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# Homonuclear and Heteronuclear Metal Complexes with a Cyclic $Cu^{II}_4$ Unit. Syntheses, Crystal Structures, and Magnetic Properties of $[Cu^{II}_4(dmap)_3(OH)(O_2CCH_3)_2(HO_2CCH_3)(H_2O)][PF_6]_2$, $[Cu^{II}_4(dmap)_2(O_2CCH_3)_4][PF_6]_2$, $[Cu^{II}_4(dmap)_2(O_2CCH_3)_2(OH)_2][Hg^{II}(O_2CCH_3)Cl_2]_2[Hg^{II}Cl_2]$, and $[Cu^{II}_4(dmap)_2(O_2CCH_3)_3(OH)_2(H_2O)][PF_6]$ (dmap = 1,3-Bis(dimethylamino)-2-propanolato)

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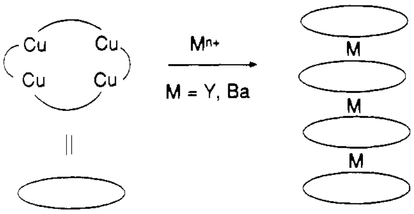
A new class of tetranuclear copper complexes with planar cyclic structures has been synthesized by using 1,3-bis(dimethylamino)-2-propanolato and acetate ligands. Four members of this class of molecules have been characterized structurally. Compound **1** with the formula $[Cu^{II}_4(dmap)_3(OH)(O_2CCH_3)_2(HO_2CCH_3)(H_2O)][PF_6]_2$ and compound **2** with the formula $[Cu^{II}_4(dmap)_2(O_2CCH_3)_4][PF_6]_2$ are discrete molecular complexes in the solid. Compound **3** with the formula $[Cu_4^{II}(dmap)_2(O_2CCH_3)_2(OH)_2][Hg^{II}(O_2CCH_3)Cl_2]_2[Hg^{II}Cl_2]$ and compound **4** with the formula of $[Cu_4^{II}(dmap)_2(O_2CCH_3)_3(OH)_2(H_2O)][PF_6]$ have one-dimensional structures in the solid state. The $Cu_4$ units in **3** are linked through $Hg^{II}_3$ chains, while the $Cu_4$ units in **4** are linked through intermolecular hydrogen bonds. **1** crystallizes in the triclinic crystal system, space group $P\bar{1}$, $a = 13.289$ (6) Å, $b = 15.737$ (6) Å, $c = 13.214$ (5) Å, $\alpha = 97.29$ (4)°, $\beta = 96.24$ (4)°, $\gamma = 103.77$ (3)°, $Z = 2$. **2** crystallizes in the monoclinic crystal system, space group $P2_1/n$, $a = 10.154$ (5) Å, $b = 12.712$ (4) Å, $c = 15.405$ (9) Å, $\beta = 99.05$ (6)°, $Z = 2$.**3** crystallizes in the monoclinic crystal system, space group $P2_1/n$, $a = 12.524$ (8) Å, $b = 12.358$ (7) Å, $c = 14.563$ (8) Å, $\beta = 94.24$ (5)°, $Z = 2$. **4** crystallizes in the triclinic crystal system, space group $P\bar{1}$, $a = 13.34$ (1) Å, $b = 13.992$ (8) Å, $c = 11.726$ (8) Å, $\alpha = 113.59$ (4)°, $\beta = 95.71$ (8)°, $\gamma = 74.54$ (7)°, $Z = 2$. The magnetic susceptibility of **3** has been measured in the temperature range 5–350 K. Results from the best fitting of the experimental data at 0.5 kG indicate that antiferromagnetic exchange dominates in this compound, $j_{12} = j_{34} = -186.5\ cm^{-1}$, $j_{23} = j_{14} = 39.7\ cm^{-1}$, $j_{24} = j_{13} = -4.4\ cm^{-1}$.

## Introduction

The search for molecular precursor complexes to synthesize high-temperature superconductors has recently stimulated intense research on the synthesis of polynuclear multiple-component molecular complexes.[1-6] We have been particularly interested in heteronuclear metal complexes with metal composition and structures resembling those of 1–2–3 superconductors since such complexes cannot only be used as precursors for superconductors but also can be used as molecular models for the study of the chemical and physical properties of superconductors. Several heteronuclear metal complexes related to high-$T_c$ superconductors have been reported recently. Among them are $Ba\{Cu[OCMe(CF_3)_2]_3\}_2$, the most volatile Ba–Cu complex,[6a] $(CuO)_3Ba_2Y(OCH_2CH_2OCH_3)_7$, used in the synthesis of the $YBa_2Cu_3O_{7-x}$ superconductor,[6c] and $Ba_2Cu_2(OCH_2CH_2OCH_3)_4(acac)_4(HOCH_2CH_2OCH_3)_2$, isolated from the precursor solution to $YBa_2Cu_3O_7$ thin films.[2] We have reported the structure of a $Y_2Cu_8$ complex.[1] The central core structure of this compound remarkably resembles that of the 1–2–3 superconductor. Heteronuclear complexes involving yttrium, barium, and copper ions are difficult to synthesize since the requirements for ligand environment of these metal ions are very different. Another problem associated with the synthesis of these heteronuclear metal complexes is that one does not have much control on the stoichiometry or the structures of the products due to the electrostatic nature of barium–ligand bonds and yttrium–ligand bonds.[7] For these reasons we believe that systematic approaches to the synthesis of such heteronuclear complexes are necessary.

The 1–2–3 superconductor has a layered structure.[8] In the unit cell these layers are $Cu_4O_2$–$BaO_4$–$Cu_4O_4$–Y–$Cu_4O_4$–$BaO_4$–$Cu_4O_2$, that is, it consists of $Cu_4O_x$ units interlayered by $BaO_4$ and Y units. If a molecular complex with a planar $Cu_4O_x$ structure can be synthesized, such a complex could be used as a building block for the construction of molecular complexes with structure resembling that of the 1–2–3 superconductor in one dimension. Such a building block will also make it possible to control the addition of different metal atoms to the complex, as shown in Scheme I.

**Scheme I**



We have synthesized a new class of planar cyclic $Cu_4$ complexes. These compounds indeed display the potential to form one-dimensional arrays. We report here the syntheses, crystal structures, and magnetic properties of some members of this family of molecules.

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**Table I.** Crystallographic Data

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| formula | $C_{27}H_{64}Cu_4P_2F_{12}O_{11}N_6 \cdot CH_2Cl_2$ | $C_{22}H_{46}Cu_4P_2F_{12}O_{10}N_4$ | $C_{22}H_{48}Hg_3Cu_4Cl_6O_{12}N_4$ | $C_{20}H_{47}Cu_4PF_6O_{11}N_4 \cdot CH_2Cl_2$ |
| fw | 1277.7 | 1070.7 | 1629.3 | 1003.7 |
| space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ |
| $a$, Å | 13.289 (6) | 10.154 (5) | 12.524 (8) | 13.40 (2) |
| $b$, Å | 15.737 (6) | 12.712 (4) | 12.358 (7) | 14.009 (7) |
| $c$, Å | 13.214 (5) | 15.405 (9) | 14.563 (8) | 11.729 (9) |
| $\alpha$, deg | 97.29 (4) | 90 | 90 | 113.65 (4) |
| $\beta$, deg | 96.24 (4) | 99.05 (6) | 94.24 (5) | 95.73 (9) |
| $\gamma$, deg | 103.77 (3) | 90 | 90 | 74.81 (7) |
| $V$, Å$^3$ | 2634 (2) | 1964 (2) | 2248 (2) | 1946 (3) |
| $Z$ | 2 | 2 | 2 | 2 |
| $d_{calc}$, g cm$^{-3}$ | 1.60 | 1.81 | 2.40 | 1.71 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 18.51 | 23.30 | 124.78 | 24.26 |
| $\lambda$, Å | 0.71069 | | 0.71069 | |
| $T$, °C | 22 | | 22 | |
| $R^a$ | 0.075 | 0.065 | 0.052 | 0.072 |
| $R_w{}^b$ | 0.082 | 0.069 | 0.049 | 0.073 |

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

## Experimental Section

**General Information.** All syntheses were performed either by using the standard Schlenk vacuum line under nitrogen atmosphere or in the inert atmosphere drybox. Solvents were distilled prior to use. 1,3-Bis(dimethylamino)-2-propanol was purchased from Aldrich Chemical Co., Inc. and Spectrum Chemical Mfg. Corp. $Cu(OCH_3)_2$ was purchased from Aldrich Chemical Co., Inc. $TlPF_6$ was obtained from Strem Chemicals, Inc. These reagents were used without further purification. $Cu_2(dmapH)_2Cl_4$ was synthesized according to the published method.[9] IR spectra were recorded on a Nicolet DX FTIR spectrometer.

