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Homonuclear Copper Complexes with Multidentate Amino Alcohol Ligands. Synthesis and Characterization of a Dicopper Zwitterion, Cu_2(1,3-bis(dimethylamino)-2-propanol)$_2Cl_4$, and a Tricopper Compound, Cu_3(1,3-bis(dimethylamino)-2-propanolato)$_2Cl_4$

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Reaction of 1,3-bis(dimethylamino)-2-propanol (dmap-H) with $CuCl_2$ in 1:1 ratio in THF yielded a dimeric Cu(II) compound with the formula Cu_2(dmap-H)$_2Cl_4$ (**1**). **1** is a zwitterion with an intramolecular ammonium group. The proton on the ammonium group can be removed by a base through an intermolecular process. **1** reacted with $Cu(OMe)_2$ in 1:1 ratio in CH_2Cl_2 to produce a trimeric Cu(II) compound with the formula Cu_3(dmap)$_2Cl_4$ (**2**). Both crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis. **1**, $C_{14}H_{36}Cu_2Cl_4O_2N_4\cdot C_7H_8$, crystallizes in the monoclinic space group $C2/c$ with a = 18.619 (3) Å, b = 12.129 (2) Å, c = 13.822 (2) Å, β = 106.69 (1)°, V = 2989.8 (7) Å^3, and Z = 4. **2**, $C_{14}H_{34}Cu_3Cl_4O_2N_4\cdot CH_2Cl_2$, crystallizes in the monoclinic space group $P2_1/a$ with a = 16.45 (2) Å, b = 10.445 (7) Å, c = 16.47 (1) Å, β = 101.52 (8)°, V = 2793 (5) Å^3, and Z = 4.

Introduction

There is much current interest in the investigation of homonuclear and heteronuclear metal alkoxide complexes, stimulated by their possible applications in MOCVD and chemical sol–gel processes.[1] We have been particularly interested in investigating those systems involving alkaline-earth-metal atoms, lanthanide atoms, and copper atoms since these elements are the major components in high-temperature superconductors.[2] Although a number of systems employing chemical sol–gel methods have been reported to produce high-temperature superconductors, the chemical reactions and intermediates involved in these processes have been poorly understood.[3] One of the systems used diethylenetriamine, alkoxide, and acetate ligands to form a gel solution of yttrium, barium, and copper. Fibres of 1–2–3 superconductor were obtained from this system. One-dimensional copper chain structures linked by diethylenetriamine for the precursor compounds were proposed.[4] This promoted us to investigate mixed-metal complexes of yttrium, barium, and copper with multidentate amine or amino alcohol ligands. We have not been able to isolate any multinuclear species from the diethylenetriamine reactions. However, our research with 1,3-bis(dimethylamino)-2-propanol ligand (dmap-H) has been quite fruitful. We have isolated several Y–Cu and Ln–Cu compounds with a dmap-H or a 1,3-bis(dimethylamino)-2-propanolato (dmap) ligand. The details will be published in a subsequent paper. We report here two new dimeric and trimeric copper compounds with a dmap-H or a dmap ligand.

Experimental Section

All reactions were performed either in a Schlenk line or in an inert-atmosphere drybox under nitrogen atmosphere. Solvents were distilled by standard procedures prior to use. $Cu(OMe)_2$ and dmap-H ligand were purchased from Aldrich Chemical Co. and used without further purification. IR spectra were recorded on a Nicolet DX FTIR spectrometer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada, and Desert Analytics, Tucson, AZ. Magnetic susceptibilities were measured on a Gouy Magnetic balance using $Hg[Co(SCN)_4]$ as standard.

Synthesis of Cu_2(dmap-H)$_2Cl_4$ (1). A 500-mg (0.0037-mol) sample of $CuCl_2$ was dissolved in 150 mL of THF. Then 540 mg (0.0037 mol) of 1,3-bis(dimethylamino)-2-propanol was added dropwise to this solution. A green crystalline solid formed and precipitated from the solution. After being stirred for 1 h at 23 °C, the solution was filtered. The bright green solid was collected. Recrystallization of this solid from ethanol and diethyl ether at 0 °C produced 620 mg (0.0011 mol) of **1** (60%). Mp 137 °C dec. Anal. Calcd for $C_{14}H_{36}Cu_2Cl_4O_2N_4$: C, 29.95; H, 6.47; N, 9.98. Found: C, 29.82; H, 6.70; N, 9.67.

Synthesis of Cu_3(dmap)$_2Cl_4$ (2). Method A. A 50-mg (0.089-mmol) sample of compound **1** was dissolved in 10 mL of CH_2Cl_2. Then 12 mg (0.096 mmol) of $Cu(OMe)_2$ was added to this solution. After the mixture was stirred for 1 h at 23 °C, the blue solid of $Cu(OMe)_2$ disappeared completely and a clear dark green solution was obtained. Then 10 mL of diethyl ether was added to this solution to crystallize the product. After the mixture was allowed to stand at 23 °C for 2–3 days, dark green crystals of **2** solvated by CH_2Cl_2 were obtained (dry weight 25 mg, 0.0402 mmol, 45%). Mp 163–165 °C dec. Anal. Calcd for $C_{14}H_{36}Cu_3Cl_4O_2N_4$: C, 26.99; H, 5.50; N, 9.00. Found: C, 27.01; H, 5.48; N, 8.72.

