yet why only diastereomer **B** was observed for the Cu_6 compound from all three reactions.

Magnetic Properties of 1. The magnetic susceptibility of compound **1** was measured over the temperature range 4–300 K at 0.49 kG. Molar susceptibility data have been corrected for diamagnetism by using Pascal's constants. Due to the complexity of this cluster compound, we have not been able to do theoretical fitting for the susceptibility data. Nevertheless, some information can be obtained by a qualitative analysis of the data. As shown in Figure 5, the plot of χ_m versus T has a minimum at about 50 K. The slight increase of the susceptibility with the decrease of temperature in the range 2–25 K is probably caused by the presence of a small percentage of monomeric impurities. The magnetic moment for a noninteracting hexanuclear copper(II) system is 4.65 μ_B, if a g value of 2.20 for a monomeric copper(II) complex is assumed. The magnetic moment of compound **1** is 2.54 μ_B at 295 K and decreases rapidly with the decrease of temperature, which suggests that compound **1** is a strongly antiferromagnetically coupled system. This is in agreement with the fact that dimeric and trimeric copper(II) complexes with

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(9) Evans, W. J.; Hain, J. H., Jr. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 39.

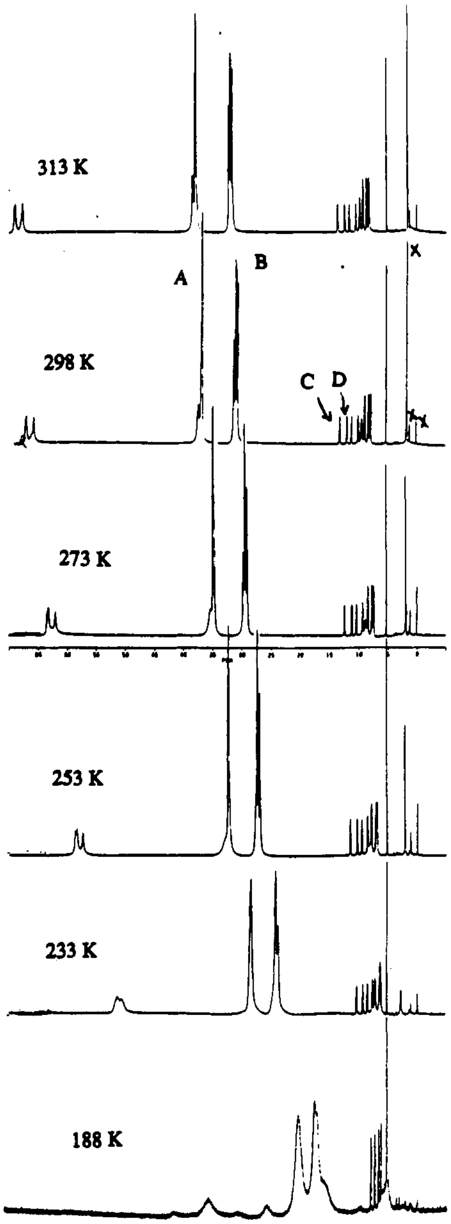


Figure 6. Variable-temperature ^1H NMR spectra of **1**.

oxygen bridges typically display antiferromagnetically coupled magnetic behavior.[10]

Solution Behavior. Since the magnetic data for compound **1** in the solid state suggest an antiferromagnetically coupled ground state and no EPR signal was detected in both solution and the solid state, one would anticipate that the behavior of compound **1** in solution could be studied by NMR spectroscopy.[11] Indeed, a moderately sharp ^1H NMR spectrum for compound **1** in CD_2Cl_2 was obtained at 298 K, as shown in Figure 6. The chemical shifts of the bdmap ligand spread from 6 to 70 ppm, a substantial shift in comparison to the 2–4 ppm range of the free ligand's chemical shifts. Undoubtedly, this dramatic shift is caused by the presence of paramagnetism, which is in agreement with the fact that compound **1** has a magnetic moment of 2.54 μ_B at 298 K. However, contrary to the typical paramagnetic shift, which usually increases with a decrease of temperature,[11] the extent of the shift in **1** decreases nearly linearly with the decrease of temperature, as shown in Figure 6. The shifts of the peaks A–D with temperature were plotted and are shown in Figure 7. The trends of these plots are similar to those of the molar susceptibility and the magnetic moment of the compound in the solid state, an indication that compound **1** has an antiferromagnetically coupled ground state in solution as well.