**Synthesis of $[Cu^{II}_4(dmap)_3(OH)(O_2CCH_3)_2(HO_2CCH_3)(H_2O)][PF_6]_2$ (1).** A 168-mg (0.30-mmol) sample of $Cu_2(dmapH)_2Cl_4$ was dissolved in 30 mL of $CH_2Cl_2$, and 150 mg (1.20 mmol) of $Ag(O_2CCH_3)$ was added to this solution. After being stirred for 2 h at 23 °C, the solution changed from green to blue and was filtered. $TlPF_6$ (99 mg, 0.28 mmol) was added to the filtrate. The mixture was stirred for an additional 5 h and then filtered. The solution was concentrated in vacuum to about 10 mL. Diethyl ether and toluene were added. After a few days standing at 23 °C, dark blue crystals of **1** (45 mg, 0.035 mmol, yield 23%) were obtained. Anal. Calcd for $C_{27}H_{64}Cu_4P_2F_{12}O_{11}N_6 \cdot CH_2Cl_2$: C, 26.31; H, 5.21; N, 6.58. Found: C, 26.36; H, 5.34; N, 6.42. IR (KBr, cm$^{-1}$): 3619 (m, OH), 3549 (m, OH), 3300 (w, br, OH), 1575 (s, C=O), 1469 (s, C=O), 1439 (s, C=O), 850 (vs, P—F).

**Synthesis of $[Cu^{II}_4(dmap)_2(O_2CCH_3)_4][PF_6]_2$ (2).** A 200-mg (1.60-mmol) sample of $Cu(OCH_3)_2$ was placed in 30 mL of $CH_2Cl_2$, and 72 mg (0.53 mmol) of $CuCl_2$, 156 mg (1.06 mmol) of 1,3-bis(dimethylamino)-2-propanol (dmapH), and 128 mg (2.13 mmol) of $HO_2CCH_3$ were added to the solution. After stirring for 3 h, a clear dark green-blue solution was obtained. $TlPF_6$ (352 mg, 1.01 mmol) was then added to this solution. After being stirred for another 4 h, the solution was filtered. Diethyl ether and toluene were added to the blue filtrate. After standing at 23 °C for several days, blue crystals of **2** were obtained (40 mg, 0.037 mmol, yield 7.5%). Anal. Calcd for $C_{22}H_{46}Cu_4P_2F_{12}O_{10}N_4$: C, 24.67; H, 4.30; N, 5.23. Found: C, 25.11; H, 4.12; N, 5.38. IR (KBr, cm$^{-1}$): 1574 (s, C=O), 1427 (s, C=O), 850 (vs, P—F).

**Synthesis of $[Cu^{II}_4(dmap)_2(O_2CCH_3)_2(OH)_2][Hg^{II}(O_2CCH_3)Cl_2]_2$-$[Hg^{II}Cl_2]$ (3).** A 300-mg (0.536-mmol) sample of $Cu_2(dmapH)_2Cl_4$ was dissolved in 15 mL of THF, and 342 mg (1.00 mmol) of $Hg(O_2CCH_3)_2$ was added to this solution. After stirring for 19 h, a clear dark blue solution was produced. Toluene and diethyl ether were added. After several days dark blue crystals were obtained (154 mg, 0.095 mmol, 35%). Anal. Calcd for $C_{22}H_{48}Hg_3Cu_4Cl_6O_{12}N_4$: C, 16.22; H, 2.95; N, 3.44. Found: C, 16.28; H, 2.89; N, 3.22. IR (KBr, cm$^{-1}$): 3400 (m, br, OH), 3200 (m, br, OH), 1573 (s, C=O), 1534 (s, C=O), 1441 (s, C=O), 1403 (s, C=O).

**Synthesis of $[Cu^{II}_4(dmap)_2(O_2CCH_3)_3(OH)_2(H_2O)][PF_6]$ (4).** The mixture of $Cu_2(dmapH)_2Cl_4$ (70 mg, 0.125 mmol) and $Cu_2(OAc)_4(H_2O)_2$ (98 mg, 0.245 mmol) was dissolved in about 10 mL of $CH_2Cl_2$, and 117 mg (0.70 mmol) of Ag(OAc) was added to this solution. After being stirred for a few hours, the solution was filtered. $TlPF_6$ (30 mg, 0.086 mmol) and 50 mg (0.223 mmol) of $Y(OC_2H_5)_3$ were added to the blue filtrate. This solution was stirred for another 4 h and filtered. Diethyl ether and toluene were added to the filtrate. After several days standing at 23 °C, blue crystals of **4** were obtained in about 10% yield. Anal. Calcd for $C_{20}H_{47}Cu_4PF_6O_{11}N_4$: C, 26.14; H, 5.11; N, 6.10. Found: C, 25.70; H, 4.77; N, 5.82. IR (KBr, cm$^{-1}$): 3270 (m, br, OH), 1559 (s, C=O), 1471 (s, C=O), 1442 (s, C=O), 840 (vs, P—F).

**Magnetic Susceptibility Measurement.** Magnetic susceptibilities for compound **3** were measured on a SQUID device (S. H. F. variable-temperature susceptometer) at Michigan State University. The sample was quenched to 5 K at zero applied field. The field was cycled to minimize residual field. The sample was loaded in a nitrogen-filled glovebag and run in a Al–Si alloy bucket.

**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 blue single crystals of **2** were obtained from the solution of $CH_2Cl_2$ and diethyl ether at 23 °C. Dark blue crystals of **3** with a recentangular shape were obtained by slow diffusion of toluene/diethyl ether into the THF solution of **3**. Dark blue crystals of **4** with a thin plate shape were obtained from the solution of $CH_2Cl_2$/diethyl ether. The crystals were mounted on glass fibres and sealed with epoxy glue. Data were collected over the range $3 < 2\theta < 45°$ for **1**, $3 < 2\theta < 45°$ for **2**, $3 < 2\theta < 50°$ for **3**, and $3 < 2\theta < 47°$ for **4** on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo K$\alpha$ radiation operated at 50 kV and 35 mA. The initial orientation matrix for **1** was obtained from 20 reflections ($7 < 2\theta < 13°$). This matrix was refined by using 25 high-angle reflections ($30 < 2\theta < 33°$). The initial orientation matrix for **2** was obtained from 13 reflections ($7 < 2\theta < 13°$). This matrix was refined by using 25 high-angle reflections ($26 < 2\theta < 30°$). The initial orientation matrix for **3** was obtained from 20 reflections ($8 < 2\theta < 15°$) located by the search routine. High-angle cell refinement was not successful due to too few available strong reflections. The orientation matrix for **4** was initially obtained from 20 reflections ($5 < 2\theta < 12°$) and refined using 22 reflections of the range $25 < 2\theta < 30°$. Three standard reflections were measured every 147 reflections for each data set. Data were processed on a VAX workstation 3520 using the TEXSAN crystallographic package (version 5.0). Data were corrected for Lorentz–polarization effects. Empirical absorption corrections were applied for all data. Extinction corrections were not applied. Neutral-atom scattering factors were calculated by the standard procedures.[10]

Compounds **1** and **4** crystallize in the triclinic crystal system. **2** and **3** crystallize in the monoclinic crystal system. The space group $P2_1/n$ for both was uniquely determined by the systematic absences. The positions of metal atoms were determined by the direct method of the SHELXS option. Other non-hydrogen atoms were located by subsequent difference Fourier syntheses. **2** and **3** have a center of symmetry. The positions of the hydrogen atoms were calculated. Their temperature factors were tied to the temperature factors of the carbon atoms to which they are bonded (multiplied by 1.10). Their contribution in the structure factor calculations was included. Atoms heavier than nitrogen were refined anisotropically in **1**. Atoms heavier than carbon were refined anisotropically in **2**. All atoms except carbon and hydrogen in **3** were refined anisotropically. Atoms heavier than oxygen in **4** were refined anisotropically. The largest peak in the final difference Fourier map of **1** is 0.977 e Å$^{-3}$, 0.82 Å away from the F(12) atom. The largest peak in the final difference Fourier map of **2** is 1.033 e Å$^{-3}$, 1.65 Å away from N(1). The largest peak in the final difference Fourier map of **3** is 1.078