Method B. $CuCl_2$ (135 mg, 1 mmol) was dissolved in THF (75 mL). Na(dmap) (168 mg, 1 mmol) was then added to this solution. The mixture was stirred overnight at 23 °C. Dark green solid precipitated and was collected by filtration. After being washed with ethanol (20 mL), the dark green solid was recrystallized from CH_2Cl_2 (25 mL) and diethyl ether (10 mL). A yield of 86 mg (dry weight 0.140 mmol, 41%) of compound **2** was obtained.

X-ray Diffraction Analysis. Single crystals of **1** with rectangular shapes were grown by slow diffusion of diethyl ether into the CH_2Cl_2/toluene solution of **1** at 23 °C. Dark green single crystals of **2** were obtained from the solution of CH_2Cl_2 and diethyl ether at 23 °C. Both crystals were mounted on glass fibers and sealed with epoxy glue. Data were collected over the range $3 < 2\theta \leq 50°$ for **1** and $2 < 2\theta < 45°$ for **2** at 23 °C on a Rigaku four-circle AFC6-S diffractometer with graphite-monochromated Mo Kα radiation operated at 50 kV and 35 mA. The initial orientation matrix for **1** was obtained from 20 reflections ($8 < 2\theta < 15°$) located by the SEARCH routine. This matrix was refined by using 25 high-angle reflections ($34 < 2\theta < 42°$). The orientation matrix for **2** was obtained from 20 reflections ($13 < 2\theta < 16°$) located by the SEARCH routine. Attempted high-angle cell refinements were unsuccessful due to too few available strong reflections at $2\theta > 35°$. Three standard reflections were measured every 147 reflections. Crystals of **1** contain a toluene molecule in the lattice (one toluene per molecule of **1**). No significant decay was observed for this crystal. Crystals of **2** contain a CH_2Cl_2 solvent molecule (one CH_2Cl_2 per molecule of **2**). Upon isolation from the solution, crystals of **2** rapidly lost CH_2Cl_2 molecules and became powders. Despite our effort to mount the crystal and seal it quickly in epoxy glue, it had partially decomposed. However, no further decay was observed after the crystal was sealed. All data processing were performed on a VAX workstation 3520 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.

Crystals of **1** and **2** both belong to the monoclinic crystal system. The space group $P2_1/a$ for **2** was uniquely determined by the systematic

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

	1	**2**
formula	$C_{14}H_{36}Cu_2Cl_4O_2N_4{\cdot}C_7H_8$	$C_{14}H_{34}Cu_3Cl_4O_2N_4{\cdot}CH_2Cl_2$
fw	653.50	707.80
space group	*C*2/*c* (No. 15)	*P*2$_1$/*a* (No. 14)
a, Å	18.619 (3)	16.45 (2)
b, Å	12.129 (2)	10.445 (7)
c, Å	13.822 (2)	16.47 (1)
β, deg	106.69 (1)	101.52 (8)
V, Å^3	2989.8 (7)	2793 (5)
Z	4	4
d_{calc}, g cm^{-3}	1.45	1.65
μ(Mo K*α*), cm^{-1}	18.1	28.7
λ, Å	0.71069	0.71069
T, °C	22	22
R^a	0.036	0.078
$R_w{}^b$	0.039	0.080

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

absences. The systematic absences for **1** agree with both space groups *Cc* and *C*2/*c*. *C*2/*c* was chosen. The correctness of this choice was confirmed by the successful solution and refinements. The positions of metal atoms in both crystals were determined by the direct method (MITHRIL). The other non-hydrogen atoms were located by subsequent difference Fourier synthesis. The hydrogen atom H(21) on the noncoordinated amino group N(1) in **1** was located directly from difference Fourier synthesis. The positions of all other hydrogen atoms were calculated. Their temperature factors were tied to the temperature factor of the carbon atoms to which they are bonded (multiplied by 1.10). Their contribution in structural factor calculations were included. Molecule **1** possesses a C_2 symmetry. C(8) and C(11) in the toluene molecule lie on the 2-fold axis. The methyl group C(12) disorders over two sites, related by a C_2 symmetry of operation, with 50% occupancy for each site. This solvent molecule and the CH_2Cl_2 molecule in **2** were refined successfully. ORTEP drawings for these solvent molecules are given in the supplementary material. C(3) in **2** shows substantial high-temperature factor. We believe it was caused by some degree of disorder or the poor quality of the crystal. Efforts to model this disorder were unsuccessful. All non-hydrogen atoms in **1** were refined anisotropically. All non-hydrogen atoms except N(2) in **2** were refined anisotropically. The largest peak in the final difference Fourier map for **1** is 0.30 e Å^{-3}, located 1.21 Å from C(8). The largest peak in the final difference Fourier map for **2** is 1.04 e Å^{-3}, located 1.29 Å from Cu(1) and 1.22 Å from O(2). The data of X-ray diffraction analysis were given in Table I.

Molecular Orbital Calculations. Molecular orbital calculations were conducted on a VAX 3520 computer operating under the VMS operating system. The molecular model for compound **1** was constructed from crystallographic bond lengths, bond angles, and dihedral angles for all atoms except hydrogen atoms. Methyl groups on the nitrogen atoms of the dmap ligand were replaced by hydrogen atoms. All hydrogen atoms were added using standard C–H and N–H bond lengths. Bond angles and dihedral angles were optimized using the extended Hückel option of the OPT9 program in the TRIBLE package.[5] Cartesian coordinates obtained from this optimization were used for MO calculations using the Fenske–Hall (FH) method.[6] The calculation was converged within a deviation of less than 0.01 in 10 iterations. AM1 calculations[7] on the molecule of dmap-H and its zwitterion form were conducted using the AM1 option in the AMPAC program included in the TRIBLE package. A full geometric optimization was performed on both structures.