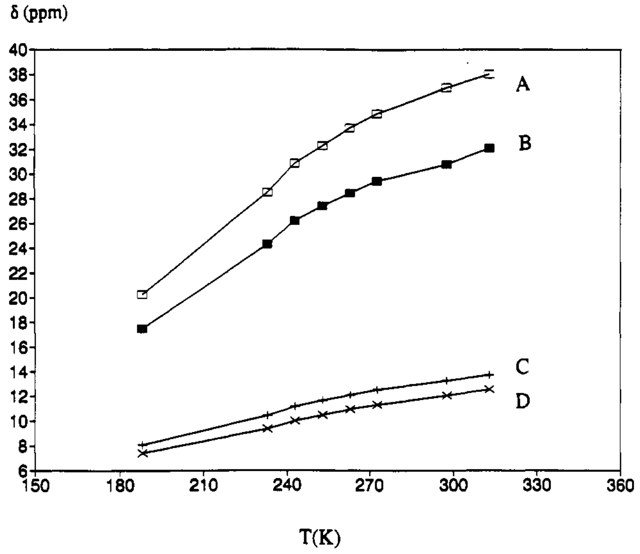
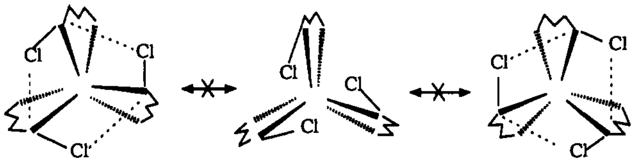


Figure 7. Plots of the change of chemical shifts of **1** versus T.

Scheme II



In the 298 K spectrum, the chemical shifts at 66.96 and 65.73 ppm were tentatively assigned to the CH groups, the chemical shifts at 36.96 and 31.04 ppm were assigned to the CH_3 groups, and the chemical shifts between 14 and 7 ppm were assigned to the CH_2 groups. As the first approximation, the methyl groups can be divided into two subgroups: group **a**, *cis* to the CH bond, and group **b**, *trans* to the CH bond in the five-membered ring. We believe that the two chemical shifts centered at 36.96 and 31.04 ppm at 298 K belong to group **a** and group **b**, respectively. If the compound retains conformation **B** in solution and no interconversion of the enantiomers occurs, the chemical environments for all 12 methyl groups are not equivalent. Therefore, the total number of chemical shifts for the methyl groups should be 12, 6 for each subgroup. On the other hand, if the interconversion of the enantiomers does occur in solution, the equilibrium structure would have a mirror plane as shown in Scheme II, which would make the dimethylamino groups in the front have chemical environments identical to those in the back. As a consequence, the total number of chemical shifts for the methyl groups should be 6, 3 for each subgroup. The fact that at least four chemical shifts were observed for one of the subgroups at 313 K implies that the enantiomer interconversion does not occur at this temperature. We believe that the enantiomer interconversion process is hindered mainly by the chlorine ligands in the molecule. As indicated by crystal struture data, each chlorine atom is covalently bonded to one copper center and weakly bonded to the second copper center in the same trimer unit as the fifth ligand. Hence the conformation of the molecule is locked. By molecular modeling, it can be demonstrated readily that, in order for the molecule to undergo the enantiomer interconversion, not only do the weak Cu–Cl bonds have to be broken but all three chlorine atoms in each of the trimer unit also have to be in very close contact distances in the intermediate, which would require a very high activation energy. As a result, the interconversion

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(10) (a) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986. (b) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259. (c) Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *92*, 45.

(11) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, PA, 1977.