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**Table II.** Positional and Thermal Parameters for **1**

| atom | *x* | *y* | *z* | *B*(eq),[a] Å$^2$ |
|---|---|---|---|---|
| Cu(1) | −0.0012 (1) | 0.3153 (1) | 0.2188 (2) | 2.8 (1) |
| Cu(2) | 0.2874 (1) | 0.3884 (1) | 0.2470 (2) | 2.9 (1) |
| Cu(3) | 0.2971 (1) | 0.1826 (1) | 0.2646 (2) | 2.7 (1) |
| Cu(4) | 0.0083 (1) | 0.1199 (1) | 0.2383 (2) | 2.31 (8) |
| Cl(1) | 0.456 (1) | 0.100 (1) | 0.773 (1) | 28 (1) |
| Cl(2) | 0.555 (1) | 0.258 (1) | 0.896 (1) | 28 (1) |
| P(1) | 0.7448 (4) | 0.1989 (3) | 0.5331 (4) | 4.1 (2) |
| P(2) | 0.2105 (5) | 0.3189 (4) | 0.6486 (6) | 7.0 (3) |
| O(1) | 0.1531 (7) | 0.1178 (6) | 0.2798 (7) | 2.0 (4) |
| O(2) | 0.2504 (7) | 0.2645 (6) | 0.1815 (8) | 2.2 (4) |
| O(3) | 0.1423 (7) | 0.3915 (6) | 0.2584 (8) | 2.7 (4) |
| O(4) | −0.1484 (8) | 0.2455 (7) | 0.193 (1) | 3.9 (5) |
| O(5) | −0.1397 (7) | 0.1063 (7) | 0.1932 (8) | 2.9 (5) |
| O(6) | 0.4365 (8) | 0.3878 (7) | 0.272 (1) | 4.6 (6) |
| O(7) | 0.4434 (8) | 0.2483 (7) | 0.270 (1) | 4.0 (5) |
| O(8) | 0.0461 (7) | 0.2155 (6) | 0.1620 (7) | 2.2 (4) |
| O(9) | −0.366 (1) | 0.3347 (9) | 0.021 (1) | 5.7 (7) |
| O(10) | −0.046 (1) | 0.1925 (8) | −0.028 (1) | 5.2 (6) |
| O(11) | 0.0062 (9) | 0.2299 (8) | 0.389 (1) | 4.7 (6) |
| N(1) | −0.031 (1) | 0.0047 (8) | 0.293 (1) | 2.6 (3) |
| N(2) | 0.347 (1) | 0.1243 (9) | 0.378 (1) | 3.2 (3) |
| N(3) | 0.290 (1) | 0.1036 (9) | 0.093 (1) | 3.5 (3) |
| N(4) | 0.286 (1) | 0.410 (1) | 0.070 (1) | 4.2 (3) |
| N(5) | 0.329 (1) | 0.5055 (9) | 0.339 (1) | 3.5 (3) |
| N(6) | −0.052 (1) | 0.4222 (8) | 0.269 (1) | 3.2 (3) |
| C(1) | 0.064 (2) | 0.007 (2) | 0.365 (2) | 7.6 (6) |
| C(2) | 0.159 (1) | 0.052 (1) | 0.341 (1) | 3.0 (3) |
| C(3) | 0.254 (2) | 0.071 (2) | 0.415 (2) | 8.7 (7) |
| C(4) | −0.054 (2) | −0.068 (2) | 0.209 (2) | 7.9 (6) |
| C(5) | −0.117 (2) | −0.005 (1) | 0.352 (2) | 6.4 (5) |
| C(6) | 0.413 (2) | 0.067 (1) | 0.346 (2) | 6.4 (5) |
| C(7) | 0.404 (2) | 0.186 (2) | 0.469 (2) | 8.6 (7) |
| C(8) | 0.248 (1) | 0.160 (1) | 0.034 (1) | 3.3 (4) |
| C(9) | 0.284 (1) | 0.255 (1) | 0.082 (1) | 2.7 (3) |
| C(10) | 0.246 (1) | 0.320 (1) | 0.023 (1) | 3.9 (4) |
| C(11) | 0.396 (1) | 0.098 (1) | 0.071 (1) | 4.6 (4) |
| C(12) | 0.223 (2) | 0.012 (1) | 0.070 (2) | 5.8 (5) |
| C(13) | 0.392 (1) | 0.447 (1) | 0.045 (2) | 5.5 (5) |
| C(14) | 0.219 (2) | 0.466 (1) | 0.036 (2) | 5.8 (5) |
| C(15) | 0.233 (2) | 0.538 (1) | 0.331 (2) | 6.8 (6) |
| C(16) | 0.136 (1) | 0.471 (1) | 0.321 (1) | 3.4 (4) |
| C(17) | 0.042 (2) | 0.494 (1) | 0.292 (2) | 6.6 (6) |
| C(18) | 0.412 (2) | 0.573 (2) | 0.313 (2) | 7.2 (6) |
| C(19) | 0.347 (2) | 0.487 (2) | 0.441 (2) | 10.2 (8) |
| C(20) | −0.126 (2) | 0.439 (1) | 0.197 (2) | 6.5 (6) |
| C(21) | −0.095 (2) | 0.411 (1) | 0.361 (2) | 5.6 (5) |
| C(22) | −0.188 (1) | 0.165 (1) | 0.184 (1) | 2.8 (3) |
| C(23) | −0.308 (1) | 0.135 (1) | 0.162 (1) | 4.1 (4) |
| C(24) | 0.483 (1) | 0.328 (1) | 0.269 (1) | 3.0 (4) |
| C(25) | 0.600 (1) | 0.356 (1) | 0.270 (1) | 4.6 (4) |
| C(26) | −0.058 (2) | 0.269 (2) | −0.044 (2) | 5.2 (5) |
| C(27) | −0.100 (2) | 0.271 (2) | −0.150 (2) | 9.0 (7) |
| C(28) | 0.498 (3) | 0.209 (3) | 0.773 (3) | 15 (1) |
| F(1) | 0.673 (2) | 0.110 (1) | 0.470 (2) | 4.4 (9) |
| F(2) | 0.839 (2) | 0.155 (2) | 0.524 (3) | 6 (1) |
| F(3) | 0.729 (3) | 0.151 (2) | 0.633 (2) | 13 (2) |
| F(4) | 0.762 (3) | 0.236 (2) | 0.440 (2) | 14 (2) |
| F(5) | 0.652 (2) | 0.233 (2) | 0.549 (3) | 9 (1) |
| F(6) | 0.818 (2) | 0.277 (2) | 0.603 (3) | 10 (2) |
| F(7) | 0.119 (1) | 0.364 (1) | 0.607 (1) | 8.8 (7) |
| F(8) | 0.121 (1) | 0.2273 (9) | 0.614 (2) | 10.1 (8) |
| F(9) | 0.178 (2) | 0.327 (1) | 0.750 (1) | 11.3 (9) |
| F(10) | 0.227 (1) | 0.306 (1) | 0.529 (1) | 8.9 (7) |
| F(11) | 0.285 (1) | 0.406 (1) | 0.665 (2) | 13 (1) |
| F(12) | 0.286 (1) | 0.269 (1) | 0.671 (2) | 15 (1) |
| F(13) | 0.683 (1) | 0.2556 (8) | 0.478 (1) | 6.3 (4) |
| F(14) | 0.709 (1) | 0.229 (1) | 0.6343 (8) | 9.9 (6) |
| F(15) | 0.8407 (8) | 0.2814 (7) | 0.558 (1) | 7.0 (5) |
| F(16) | 0.652 (1) | 0.1203 (7) | 0.508 (1) | 9.1 (7) |
| F(21) | 0.783 (1) | 0.173 (1) | 0.431 (1) | 12.6 (8) |
| F(22) | 0.809 (1) | 0.1461 (8) | 0.587 (1) | 8.1 (5) |
| F(17) | 0.326 (2) | 0.337 (2) | 0.620 (2) | 8.5 (8) |
| F(18) | 0.274 (2) | 0.391 (1) | 0.758 (2) | 13 (1) |
| F(19) | 0.250 (2) | 0.249 (1) | 0.718 (2) | 10 (1) |
| F(20) | 0.194 (2) | 0.394 (2) | 0.608 (2) | 12 (1) |
| F(23) | 0.170 (2) | 0.253 (2) | 0.568 (2) | 16 (1) |
| F(24) | 0.118 (2) | 0.307 (2) | 0.706 (2) | 16 (2) |

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

e Å$^{-3}$, 1.08 Å away from C(1) atom. The largest peak in the final difference Fourier map of **4** is 0.743 e Å$^{-3}$, 1.11 Å away from Cu(2). **1** and **4** contain a $CH_2Cl_2$ solvent molecule in the lattice (one $CH_2Cl_2$ per molecule of **1** or **4**). Upon mounting of the crystal, **4** already has undergone partial decay due to the partial loss of the $CH_2Cl_2$ molecule. The occupancy factor for this $CH_2Cl_2$ molecule was refined initially and then fixed at 0.80. The two $PF_6^-$ anions in **1** are disordered. Two sets of fluorine atoms were located for each $PF_6^-$. For one $PF_6^-$ the occupancy factors for these two sets were refined to 31% and 69%, respectively. For the other $PF_6^-$ the occupancy factors for the two sets were refined to 45% and 55%, respectively. The ORTEP diagram showing the disorder of these $PF_6^-$ anions are given in the supplementary material. The data for the X-ray diffraction analysis are 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 the cation $[Cu_4(dmap)_2(OAc)_2(OH)_2]^{2+}$ was constructed from crystallographic bond lengths, bond angles, and dihedral angles for all atoms except hydrogen atoms using the $C_{2h}$ point group. The dmap ligand was replaced by two $NH_3$ groups and one OH group. The methyl group on the acetate ligand was replaced by a hydrogen atom. All hydrogen atoms were added using standard C–H and N–H bond lengths. MO calculations were performed by using the Fenske–Hall (FH) method.[11] The calculation was converged within a deviation of less than 0.001 in 10 iterations.