Results and Discussion

Synthesis, Crystal Structure, and Bondings of $Cu_2(dmap\text{-}H)_2Cl_4$ (1). Compound **1** was initially isolated from the reaction of $Ba(dmap)_2$, $CuCl_2$, and dmap-H ligand. This compound was also synthesized directly from the reaction of $CuCl_2$ with DMAP-H ligand in a 1:1 ratio. **1** was fully characterized by IR spectroscopy and elemental and single-crystal X-ray diffraction analyses.

Table II. Positional Parameters and *B*(eq) for Compound **1**

atom	*x*	*y*	*z*	*B*(eq),^{a} Å^2
Cu	0.42124 (3)	0.19953 (5)	0.23624 (4)	2.54 (2)
Cl(1)	0.33413 (7)	0.3640 (1)	0.19663 (9)	3.36 (5)
Cl(2)	0.36128 (7)	0.0658 (1)	0.12559 (9)	3.74 (5)
O	0.5118 (1)	0.2509 (3)	0.3408 (2)	2.6 (1)
N(1)	0.6223 (2)	0.3572 (3)	0.5070 (3)	2.9 (2)
N(2)	0.3918 (2)	0.1405 (3)	0.3578 (3)	3.0 (2)
C(1)	0.5110 (2)	0.2342 (4)	0.4405 (3)	2.6 (2)
C(2)	0.4298 (3)	0.2165 (4)	0.4400 (3)	3.4 (2)
C(3)	0.5421 (3)	0.3365 (4)	0.5012 (3)	3.3 (2)
C(4)	0.6450 (3)	0.4712 (4)	0.5426 (4)	4.5 (2)
C(5)	0.6749 (3)	0.2760 (4)	0.5702 (4)	4.1 (2)
C(6)	0.4210 (3)	0.0279 (4)	0.3809 (4)	4.3 (2)
C(7)	0.3105 (3)	0.1404 (5)	0.3463 (4)	4.7 (3)
C(8)	0.5000	0.2029 (7)	0.7500	4.8 (4)
C(9)	0.5657 (4)	0.2624 (7)	0.7877 (4)	6.1 (3)
C(10)	0.5611 (8)	0.379 (1)	0.7846 (8)	10.6 (8)
C(11)	0.5000	0.428 (2)	0.7500	14 (2)
C(12)	0.6395 (7)	0.232 (1)	0.836 (1)	6.4 (7)

[a] $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i{}^*a_j{}^*\vec{a}_i{\cdot}\vec{a}_j$.

Table III. Bond Distances (Å) and Angles (deg) for Compound **1**^{a}

	(a) Bond Distances		
Cu–Cu	2.847 (1)	N(2)–C(2)	1.476 (6)
Cu–Cl(1)	2.530 (1)	N(2)–C(6)	1.470 (6)
Cu–Cl(2)	2.288 (1)	N(2)–C(7)	1.476 (6)
Cu–O	1.980 (3)	C(1)–C(2)	1.524 (6)
Cu–O′	1.959 (3)	C(1)–C(3)	1.516 (6)
Cu–N(2)	2.041 (4)	C(8)–C(9)	1.386 (8)
O–C(1)	1.398 (5)	C(8)–C(9)	1.386 (8)
N(1)–C(3)	1.494 (6)	C(9)–C(10)	1.41 (1)
N(1)–C(4)	1.488 (6)	C(9)–C(12)	1.39 (1)
N(1)–C(5)	1.483 (6)	C(10)–C(11)	1.25 (2)
N(1)–H(21)	1.001		
	(b) Bond Angles		
Cu–Cu–Cl(1)	126.93 (3)	C(3)–N(1)–C(5)	113.7 (4)
Cu–Cu–Cl(2)	112.05 (4)	C(4)–N(1)–C(5)	110.2 (4)
Cu–Cu–O	43.42 (8)	Cu–N(2)–C(2)	103.4 (3)
Cu–Cu–O	44.02 (8)	Cu–N(2)–C(6)	109.5 (3)
Cu–Cu–N(2)	113.6 (1)	Cu–N(2)–C(7)	114.9 (3)
Cl(1)–Cu–Cl(2)	104.76 (5)	C(2)–N(2)–C(6)	110.3 (4)
Cl(1)–Cu–O	105.59 (9)	C(2)–N(2)–C(7)	109.5 (4)
Cl(1)–Cu–O′	95.74 (9)	C(6)–N(2)–C(7)	109.1 (4)
Cl(1)–Cu–N(2)	98.5 (1)	O–C(1)–C(2)	108.0 (3)
Cl(2)–Cu–O	149.4 (1)	O–C(1)–C(3)	108.5 (4)
Cl(2)–Cu–O′	97.27 (9)	C(2)–C(1)–C(3)	109.8 (4)
Cl(2)–Cu–N(2)	96.1 (1)	N(2)–C(2)–C(1)	110.3 (4)
O–Cu–O′	75.8 (1)	N(1)–C(3)–C(1)	112.6 (4)
O–Cu–N(2)	83.3 (1)	C(9)–C(8)–C(9)	117.3 (9)
O–Cu–N(2)	157.3 (1)	C(8)–C(9)–C(10)	117.9 (8)
Cu–O–Cu	92.6 (1)	C(8)–C(9)–C(12)	133.2 (9)
Cu–O–C(1)	115.2 (2)	C(10)–C(9)–C(12)	109 (1)
Cu–O–C(1)	132.8 (3)	C(9)–C(10)–C(11)	122 (2)
C(3)–N(1)–C(4)	111.0 (4)	C(10)–C(11)–C(10)	123 (2)
C(3)–N(1)–H(21)	108.03	C(4)–N(1)–H(21)	105.08
C(5)–N(1)–H(21)	108.50		