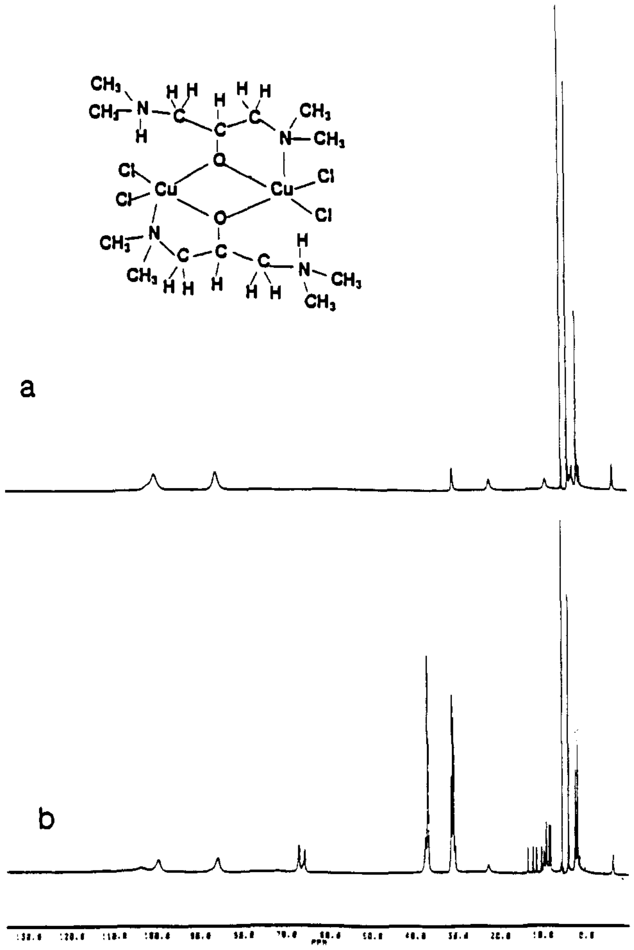

Figure 8. (a) ^{1}H NMR spectrum of $Cu_2(bdmapH)_2Cl_4$ at 298 K. ^{1}H NMR spectrum of **2a** at 298 K.

does not occur in solution. Scheme II illustrates the enantiomer interconversion process, and only three chlorine atoms are shown. The fact that not all 12 chemical shifts were observed for the methyl groups can be explained by accidental overlaps. Similar argument is also applicable to the CH_2 chemical shifts. Each proton of the CH_2 groups has a distinct chemical environment. A total of 12 chemical shifts would be expected for the CH_2 groups. In the 298 K spectrum, eight chemical shifts were observed for the CH_2 groups and the integrals of four of them are twice those of the remaining four, again caused by accidental overlap. The chemical shift of the OH group could not be assigned unambiguously. The attempted proton-exchange experiment with D_2O was unsuccessful due to the decomposition of compound **1**.

The pure $Cu_2(bdmapH)_2Cl_4$ compound is also an antiferromagnetically coupled system.[3a] The ^{1}H NMR spectrum of this compound at 298 K in CD_2Cl_2 is shown in Figure 8a. The chemical shifts at 1.78 and 3.86 ppm are tentatively assigned to the ammonium methyl groups while the two chemical shifts at 100.17 and 85.88 ppm are assigned to the methyl groups of the amino group bonded to the copper center. The four chemical shifts at 30.65, 22.01, 9.10, and –6.47 ppm are assigned to the four protons of the two CH_2 groups. The peak at 2.50 ppm is probably caused by the NH group because the position of this peak changes with the concentration of the solution. The shoulder peak at about 102 ppm is probably the chemical shift of the CH group. We have performed several 2D ^{1}H NMR experiments to confirm our assignments. However, every attempt failed to give definitive correlations of the chemical shifts in the spectra. Therefore, our assignment for the chemical shifts of these two compounds was tentative and was based mainly on the relative integrals and the chemical environment of the protons.

Since compound **2** is a 1:1 mixture of the $Cu_6(bdmap)_3Cl_6(O)(OH)$ and $Cu_2(bdmapH)_2Cl_4$ compounds, the ^{1}H NMR spectrum of **2** should have all the features of both compounds. Indeed, as shown in Figure 8, the spectrum of compound **2** is a combination of those of compound **1** and $Cu_2(bdmapH)_2$, implying that there is no interaction between these two compounds in solution.

Conclusion. Copper(II) halide complexes with the bdmap ligand display versatile compositions and structures. A new hexanuclear copper(II) compound (**1**) with a propeller structure has been characterized. This compound can be readily cocrystallized with the $Cu_2(bdmapH)_2Cl_4$ compound in a 1:1 ratio. Compound **1** is a chiral molecule and an antiferromagnetically coupled magnetic system. The ^{1}H NMR spectroscopic study suggested that no enantiomer interconversion occurs in solution.

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Supplementary Material Available: Tables S1–S11, giving crystallographic data, atomic coordinates, anisotropic thermal parameters, atomic positional and isotropic thermal parameters, and bond lengths and angles (27 pages). Ordering information is given on any current masthead page.