## Results and Discussion

**Synthesis and Crystal Structure of $[Cu^{II}_4(dmap)_3(OH)(O_2CCH_3)_2(HO_2CCH_3)(H_2O)][PF_6]_2$ (1).** We have recently reported a zwitterion dicopper complex[9] $[Cu_2(dmapH)_2Cl_4]$ (**5**). This compound is a good precursor for the synthesis of homo and heteropolynuclear complexes, especially for the planar tetranuclear copper complexes. The reaction of **5** with Ag(OAc) and $TlPF_6$ in $CH_2Cl_2$ in a 1:4:1 ratio produced the blue compound **1** in about 23% yield (eq 1). This compound has been characterized by IR

$$1Cu_2(dmapH)_2Cl_4 + 4Ag(OAc) + 1TlPF_6 \rightarrow [Cu_4(dmap)_3(OH)(OAc)_2(HOAc)(H_2O)][PF_6]_2 + HOAc \quad (1)$$

spectroscopy, elemental, and single-crystal X-ray diffraction analyses. The ORTEP diagram for the $Cu_4$ cation is given in Figure 1. Positional and isotropic thermal parameters are listed in Table

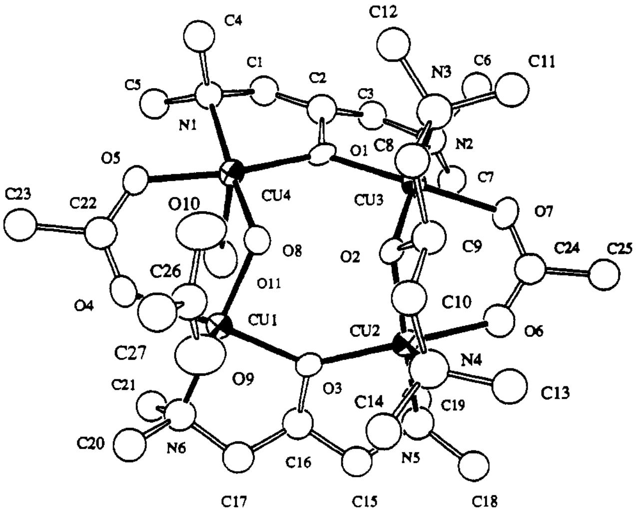

**Figure 1.** ORTEP diagram for the cation of **1** with labeling scheme and 50% thermal ellipsoids.

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(11) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

**Table III.** Bond Lengths (Å) and Angles (deg) for **1**[a]

| | | | |
|---|---|---|---|
| | (a) Lengths | | |
| Cu(1)–O(3) | 1.970 (9) | N(1)–C(4) | 1.44 (3) |
| Cu(1)–O(4) | 1.97 (1) | N(2)–C(3) | 1.49 (3) |
| Cu(1)–O(8) | 1.92 (1) | N(2)–C(7) | 1.46 (3) |
| Cu(1)–N(6) | 2.02 (1) | N(3)–C(11) | 1.48 (2) |
| Cu(2)–O(2) | 1.954 (9) | N(4)–C(10) | 1.43 (2) |
| Cu(2)–O(3) | 1.96 (1) | N(4)–C(14) | 1.46 (3) |
| Cu(2)–O(6) | 1.98 (1) | N(5)–C(18) | 1.45 (3) |
| Cu(2)–N(5) | 2.00 (1) | N(6)–C(17) | 1.45 (2) |
| Cu(3)–O(1) | 1.988 (9) | N(6)–C(21) | 1.41 (3) |
| Cu(3)–O(2) | 1.96 (1) | C(2)–C(3) | 1.46 (3) |
| Cu(3)–O(7) | 1.96 (1) | C(9)–C(10) | 1.50 (3) |
| Cu(3)–N(2) | 1.99 (1) | C(16)–C(17) | 1.42 (3) |
| Cu(4)–O(1) | 1.95 (1) | C(24)–C(25) | 1.50 (2) |
| Cu(4)–O(5) | 1.94 (1) | N(1)–C(5) | 1.44 (3) |
| Cu(4)–O(8) | 1.92 (1) | N(2)–C(6) | 1.46 (3) |
| Cu(4)–N(1) | 2.01 (1) | N(3)–C(8) | 1.43 (2) |
| | | N(3)–C(12) | 1.48 (2) |
| | | N(4)–C(13) | 1.48 (2) |
| O(1)–C(2) | 1.40 (2) | N(5)–C(15) | 1.48 (3) |
| O(2)–C(9) | 1.43 (2) | N(5)–C(19) | 1.42 (3) |
| O(3)–C(16) | 1.43 (2) | N(6)–C(20) | 1.40 (3) |
| O(4)–C(22) | 1.23 (2) | C(1)–C(2) | 1.38 (3) |
| O(5)–C(22) | 1.25 (2) | C(8)–C(9) | 1.50 (2) |
| O(6)–C(24) | 1.24 (2) | C(15)–C(16) | 1.43 (3) |
| O(7)–C(24) | 1.25 (2) | C(22)–C(23) | 1.53 (2) |
| O(9)–C(26) | 1.20 (3) | C(26)–C(27) | 1.45 (4) |
| O(10)–C(26) | 1.30 (3) | N(1)–C(1) | 1.48 (3) |
| | (b) Angles | | |
| O(3)–Cu(1)–O(4) | 173.8 (5) | Cu(3)–O(1)–Cu(4) | 139.3 (5) |
| O(3)–Cu(1)–O(8) | 93.1 (4) | Cu(3)–O(1)–C(2) | 109.3 (8) |
| O(3)–Cu(1)–N(6) | 87.1 (5) | Cu(4)–O(1)–C(2) | 111.3 (8) |
| O(4)–Cu(1)–O(8) | 91.9 (4) | Cu(2)–O(2)–Cu(3) | 115.4 (5) |
| O(4)–Cu(1)–N(6) | 88.1 (5) | Cu(2)–O(2)–C(9) | 111.3 (8) |
| O(8)–Cu(1)–N(6) | 176.4 (5) | Cu(3)–O(2)–C(9) | 110.6 (9) |
| O(2)–Cu(2)–O(3) | 94.4 (4) | Cu(1)–O(3)–Cu(2) | 140.0 (5) |
| O(2)–Cu(2)–O(6) | 90.6 (4) | Cu(1)–O(3)–C(16) | 107.7 (9) |
| O(2)–Cu(2)–N(5) | 168.9 (5) | Cu(2)–O(3)–C(16) | 112.1 (8) |
| O(3)–Cu(2)–O(6) | 166.1 (5) | Cu(1)–O(4)–C(22) | 132 (1) |
| O(3)–Cu(2)–N(5) | 86.3 (5) | Cu(4)–O(5)–C(22) | 128.9 (9) |
| O(6)–Cu(2)–N(5) | 86.3 (5) | Cu(2)–O(6)–C(24) | 134 (1) |
| O(1)–Cu(3)–O(2) | 94.5 (4) | Cu(3)–O(7)–C(24) | 131 (1) |
| O(1)–Cu(3)–O(7) | 172.1 (5) | Cu(1)–O(8)–Cu(4) | 110.3 (5) |
| O(1)–Cu(3)–N(2) | 86.6 (5) | Cu(4)–N(1)–C(1) | 103 (1) |
| O(2)–Cu(3)–O(7) | 90.5 (5) | Cu(4)–N(1)–C(4) | 110 (1) |
| O(2)–Cu(3)–N(2) | 165.4 (5) | Cu(4)–N(1)–C(5) | 115 (1) |
| O(7)–Cu(3)–N(2) | 87.0 (5) | O(6)–Cu(2)–N(4) | 96.1 (5) |
| O(1)–Cu(4)–O(5) | 173.0 (4) | O(7)–Cu(3)–N(3) | 93.1 (5) |
| O(1)–Cu(4)–O(8) | 93.8 (4) | N(5)–Cu(2)–N(4) | 109.8 (6) |
| O(1)–Cu(4)–N(1) | 85.7 (5) | O(2)–Cu(3)–N(3) | 80.0 (5) |
| O(5)–Cu(4)–O(8) | 91.2 (4) | N(2)–Cu(3)–N(3) | 114.4 (5) |
| O(5)–Cu(4)–N(1) | 88.4 (5) | Cu(1)–N(6)–C(17) | 104 (1) |
| O(8)–Cu(4)–N(1) | 168.9 (5) | Cu(1)–N(6)–C(20) | 113 (1) |
| Cu(3)–N(2)–C(3) | 109 (1) | Cu(1)–N(6)–C(21) | 111 (1) |
| Cu(3)–N(2)–C(6) | 113 (1) | Cu(2)–N(5)–C(15) | 104 (1) |
| Cu(3)–N(2)–C(7) | 114 (1) | Cu(2)–N(5)–C(18) | 117 (1) |
| | | Cu(2)–N(5)–C(19) | 106 (1) |