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

Atomic positional and thermal parameters are given in Table II. Bond distances and angles are given in parts a and b of Table III, respectively. The molecular structure of **1** is shown in Figure 1. **1** consists of two copper atoms, two dmap-H, and four chlorine ligands. The molecule has a C_2 symmetry. Each Cu atom is coordinated by two chlorine atoms and one nitrogen atom and is bridged to the other Cu atom by two oxygen atoms. The coordination geometry around Cu atom is, therefore, a distorted square pyramid with Cl(1) as a weekly coordinated axial ligand: Cu–Cl(1) = 2.530 (1) Å. Such distorted-square-pyramidal geometry has been observed in some Cu(II) complexes.[8] The Cu–Cu distance, 2.847 (1) Å, is considerably shorter than those of known dimeric Cu(II) compounds with similar aminoalkoxo

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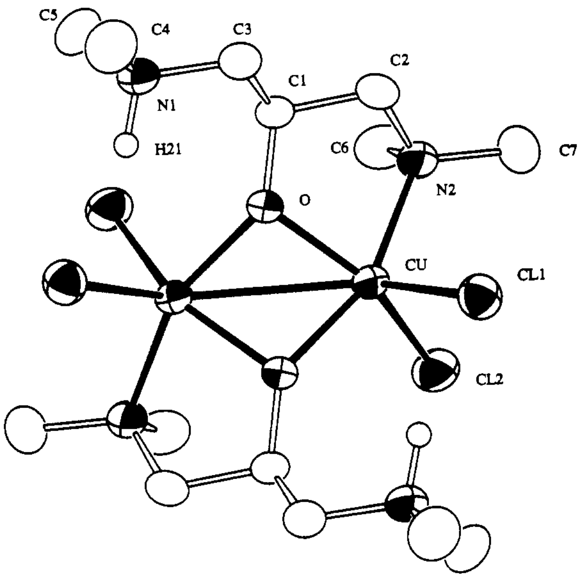

Figure 1. Molecular structure of **1** showing 50% thermal ellipsoids and the labeling scheme. Hydrogen atoms except H(21) are omitted for clarity.

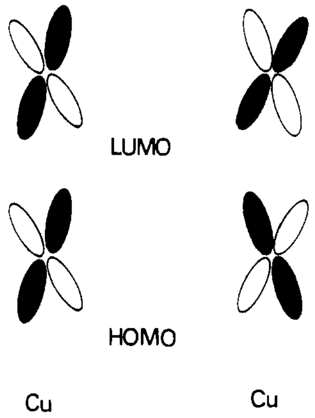

Figure 2. d orbitals of Cu atoms in the HOMO and LUMO of **1**.

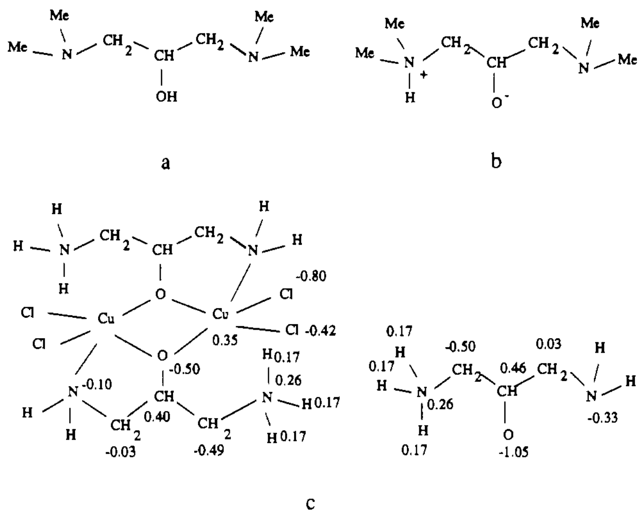

Figure 3. (a) dmap-H ligand. (b) Zwitterion form of the dmap-H ligand; (c) Mulliken atomic charge distribution on b and **1**.

ligands. For example, in $[(Cu(deae)Cl_2]_2$, deae = 2-(diethylamino)ethanolato, Cu–Cu distances[9a] within the dimer are 2.931 (2) and 2.940 (2) Å. In $[(Cu(deae)Br)_2]_2$, the Cu–Cu distance[9b] in the dimer is 3.176 (2) Å. The Cu_2O_2 unit in **1** is nonplanar. The dihedral angle between the planes of Cu–O–Cu′ and Cu–O′–Cu′ is 125.5°. The two dmap-H ligands have a cis configuration in respect to the Cu–Cu′ vector. The results from MO calculations using FH method indicate no net metal–metal bonds are present. The HOMO and the LUMO contain about 20% contribution from d_δ orbitals of Cu atoms as shown in Figure 2. The gap between the HOMO and the LUMO appears small (about 1 eV). Compound **1** has an effective magnetic moment $\mu_{eff} = 1.14\ \mu_B$ at 23 °C. This is attributed to the presence of antiferromagnetic coupling of the unpaired electron on the copper atom. Strong antiferromagnetic couplings have been frequently observed in dimeric copper(II) compounds with oxygen as the bridging atom.[8b,9]