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

II. Selected bond lengths and angles are given in parts a and b of Table III.

The cation of **1** consists of four $Cu^{II}$ ions bridged by two acetate ligands and two dmap ligands in a cyclic fashion. The dmap ligand functions as a tridentate ligand and bridges two copper atoms through oxygen and two nitrogen atoms. A similar bonding situation has been observed in the compound[9] $Cu_3(dmap)_2Cl_4$. The twelve-membered ring formed by the four copper atoms, two $CO_2$ groups, and two oxygen atoms from the dmap ligands is essentially planar with the maximum deviation (0.37 Å) of O(3) from the plane. Cu(2) and Cu(3) are further bridged by an oxygen atom from the additional dmap ligand, while Cu(1) and Cu(4) are further bridged by a hydroxy ligand. The four copper atoms have an approximate rectangular arrangement, Cu(1)–Cu(2) = 3.695 (3) Å, Cu(2)–Cu(3) = 3.307 (3) Å, Cu(3)–Cu(4) = 3.694 (3) Å, Cu(1)–Cu(4) = 3.149 (3) Å. In comparison with the Cu(1)–Cu(2) and Cu(3)–Cu(4) distances, the shorter Cu–Cu separations between Cu(2)–Cu(3) and Cu(1)–Cu(4) can be attributed to the double bridges over these two pairs of Cu atoms. Such bridging effects on Cu–Cu distances have been frequently observed.[9,12] The most common arrangement of tetranuclear copper(II) compounds is tetrahedral.[12] The rectangular planar arrangement of tetranuclear Cu(II) compounds with Cu(II) atoms in close proximity is rare. Among the few known examples are[13a] $[Cu_4(mpz)_4(acmpz)_2(NO_3)_2]$, mpzH = 3(5)-methylpyrazole and acmpzH = 1-(1-ethanoyl)-5-methylpyrazole, and[13b] $Cu_4Zr_4O_3(O^iPr)_{18}$, in which the arrangement of the four Cu(II) atoms resembles that found in **1**.

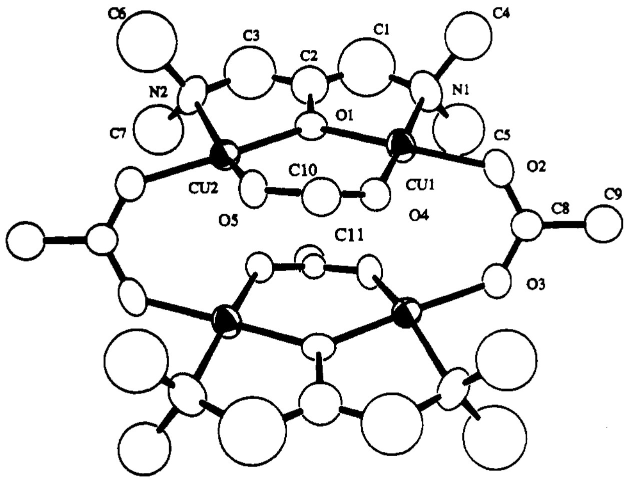

**Figure 2.** ORTEP diagram for the cation of **2** with labeling scheme and 50% thermal ellipsoids.

Each copper atom in **1** is five-coordinate with a square-pyramidal geometry. The four copper–ligand bonds in the plane have normal bond distances, while the fifth ligand coordinates to the Cu center with a long copper–ligand bond length. Cu(2) and Cu(3) are both weakly coordinated by a nitrogen atom from the dmap ligand. Cu(2)–N(4) = 2.41 (1) Å, Cu(3)–N(3) = 2.42 (1) Å. Cu(1) is coordinated weakly by an oxygen atom from an acetic acid ligand, Cu(1)–O(9) = 2.68 (2) Å. Cu(4) is coordinated by an $H_2O$ ligand, Cu(4)–O(11) = 2.47 (1) Å. Five-coordinate copper(II) complexes often display trigonal-bipyramidal structures.[12] Square-pyramidal structures are relatively less common. The assignments of the acetic acid and water ligands were based on the charge of the cation and the long Cu–O distances. It has been well established that a neutral ligand tends to occupy the fifth position in a square-pyramidal Cu(II) complex.[12] A hydrogen bond[14] is present between the hydroxy ligand and the acetic acid ligand, as evidence by the C(26)–O(10)–O(8) angle of 106 (1)° and O(8)–O(10) distance of 2.61 (2) Å, much shorter than the sum of the van der Waals radii[15] of oxygen atoms (2.80 Å). Such an unusual hydrogen bond between an acid and a strong base is apparently stabilized by the coordination of the hydroxy group to the Cu atoms. The hydroxy ligand and the dmap ligand on the ring are cis to each other. Hence, the other two dmap ligands are cis to each other as well. The dmap ligand bonded to the $Cu_4$

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**Table IV.** Positional and Thermal Parameters for **2**

| atom | *x* | *y* | *z* | *B*(eq),[a] Å$^2$ |
|---|---|---|---|---|
| Cu(2) | 0.1453 (1) | 0.8556 (1) | 0.5241 (1) | 2.80 (7) |
| Cu(1) | −0.1854 (1) | 0.8895 (1) | 0.4389 (1) | 2.94 (7) |
| P(1) | 0.2165 (6) | 0.3520 (4) | 0.3847 (3) | 5.6 (2) |
| F(1) | 0.153 (2) | 0.404 (1) | 0.4574 (9) | 13 (1) |
| F(2) | 0.272 (3) | 0.300 (1) | 0.313 (1) | 21 (2) |
| F(3) | 0.263 (1) | 0.2580 (8) | 0.4462 (7) | 8.7 (6) |
| F(4) | 0.177 (2) | 0.445 (1) | 0.3256 (8) | 14 (1) |
| F(5) | 0.338 (1) | 0.409 (1) | 0.416 (1) | 17 (1) |
| F(6) | 0.082 (2) | 0.295 (1) | 0.363 (2) | 20 (1) |
| O(1) | −0.0143 (7) | 0.8290 (6) | 0.4482 (5) | 2.8 (4) |
| O(2) | −0.3615 (8) | 0.9519 (7) | 0.4172 (6) | 3.8 (4) |
| O(3) | −0.3170 (8) | 1.1219 (7) | 0.4063 (6) | 3.6 (4) |
| O(4) | −0.1476 (8) | 0.9653 (6) | 0.5500 (5) | 2.7 (4) |
| O(5) | 0.0604 (7) | 0.9273 (7) | 0.6135 (5) | 2.9 (4) |
| N(1) | −0.233 (1) | 0.798 (1) | 0.3322 (8) | 4.3 (6) |
| N(2) | 0.223 (1) | 0.7386 (9) | 0.4593 (7) | 3.6 (5) |
| C(1) | −0.116 (3) | 0.735 (2) | 0.324 (2) | 11.7 (7) |
| C(2) | −0.005 (2) | 0.753 (1) | 0.383 (1) | 4.8 (4) |
| C(3) | 0.118 (2) | 0.710 (2) | 0.389 (2) | 9.6 (6) |
| C(4) | −0.341 (2) | 0.730 (2) | 0.337 (1) | 7.4 (5) |
| C(5) | −0.273 (2) | 0.860 (2) | 0.253 (2) | 9.8 (6) |
| C(6) | 0.270 (2) | 0.653 (2) | 0.519 (2) | 11.4 (7) |
| C(7) | 0.335 (2) | 0.772 (2) | 0.417 (1) | 9.1 (6) |
| C(8) | −0.393 (1) | 1.046 (1) | 0.3986 (8) | 3.0 (3) |
| C(9) | −0.536 (1) | 1.065 (1) | 0.365 (1) | 4.3 (3) |
| C(10) | −0.057 (1) | 0.9528 (9) | 0.6158 (8) | 2.1 (2) |
| C(11) | −0.097 (1) | 0.967 (1) | 0.7039 (9) | 3.5 (3) |

[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 V.** Bond Lengths (Å) and Angles (deg) for **2**[a]

(a) Lengths

| | | | |
|---|---|---|---|
| Cu(2)–O(1) | 1.874 (8) | O(2)–C(8) | 1.26 (1) |
| Cu(2)–O(3′) | 1.919 (8) | O(3)–C(8) | 1.23 (1) |
| Cu(2)–O(5) | 1.961 (8) | O(4)–C(10) | 1.27 (1) |
| Cu(2)–N(2) | 2.02 (1) | O(5)–C(10) | 1.24 (1) |
| Cu(1)–O(1) | 1.884 (8) | N(1)–C(1) | 1.45 (3) |
| Cu(1)–O(2) | 1.938 (9) | N(1)–C(4) | 1.41 (2) |
| Cu(1)–O(4) | 1.949 (8) | N(1)–C(5) | 1.46 (2) |
| Cu(1)–N(1) | 2.01 (1) | N(2)–C(3) | 1.44 (2) |
| O(1)–C(2) | 1.40 (2) | N(2)–C(6) | 1.46 (3) |
| C(2)–C(3) | 1.35 (2) | N(2)–C(7) | 1.46 (2) |
| C(8)–C(9) | 1.48 (2) | C(1)–C(2) | 1.36 (2) |
| C(10)–C(11) | 1.49 (2) | | |