The most interesting feature of this molecule is the zwitterion form. The hydrogen atom H(21) bonded to N(1) was located directly from a difference Fourier map in the X-ray crystal structure analysis. H(21) atom is more than 4 Å from the Cl(1) and Cl(2) atoms. Therefore, no hydrogen bonds are present between H(21) and the chlorine atoms. Although the distance of N(1) to O, 2.908 Å, is close to the sum of van der Waals radii[10] of O and N atoms (2.94 Å), H(21) is 2.51 Å from O, and the N(1)–H(21)–O angle, 103.0°, is nonlinear. Therefore, no intramolecular hydrogen bonds are present.[11] Crystallographic data also indicated that there is no intermolecular hydrogen bonds. The proton bonded originally to the oxygen atom was apparently shifted to the nitrogen atom, and an intramolecular ammonium ion is formed. The presence of a N–H bond was also confirmed by the IR spectrum, ν(N–H) = 3420 cm^{-1}. Hydrogen bonds play important roles in biological systems.[12] Complexation of the dmap-H ligand to Cu(II) centers not only resulted in a proton shift but also appeared to prevent the formation of hydrogen bonds to the oxygen center. The zwitterion form, b, of dmap-H is thermodynamically unstable. Results from the AM1 molecular orbital calculations indicate that the heat of formation $\Delta H_f°$ of zwitterion b is about 53 kcal/mol higher than that of a. Zwitterion b was apparently stabilized by the complexation to $CuCl_2$ centers, since the formation of two Cu–O bonds and one Cu–N bond can provide about 180 kcal/mol energy.[10] MO calculations on **1** and zwitterion b using the Fenske–Hall method indicate that the charges on zwitterion b are substantially delocalized over the entire molecule in the complex **1**. Although the positive charge still concentrates on the ammonium group, the negative charge is delocalized over copper, oxygen, and chlorine centers in the complex. We believe that the zwitterion was further stabilized by such delocalization of charges in the complex and chelating effects. The results of a Mulliken atomic charge distribution for **1** and zwitterion b from Fenske–Hall calculations are shown in Figure 3.

Deprotonation of a hydroxy group in aminoalcohol in the presence of Cu(II) has been observed before. For example the reactions of CuX_2 with excess (diethylamino)ethanol resulted in the formation[9] of $[(Cu((diethylamino)ethanolato)X)_2]_2$, X = Cl, Br. In these cases the proton was probably removed by the excess amino alcohol ligand through an intermolecular process. If the proton in complex **1** could also be removed by a similar intermolecular process, an additional coordination site can be created which may be used to incorporate the third metal center. This was demonstrated by the formation of a trinuclear copper compound from the reaction of **1** with $Cu(OMe)_2$ in a 1:1 ratio.

Synthesis and Crystal Structure of $Cu_3(dmap)_2Cl_4$ (2). Reaction of **1** with $Cu(OMe)_2$ in a 1:1 ratio in CH_2Cl_2 yielded a new trimetallic copper compound, $Cu_3(dmap)_2Cl_4$ (**2**), nearly quan-

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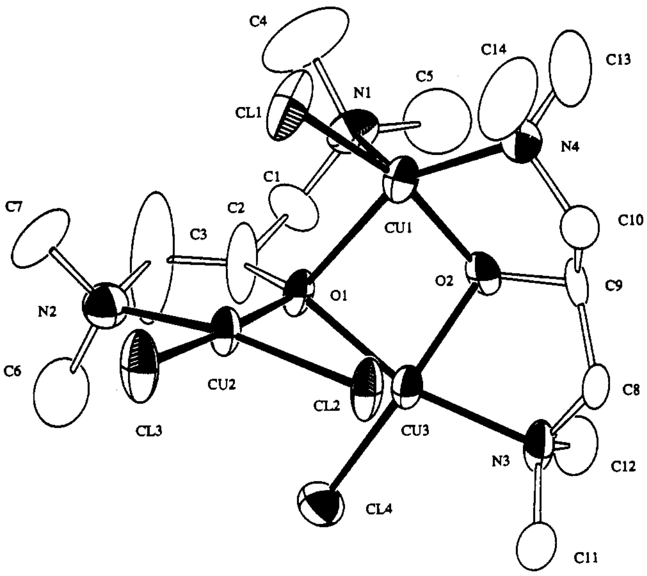

Figure 4. Molecular structure of **2** showing 50% thermal ellipsoids and the labeling scheme.