(b) Angles

| | | | |
|---|---|---|---|
| O(1)–Cu(2)–O(3) | 174.9 (4) | Cu(2)–O(1)–Cu(1) | 132.1 (4) |
| O(1)–Cu(2)–O(5) | 95.1 (3) | Cu(2)–O(1)–C(2) | 114.7 (8) |
| O(1)–Cu(2)–N(2) | 85.7 (4) | Cu(1)–O(1)–C(2) | 113.1 (8) |
| O(3)–Cu(2)–O(5) | 89.9 (3) | Cu(1)–O(2)–C(8) | 128.7 (9) |
| O(3)–Cu(2)–N(2) | 89.7 (4) | Cu(2)–O(3)–C(8) | 132.4 (9) |
| O(5)–Cu(2)–N(2) | 159.8 (4) | Cu(1)–O(4)–C(10) | 131.2 (8) |
| O(1)–Cu(1)–O(2) | 174.5 (4) | Cu(2)–O(5)–C(10) | 132.2 (8) |
| O(1)–Cu(1)–O(4) | 94.8 (3) | Cu(1)–N(1)–C(1) | 107 (1) |
| O(1)–Cu(1)–N(1) | 85.9 (4) | Cu(1)–N(1)–C(4) | 114 (1) |
| O(2)–Cu(1)–O(4) | 89.9 (4) | Cu(1)–N(1)–C(5) | 112 (1) |
| O(2)–Cu(1)–N(1) | 89.9 (4) | C(1)–N(1)–C(4) | 109 (2) |
| O(4)–Cu(1)–N(1) | 173.4 (4) | C(1)–N(1)–C(5) | 110 (2) |
| C(6)–N(2)–C(7) | 107 (1) | C(4)–N(1)–C(5) | 105 (1) |
| N(1)–C(1)–C(2) | 117 (2) | Cu(2)–N(2)–C(3) | 105 (1) |
| O(1)–C(2)–C(1) | 117 (2) | Cu(2)–N(2)–C(6) | 111 (1) |
| O(1)–C(2)–C(3) | 114 (2) | Cu(2)–N(2)–C(7) | 113 (1) |
| C(1)–C(2)–C(3) | 129 (2) | C(3)–N(2)–C(6) | 115 (2) |
| N(2)–C(3)–C(2) | 121 (2) | C(3)–N(2)–C(7) | 106 (1) |
| O(2)–C(8)–O(3) | 126 (1) | | |
| O(2)–C(8)–C(9) | 116 (1) | | |
| O(3)–C(8)–C(9) | 119 (1) | | |
| O(4)–C(10)–O(5) | 126 (1) | | |
| O(4)–C(10)–C(11) | 117 (1) | | |
| O(5)–C(10)–C(11) | 117 (1) | | |

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

ring may be used to incorporate other metal centers through the two nitrogen atoms that are weakly bonded to the copper centers. The formation of the hydroxy ligand in this complex has not been understood. The trace amount of water in the solvent might be the source of the OH ligand. The presence of Ag(OAc) might have promoted the formation of the hydroxy ligand. This is supported by the fact that the hydroxy ligands were also formed in compounds **3** and **4** where $Hg(OAc)_2$ or Ag(OAc) was used in the syntheses, while no hydroxy ligand was formed in **2** where neither Ag(OAc) nor $Hg(OAc)_2$ was involved in the synthesis.

**Synthesis and Crystal Structure of $[Cu^{II}_4(dmap)_2(O_2CCH_3)_4][PF_6]_2$ (2).** The reaction of $Cu(OCH_3)_2$ and $CuCl_2$ with dmapH and HOAc ligands in a 3:1:2:4 ratio in the presence of $TlPF_6$ yielded the blue compound **2** in about 10% isolated yield (eq 2). The low yield of this compound was caused by the poor

$$3Cu(OCH_3)_2 + 1CuCl_2 + 2dmapH + 4HO_2CCH_3 + 2Tl[PF_6] \rightarrow [Cu_4(dmap)_2(OAc)_4][PF_6]_2 \quad (2)$$

solubility of the product. Most of the product was lost due to the coprecipitation with TlCl. This compound was fully characterized by IR, elemental, and X-ray analyses. Positional and isotropic thermal parameters are given in Table IV. Bond lengths and angles are listed in Table V (a and b). ORTEP diagrams for the cation and the molecule are given in Figures 2 and 3, respectively.

The molecule of **2** has an inversion center. Two acetate ligands and two dmap ligands bridge the four copper atoms in a square-planar arrangement, Cu(1)–Cu(2) = 3.435 (3) Å, Cu(1)–Cu(2′) = 3.305 (2) Å. Interestingly, the double-bridged Cu(1)–Cu(2) distance is slightly longer than the single-bridged Cu(1)–Cu(2′) distance. The twelve-membered ring composed of the four copper atoms, two $CO_2$ units, and two oxygen atoms is similar to that of **1**. This ring unit is essentially planar with the maximum deviation (±0.44 Å) of O(1) from the plane. In **1**, the additional ligands bridge the two pairs of Cu atoms bridged by the acetate ligands. In contrast, the two additional acetate ligands in **2** bridge Cu(1) and Cu(2) or Cu(1′) and Cu(2′) that are bridged by the dmap ligand. Several factors might contribute to the preference of bridging Cu(1) and Cu(2) instead of Cu(1) and Cu(2′). First of all, each Cu(II) center requires a square-planar geometry. Secondly, the geometry of the dmap ligand requires that the oxygen and nitrogen atoms coordinate to the Cu(II) center in a cis fashion. As a result, the oxygen atoms from the acetate ligands have to coordinate to the Cu(II) center in a cis fashion as well. It can be demonstrated easily by simple molecular models that in order to minimize the steric interactions of ligand atoms, the acetate bridging of Cu(1) and Cu(2) is the preferred geometry. The two dimeric units of $Cu_2(dmap)(OAc)$ are parallel to each other. The dihedral angle between the twelve-membered ring and the plane defined by Cu(1) and Cu(2) and atoms coordinated to these two copper atoms is about 45°. The two acetate ligands coordinate to the ring in a trans configuration. As a consequence, the two dmap ligands are trans to

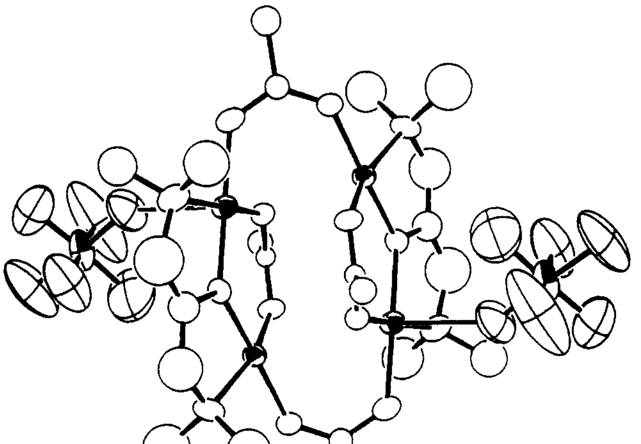

**Figure 3.** ORTEP diagram for the entire molecule of **2** with 50% thermal ellipsoids showing the interaction of the $PF_6^-$ anions with the cation of **2**.

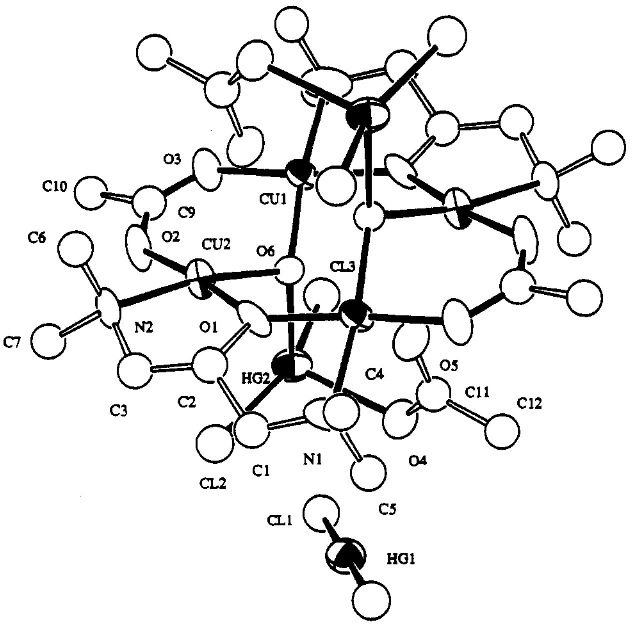

**Figure 4.** ORTEP diagram for the molecule of 3 with labeling scheme and 50% thermal ellipsoids.

each other. The O(4′) atom is weakly bonded to Cu(2), Cu(2)–O(4′) = 2.549 (8) Å. The geometry of Cu(2) is square-pyramidal. The shortest contact between the ligand atoms and the Cu(1) atom are between Cu(1) and O(5′) (2.830 (8) Å), and Cu(1) and F(3) of the $PF_6^-$ anion (2.77 (1) Å). These O(5′) and F(3) atoms occupy the fifth and sixth positions of the Cu(1) atom, as shown in Figure 4. As a result the geometry of Cu(1) is an elongated octahedron. All other contact distances between the Cu atoms and the $PF_6^-$ anion are larger than 3.60 Å and therefore can be ignored. A similar $PF_6^-$ anion interaction with a Cu(II) center has been reported recently.[16]