Table IV. Positional Parameters and B(eq) for Compound **2**

atom	x	y	z	B(eq),[a] Å^2
Cu(1)	0.4645 (1)	0.0445 (2)	0.2904 (2)	3.6 (1)
Cu(2)	0.4124 (1)	0.3367 (2)	0.2089 (2)	3.2 (1)
Cu(3)	0.3917 (1)	0.0730 (2)	0.1086 (2)	3.0 (1)
Cl(1)	0.4935 (4)	0.1961 (6)	0.3851 (4)	6.7 (3)
Cl(2)	0.2945 (3)	0.2167 (4)	0.1856 (4)	4.7 (3)
Cl(3)	0.3521 (3)	0.5140 (5)	0.2375 (4)	6.2 (3)
Cl(4)	0.4035 (3)	0.1792 (5)	−0.0039 (3)	4.9 (3)
Cl(5)	0.8194 (5)	0.2049 (8)	0.5142 (6)	12.5 (6)
Cl(6)	0.8621 (8)	−0.050 (1)	0.5022 (7)	16.1 (8)
O(1)	0.4695 (6)	0.181 (1)	0.1903 (7)	3.0 (6)
O(2)	0.4165 (7)	−0.050 (1)	0.1950 (8)	3.1 (5)
N(1)	0.594 (1)	0.011 (2)	0.267 (1)	4.1 (9)
N(2)	0.522 (1)	0.426 (2)	0.196 (1)	4.4 (4)
N(3)	0.311 (1)	−0.065 (1)	0.061 (1)	4.1 (8)
N(4)	0.395 (1)	−0.073 (2)	0.347 (1)	4.1 (9)
C(1)	0.603 (1)	0.084 (2)	0.194 (1)	5 (1)
C(2)	0.553 (1)	0.199 (2)	0.182 (2)	7 (1)
C(3)	0.576 (1)	0.315 (2)	0.197 (3)	18 (3)
C(4)	0.657 (1)	0.040 (3)	0.338 (2)	10 (2)
C(5)	0.605 (1)	−0.125 (3)	0.246 (2)	7 (2)
C(6)	0.507 (2)	0.495 (3)	0.123 (2)	8 (2)
C(7)	0.555 (1)	0.504 (3)	0.266 (2)	9 (2)
C(8)	0.282 (1)	−0.118 (2)	0.131 (1)	4 (1)
C(9)	0.352 (1)	−0.137 (2)	0.202 (1)	4 (1)
C(10)	0.324 (1)	−0.111 (2)	0.283 (1)	4 (1)
C(11)	0.242 (1)	−0.014 (2)	−0.001 (1)	6 (1)
C(12)	0.356 (1)	−0.159 (2)	0.019 (1)	6 (1)
C(13)	0.448 (2)	−0.185 (3)	0.375 (2)	9 (2)
C(14)	0.366 (2)	−0.023 (3)	0.417 (2)	9 (2)
C(15)	0.870 (2)	0.098 (3)	0.463 (2)	9.3 (8)

[a] $B_{\mathrm{eq}} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i{}^*a_j{}^*\vec{a}_i\cdot\vec{a}_j$.

titatively. This trimetallic compound was also obtained from the reaction of CuCl$_2$ with Na(dmap) in THF. The formation of **2** is the direct result of proton removal from the ammonium group in **1** by the methoxide ligand as shown in eq 1. Despite of the poor quality of the crystal, we were able to determine the crystal structure of **2** by X-ray diffraction.

$$\mathrm{Cu_2(dmap\text{-}H)_2Cl_4 + Cu(OMe)_2 \rightarrow Cu_3(dmap)_2Cl_4 + 2CH_3OH} \tag{1}$$

Table V. Bond Distances (Å) and Angles (deg) for Compound **2**

(a) Bond Distances			
Cu(1)–Cl(1)	2.214 (6)	N(1)–C(1)	1.47 (2)
Cu(1)–O(1)	2.20 (1)	N(1)–C(4)	1.43 (3)
Cu(1)–O(2)	1.90 (1)	N(1)–C(5)	1.48 (3)
Cu(1)–N(1)	2.28 (1)	N(2)–C(3)	1.47 (3)
Cu(1)–N(4)	2.03 (2)	N(2)–C(6)	1.39 (3)
Cu(2)–Cl(2)	2.276 (5)	N(2)–C(7)	1.44 (3)
Cu(2)–Cl(3)	2.197 (5)	N(3)–C(8)	1.45 (2)
Cu(2)–O(1)	1.93 (1)	N(3)–C(11)	1.47 (2)
Cu(2)–N(2)	2.08 (2)	N(3)–C(12)	1.48 (2)
Cu(3)–Cl(4)	2.211 (6)	N(4)–C(10)	1.46 (2)
Cu(3)–O(1)	2.02 (1)	N(4)–C(13)	1.47 (3)
Cu(3)–O(2)	1.91 (1)	N(4)–C(14)	1.46 (3)
Cu(3)–N(3)	2.01 (1)	C(1)–C(2)	1.44 (2)
Cl(5)–C(15)	1.72 (3)	C(2)–C(3)	1.28 (3)
Cl(6)–C(15)	1.69 (3)	C(8)–C(9)	1.49 (3)
O(1)–C(2)	1.42 (2)	C(9)–C(10)	1.54 (3)
O(2)–C(9)	1.42 (2)		
(b) Bond Angles			
Cl(1)–Cu(1)–O(1)	92.0 (3)	Cu(2)–O(1)–C(2)	115 (1)
Cl(1)–Cu(1)–O(2)	163.4 (4)	Cu(3)–O(1)–C(2)	120 (1)
Cl(1)–Cu(1)–N(1)	98.9 (5)	Cu(1)–O(2)–Cu(3)	105.3 (5)
Cl(1)–Cu(1)–N(4)	99.8 (5)	Cu(1)–O(2)–C(9)	117 (1)
O(1)–Cu(1)–O(2)	77.5 (5)	Cu(3)–O(2)–C(9)	116 (1)
O(1)–Cu(1)–N(1)	78.1 (5)	Cu(1)–N(1)–C(1)	108 (1)
O(1)–Cu(1)–N(4)	148.0 (6)	Cu(1)–N(1)–C(4)	112 (1)
O(2)–Cu(1)–N(1)	91.5 (6)	Cu(1)–N(1)–C(5)	111 (1)
O(2)–Cu(1)–N(4)	83.5 (6)	C(1)–N(1)–C(4)	114 (2)
N(1)–Cu(1)–N(4)	128.3 (7)	C(1)–N(1)–C(5)	106 (2)
Cl(2)–Cu(2)–Cl(3)	95.4 (2)	C(4)–N(1)–C(5)	107 (2)
Cl(2)–Cu(2)–O(1)	86.3 (3)	Cu(2)–N(2)–C(3)	100 (1)
Cl(2)–Cu(2)–N(2)	163.0 (5)	Cu(2)–N(2)–C(6)	109 (1)
Cl(3)–Cu(2)–O(1)	176.6 (4)	Cu(2)–N(2)–C(7)	111 (1)
Cl(3)–Cu(2)–N(2)	94.6 (5)	C(3)–N(2)–C(6)	115 (3)
O(1)–Cu(2)–N(2)	84.4 (5)	C(3)–N(2)–C(7)	107 (2)
Cl(4)–Cu(3)–O(1)	97.7 (4)	C(6)–N(2)–C(7)	113 (2)
Cl(4)–Cu(3)–O(2)	158.4 (4)	Cu(3)–N(3)–C(8)	105 (1)
Cl(4)–Cu(3)–N(3)	101.1 (6)	Cu(3)–N(3)–C(11)	112 (1)
O(1)–Cu(3)–O(2)	82.1 (5)	Cu(3)–N(3)–C(12)	108 (1)
O(1)–Cu(3)–N(3)	161.3 (6)	C(8)–N(3)–C(11)	111 (2)
O(2)–Cu(3)–N(3)	80.5 (6)	C(8)–N(3)–C(12)	113 (1)
Cu(1)–O(1)–Cu(2)	109.4 (5)	C(11)–N(3)–C(12)	108 (2)
Cu(1)–O(1)–Cu(3)	91.6 (4)	Cu(1)–N(4)–C(10)	106 (1)
Cu(1)–O(1)–C(2)	110 (1)	Cu(1)–N(4)–C(13)	106 (1)
Cu(2)–O(1)–Cu(3)	108.4 (5)	Cu(1)–N(4)–C(14)	117 (1)
C(10)–N(4)–C(13)	111 (2)	N(3)–C(8)–C(9)	110 (2)
C(10)–N(4)–C(14)	109 (2)	O(2)–C(9)–C(8)	109 (2)
C(13)–N(4)–C(14)	107 (2)	O(2)–C(9)–C(10)	109 (2)
N(1)–C(1)–C(2)	114 (2)	C(8)–C(9)–C(10)	110 (2)
O(1)–C(2)–C(1)	114 (2)	N(4)–C(10)–C(9)	109 (2)
O(1)–C(2)–C(3)	111 (2)	Cl(5)–C(15)–Cl(6)	109 (2)
C(1)–C(2)–C(3)	128 (2)		
N(2)–C(3)–C(2)	126 (2)		

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

An ORTEP diagram showing the molecular structure of **2** is given in Figure 4. Atomic positional and thermal parameters are given in Table IV. Bond distances and angles are given in parts a and b of Table V, respectively. As expected, both amino groups in the dmap ligand are bonded to Cu atoms. The oxygen atom in one of the dmap ligands is bonded to three Cu centers: Cu(1)–O(1) = 2.20 (1) Å, Cu(2)–O(1) = 1.93 (1) Å, and Cu(3)–O(1) = 2.02(1) Å. The oxygen atom in the other dmap ligand bridges two Cu atoms, Cu(1) and Cu(3), in a similar fashion as found in **1**. However, the Cu(1)–O(2)–Cu(3) angle (105.3 (5)°) is much larger than that in **1** (92.6 (1)°), apparently caused by the increased degree of crowdedness. The geometry of Cu(2) is square planar: N(2)–Cu(2)–Cl(2) = 163.0(5)° and O(1)–Cu(2)–Cl(3) = 176.6 (4)°. Cu(3) has an approximate square-planar geometry: O(1)–Cu(3)–N(3) = 161.3 (6)° and O(2)–Cu(3)–Cl(4) = 158.4 (4)°. The Cl(2) atom is 2.694 (4) Å from Cu(3), which may be responsible for the small degree of distortion of Cu(3) from square-planar geometry. Cu(1) is surrounded by five ligands. Its geometry could be described as a distorted square pyramid with a weakly bonded axial ligand N(1): N(1)–Cu(1) = 2.28 (1) Å. The distances between these three metal centers span a considerable range: Cu(1)–Cu(2) = 3.378 (4) Å, Cu(1)–Cu(3) = 3.027 (4) Å, and Cu(2)–Cu(3) = 3.200 (3) Å. The relatively short Cu(1)–Cu(3) distance is probably caused by the double bridges of oxygen atoms. Cu(1), O(1), Cu(3), and O(2) are approximately in the same plane. The dihedral angle between planes of Cu(1)O(1)Cu(3) and Cu(1)O(2)Cu(3) is 21.8°. This plane is nearly perpendicular to the plane of N(2)O(1)Cu(2)-Cl(2)Cl(3); dihedral angle ≈ 80°. Since compound **2** has three different copper(II) centers and three different Cu-Cu distances, it is a complex system regarding magnetic interactions. Investigation of magnetic properties of this complex is underway.