**Synthesis and Crystal Structure of $[Cu^{II}_4(dmap)_2(O_2CCH_3)_2(OH)_2][Hg(O_2CCH_3)Cl_2]_2[HgCl_2]$ (3).** The reaction of the compound $Cu_2(dmapH)_2Cl_4$ with $Hg(O_2CCH_3)_2$ in THF in a 1:2 ratio under nitrogen atmosphere for about 19 h produced a clear dark blue solution. Upon addition of toluene and diethyl ether, dark blue crystals with the composition $[Cu^{II}_4(dmap)_2(O_2CCH_3)_2(OH)_2][Hg(O_2(CCH_3)Cl_2]_2[HgCl_2]$ (3) were obtained in good yield (eq 3). This compound was fully characterized by IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis.

$$2Cu_2(dmapH)_2Cl_4 + 4Hg(OAc)_2 \rightarrow [Cu_4(dmap)_2(OAc)_2(OH)_2][Hg_3(OAc)_2Cl_6] + HgCl_2 \quad (3)$$

The molecular structure of 3 is given in Figure 4. Positional and isotropic thermal parameters are given in Table VI. Selected bond distances and angles are listed in Table VII (a and b). The molecule of 3 possesses an inversion center. The core unit of this molecule consists of four copper atoms bridged by two dmap, two acetate, and two hydroxy ligands. Again, a twelve-membered ring similar to those in 1 and 2 is formed. This ring unit is planar with the maximum deviation (±0.073 Å) of O(2) from the plane. The two hydroxy groups are trans to each other and 0.94 Å above and below this plane. Again the formation of the two hydroxy ligands in this complex has not been understood, although it appears to be associated with the $Hg(OAc)_2$ compound. Each copper atom has an approximate square-planar geometry. The arrangement of the four copper atoms is rectangular, Cu(1)–Cu(2) = 3.195 (5) Å, Cu(1)–Cu(2′) = 3.588 (5) Å, Cu(1)–Cu(1′) = 4.777 (7) Å, Cu(2)–Cu(2′) = 4.832 (7) Å. The Cu(2)O(1)O(6)O(2)N(2) plane is parallel to the Cu(2′)O(1′)O(6′)O(2′)N(2′) plane. The Cu(1)O(3)O(1′)O(6)N(1′) plane is parallel to the Cu(1′)O(3′)O(1)O(6′)N(1) plane. The dihedral angle between these two

**Table VI.** Positional and Thermal Parameters for 3

| atom | $x$ | $y$ | $z$ | $B$(eq),[a] Å$^2$ |
|---|---|---|---|---|
| Hg(1) | 0 | 0 | 0 | 3.97 (9) |
| Hg(2) | 0.24774 (9) | 0.1639 (1) | 0.03026 (9) | 3.51 (5) |
| Cu(1) | 0.5380 (2) | 0.1894 (2) | −0.0010 (2) | 2.7 (1) |
| Cu(2) | 0.4703 (3) | 0.0332 (2) | 0.1596 (2) | 3.2 (2) |
| Cl(1) | −0.0130 (6) | 0.1856 (6) | −0.0005 (6) | 4.9 (4) |
| Cl(2) | 0.1976 (7) | 0.0533 (7) | 0.1516 (5) | 5.5 (4) |
| Cl(3) | 0.2779 (8) | 0.3269 (8) | −0.0393 (8) | 9.7 (6) |
| O(1) | 0.456 (1) | −0.115 (1) | 0.117 (1) | 3.2 (9) |
| O(2) | 0.479 (1) | 0.173 (1) | 0.216 (1) | 4 (1) |
| O(3) | 0.538 (2) | 0.280 (1) | 0.107 (1) | 4 (1) |
| O(4) | 0.188 (1) | 0.030 (1) | −0.084 (1) | 4 (1) |
| O(5) | 0.344 (1) | −0.046 (1) | −0.090 (1) | 4 (1) |
| O(6) | 0.431 (1) | 0.093 (1) | 0.038 (1) | 2.4 (8) |
| N(1) | 0.372 (2) | −0.304 (2) | 0.057 (2) | 5 (1) |
| N(2) | 0.484 (2) | −0.038 (2) | 0.286 (1) | 6 (1) |
| C(1) | 0.353 (4) | −0.262 (4) | 0.149 (4) | 11 (1) |
| C(2) | 0.430 (2) | −0.184 (2) | 0.185 (2) | 4.1 (6) |
| C(3) | 0.424 (3) | −0.139 (3) | 0.271 (3) | 9 (1) |
| C(4) | 0.419 (3) | −0.407 (3) | 0.061 (2) | 7 (1) |
| C(5) | 0.272 (4) | −0.307 (4) | 0.016 (3) | 13 (2) |
| C(6) | 0.588 (4) | −0.045 (4) | 0.322 (3) | 13 (2) |
| C(7) | 0.428 (3) | 0.016 (3) | 0.357 (3) | 8 (1) |
| C(9) | 0.511 (2) | 0.260 (2) | 0.187 (2) | 3.6 (6) |
| C(10) | 0.504 (3) | 0.361 (3) | 0.249 (3) | 10 (1) |
| C(11) | 0.249 (2) | −0.040 (2) | −0.117 (2) | 3.6 (6) |
| C(12) | 0.201 (2) | −0.112 (2) | −0.188 (2) | 4.1 (6) |

[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 VII.** Bond Lengths (Å) and Angles (deg) for 3[a]

(a) Lengths

| | | | |
|---|---|---|---|
| Hg(1)–Cl(1) | 2.300 (7) | O(2)–C(9) | 1.23 (3) |
| Hg(1)–Cl(1) | 2.300 (7) | O(3)–C(9) | 1.26 (3) |
| Hg(2)–Cl(2) | 2.355 (8) | O(4)–C(11) | 1.26 (3) |
| Hg(2)–Cl(3) | 2.298 (9) | O(5)–C(11) | 1.23 (3) |
| Hg(2)–O(4) | 2.43 (2) | N(1)–C(1) | 1.47 (5) |
| Hg(2)–O(6) | 2.45 (1) | N(1)–C(4) | 1.40 (4) |
| Cu(1)–O(1) | 1.93 (2) | N(1)–C(5) | 1.35 (5) |
| Cu(1)–O(3) | 1.93 (2) | N(2)–C(3) | 1.47 (4) |
| Cu(1)–O(6) | 1.91 (1) | N(2)–C(6) | 1.37 (5) |
| Cu(1)–N(1) | 2.02 (2) | N(2)–C(7) | 1.46 (4) |
| Cu(2)–O(1) | 1.94 (2) | C(1)–C(2) | 1.43 (5) |
| Cu(2)–O(2) | 1.91 (2) | C(2)–C(3) | 1.38 (4) |
| Cu(2)–O(6) | 1.95 (1) | C(9)–C(10) | 1.53 (4) |
| Cu(2)–N(2) | 2.03 (2) | C(11)–C(12) | 1.46 (3) |
| O(1)–C(2) | 1.37 (3) | | |

(b) Angles

| | | | |
|---|---|---|---|
| Cl(1)–Hg(1)–Cl(1) | 180.00 | Hg(2)–O(6)–Cu(2) | 110.5 (7) |
| Cl(2)–Hg(2)–Cl(3) | 154.2 (4) | Cu(1)–O(6)–Cu(2) | 111.6 (7) |
| Cl(2)–Hg(2)–O(4) | 92.0 (5) | Cu(1)–N(1)–C(1) | 105 (2) |
| Cl(2)–Hg(2)–O(6) | 93.3 (4) | Cu(1)–N(1)–C(4) | 114 (2) |
| Cl(3)–Hg(2)–O(4) | 110.3 (5) | Cu(1)–N(1)–C(5) | 112 (3) |
| Cl(3)–Hg(2)–O(6) | 98.6 (4) | C(1)–N(1)–C(4) | 112 (3) |
| O(4)–Hg(2)–O(6) | 91.6 (5) | C(1)–N(1)–C(5) | 102 (3) |
| O(1)–Cu(1)–O(3) | 172.6 (7) | C(4)–N(1)–C(5) | 111 (3) |
| O(1)–Cu(1)–O(6) | 92.1 (6) | Cu(2)–N(2)–C(3) | 103 (2) |
| O(1)–Cu(1)–N(1) | 85.3 (9) | Cu(2)–N(2)–C(6) | 113 (3) |
| O(3)–Cu(1)–O(6) | 94.4 (7) | Cu(2)–N(2)–C(7) | 116 (2) |
| O(3)–Cu(1)–N(1) | 88 (1) | C(3)–N(2)–C(6) | 117 (3) |
| O(6)–Cu(1)–N(1) | 169.2 (8) | C(3)–N(2)–C(7) | 103 (3) |
| O(1)–Cu(2)–O(2) | 173.0 (7) | C(6)–N(2)–C(7) | 105 (3) |
| O(1)–Cu(2)–O(6) | 93.2 (6) | N(1)–C(1)–C(2) | 115 (4) |
| O(1)–Cu(2)–N(2) | 83.2 (9) | O(1)–C(2)–C(1) | 110 (3) |
| O(2)–Cu(2)–O(6) | 92.9 (7) | O(1)–C(2)–C(3) | 116 (3) |
| O(2)–Cu(2)–N(2) | 90.2 (9) | C(1)–C(2)–C(3) | 122 (4) |
| O(6)–Cu(2)–N(2) | 169.7 (9) | N(2)–C(3)–C(2) | 115 (4) |
| Cu(1)–O(1)–Cu(2) | 136.2 (8) | O(2)–C(9)–O(3) | 127 (3) |
| Cu(1)–O(1)–C(2) | 111 (2) | O(2)–C(9)–C(10) | 119 (3) |
| Cu(2)–O(1)–C(2) | 112 (2) | O(3)–C(9)–C(10) | 114 (3) |
| Cu(2)–O(2)–C(9) | 131 (2) | O(4)–C(11)–O(5) | 122 (3) |
| Cu(1)–O(3)–C(9) | 131 (2) | O(4)–C(11)–C(12) | 117 (3) |
| Hg(2)–O(4)–C(11) | 124 (2) | O(5)–C(11)–C(12) | 121 (3) |
| Hg(2)–O(6)–Cu(1) | 116.0 (7) | | |