Cu(II) complexes with mono(amino alcohol) ligands have been known to form[9] dimers or a dimer-dimer linked by weak intermolecular Cu-O bonds. Trimeric species with amino alcohol ligands were previously unknown. The formation of **2** demonstrated that (a) dmap ligand is able to bind to more than two metal centers and (b) compound **1** is an useful precursor for the synthesis of multinuclear Cu compounds. Heterometallic compounds with the dmap ligand using **1** as precursor are currently under investigation in our laboratory.

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Supplementary Material Available: Tables S1-S5, listing crystallographic data, H atom parameters, and anisotropic temperature factors for **1** and **2**, and Figures S8 and S9, showing the structures of a disordered toluene molecule in **1** and a CH_2Cl_2 molecule in **2** (9 pages); Tables S6 and S7, listing observed and calculated structure factors for **1** and **2** (27 pages). Ordering information is given on any current masthead page.

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Ferromagnetically Coupled $Gd^{III}Cu^{II}$ Molecular Material

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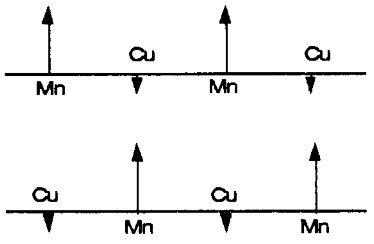
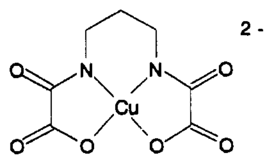
The compound $Gd_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$ (**1**), where ox stands for oxalato and pba for 1,3-propylenebis(oxamato), has been synthesized. **1** crystallizes in the monoclinic system, space group *C*2/*m*. The lattice parameters are a = 21.186 (7) Å, b = 21.098 (2) Å, c = 15.079 (1) Å, and β = 92.06 (2)°, with Z = 4. The crystal structure consists of layers of double-sheet polymers separated by water molecules. A puckered ladderlike arrangement of Gd[Cu(pba)] units forms a two-dimensional honeycomb pattern connected by oxalato groups. Discrete $[Cu(H_2O)_5]^{2+}$ entities are interspersed in the gap between the layers. The temperature dependence of the zero-field magnetic susceptibility down to 1.3 K and the field dependence of the magnetization in both the low-field regime (below 200 G) and the high-field regime (up to 20 T) have been investigated. The magnetic data are consistent with a rather strong spin correlation within the lattice and reveal that the Gd(III)-Cu(II) interaction through the oxamato bridge is ferromagnetic in spite of the large Gd···Cu separations (between 5.693 (1) and 5.739 (1) Å).

Introduction

In the last three years, we[2,3] and Gatteschi, Rey, et al.[4] have synthesized several molecular-based compounds exhibiting a spontaneous magnetization below a critical temperature T_c by assembling ferrimagnetic chains $[AB]_n$ within the crystal lattice in a ferromagnetic fashion. Two of the requirements of this approach are the following: (i) The local spins S_A and S_B of the nearest-neighbor magnetic centers along the chain must be as different as possible, and the antiferromagnetic interaction between them as large as possible. If so, the distance along which the spins S_A are oriented in an upward fashion and the neighboring spins S_B in a downward fashion (or correlation length between $|S_A-S_B|$ units) is important even at relatively high temperature. Up to now, we have used A = Mn(II) and B = Cu(II) ions, with $S_{Mn} = {}^5/_2$ and $S_{Cu} = {}^1/_2$, and bisbidentate-conjugated bridges which possess a remarkable ability to transmit rather strong antiferromagnetic interactions between magnetic centers far apart from each other.[5] (ii) The overall interchain interaction must be ferromagnetic and also as large as possible. Thus, the one-dimensional character is an obvious limitation to obtain relatively high ordering temperatures. In our case, the ferromagnetic interchain interaction has been realized by imposing Mn···Cu instead of Mn···Mn and Cu···Cu as shortest interchain separations along one of the directions perpendicular to the chain axis. The spin structure is then as follows with all the S_{Mn} local spins aligned along the same direction:[6]



All the copper(II) precursors used until now were divalent anions. One of them is $[Cu(pba)]^{2-}$, pba standing for 1,3-propylenebis(oxamato),[7] shown as follows:



The reaction of $[Cu(pba)]^{2-}$ with a divalent metal ion M(II) in a solvent S affords a one-dimensional compound of formula $MCu(pba)S_n$.[7,8] If $[Cu(pba)]^{2-}$ reacts with a trivalent metal ion M(III), one can expect to obtain a two- or three-dimensional compound of formula $M_2[Cu(pba)]_3S_n$. Increasing the dimensionality is one way to favor bulk magnetic properties. Moreover, if Mn(II) is replaced by Gd(III) with the local spin $S_{Gd} = {}^7/_2$, the spin difference $|S_A-S_B|$ is maximized. In this paper, we report on our first molecular-based compound involving Gd(III) and Cu(II) ions, of formula $Gd_2(ox)[Cu(pba)]_3Cu(H_2O)_5\cdot 20H_2O$ (**1**), where ox stands for oxalato and arises from the hydrolysis of a Cu(pba) group during the reaction. We will successively describe the crystal structure of this compound and its magnetic properties.

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