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

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[16] Sletten, J.; Sørensen, A.; Julve, M.; Journaux, Y. *Inorg. Chem.* **1990**, *29*, 5054.

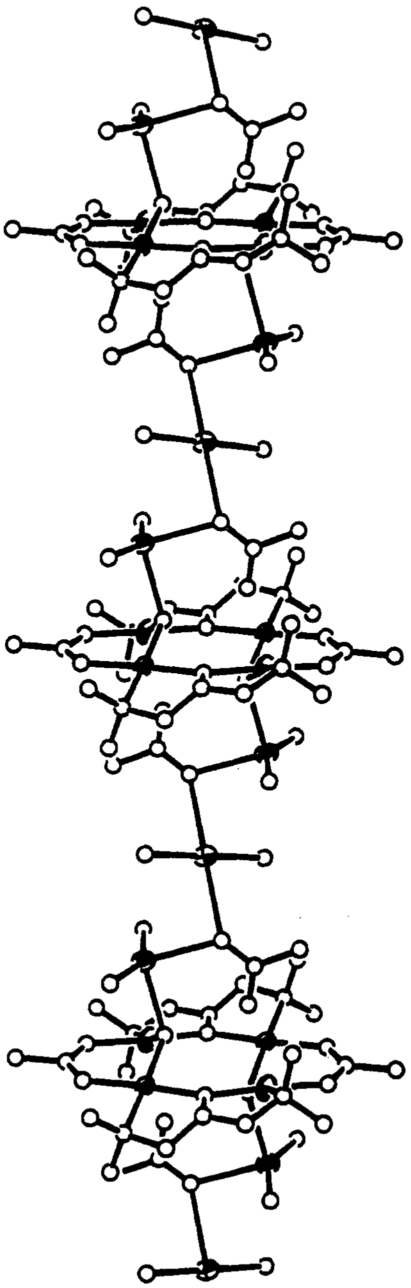

**Figure 5.** ORTEP diagram showing the polymeric structure of **3**.

sets of planes is 47.5°. These planes have a dihedral angle of 25° with the twelve-membered ring.

Interestingly, there are two $[Hg(O_2CCH_3)Cl_2]^-$ moieties attached to the twelve-membered ring through the formation of a Hg–O bond, Hg(2)–O(6) = 2.45 (1) Å, and a hydrogen bond between the hydroxy O(6) and the acetate O(5). The presence of a hydrogen bond between O(5) and O(6) is supported by the C(11)–O(5)–O(6) angle of 120 (2)° and the O(5)–O(6) distance of 2.70 (2) Å. The geometry of Hg(2) is distorted-tetrahedral, Cl(2)–Hg(2)–Cl(3) = 154.2 (4)°, O(4)–Hg(2)–O(6) = 91.6 (5)°. The distances of Hg(2) to Cu(1) and Cu(2) are 3.711 (4) and 3.626 (4) Å, respectively. The most interesting feature of the crystal structure is the presence of a neutral $HgCl_2$ moiety and the formation of a one-dimensional structure in the solid state. The Hg(1) atom is linearly coordinated by two chlorine atoms with normal Hg–Cl bond distances. It is also coordinated linearly by two oxygen atoms on the acetate ligands through the formation of two weak Hg–O bonds, Hg(1)–O(4) = 2.76 (2) Å. As a consequence, a one-dimensional structure with alternating $Hg_3$ chains and $Cu_4$ ring units is achieved in the solid state, as shown in Figure 5. To our knowledge such an unusual structure is previously unknown. The Hg(1)–Hg(2) separation is 3.704 (2) Å. Formation of polymeric one-dimensional structures in the solid state through weak metal–ligand bonds has been previously observed in some mercury(II) complexes.[17] The ability of the $HgCl_2$ molecule to form a 1:1 adduct with electron-donor ligands resulting in extended structures in the solid state has also been known.[18] Most of the reported adducts involve S or N atoms. $HgCl_2$ adducts involving oxygen atoms with a square-planar geometry and long Hg–O bonds are less common. The common coordination geometry for the Hg(II) ion is tetrahedral or linear. Square-planar geometry with two long and two short metal–ligand bonds for Hg(II) complexes have been reported recently.[17a,d]

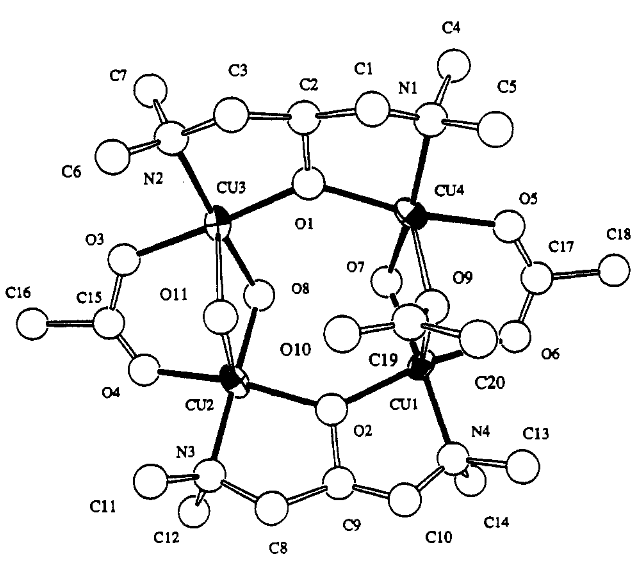

**Figure 6.** ORTEP diagram for the cation of **4** with labeling scheme and 50% thermal ellipsoids.

The structure of **3** demonstrates that it is possible to link the cyclic $Cu_4$ units together along one dimension through heteronuclear metal–ligand bonds. The one-dimensional structure displayed by compound **3** could also be achieved without the presence of the mercury ion, as illustrated by the synthesis and structure of the compound **4**.

**Synthesis and Crystal Structure of $[Cu_4(dmap)_2(O_2CCH_3)_3(OH)_2(H_2O)][PF_6]$ (4).** Compound **4** was isolated as a minor crystalline product from the reaction of $Cu_2(dmapH)_2Cl_4$ with $Cu_2(O_2CCH_3)_4(H_2O)_2$, $Y(OC_2H_5)_3$, and $Ag(O_2CCH_3)$ in the presence of $TlPF_6$. The yield of the product varied with the reaction conditions. Independent synthesis was unsuccessful. However, in the presence of $Y(OC_2H_5)_3$ the synthesis was reproducible. $Y(OC_2H_5)_3$ may have promoted the formation of hydroxy ligands in the product. **4** was fully characterized by IR spectroscopy, elemental, and single-crystal X-ray diffraction analyses. The structure of the cation is shown in Figure 6. Positional and thermal parameters are given in Table VIII. Selected bond lengths and angles are given in Table IX (a and b).

The features of the twelve-membered ring in the cation are similar to those of **1**–**3**. The arrangement of the four copper atoms is rectangular, Cu(1)–Cu(2) = 3.676 (6) Å, Cu(2)–Cu(3) = 3.109 (5) Å, Cu(3)–Cu(4) = 3.746 (5) Å, Cu(1)–Cu(4) = 2.998 (5) Å, Cu(1)–Cu(3) = 4.444 (6) Å, Cu(2)–Cu(4) = 4.739 (4) Å. There are two hydroxy ligands bridging two pairs of Cu atoms. In contrast to the trans configuration of the two hydroxy groups in **3**, the two hydroxy groups in **4** have a cis configuration with respect to the twelve-membered ring. An $H_2O$ ligand and an acetate ligand bridge Cu(2)–Cu(3) and Cu(1)–Cu(4), respectively,

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[17] (a) Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2615. (b) Bradley, D. C.; Kunchur, N. R. *J. Chem. Phys.* **1964**, *8*, 2258. (c) Kunchur, N. R. *Nature* **1964**, *204*, 468. (d) Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 6724.

[18] (a) Einstein, F. W. B.; Jones, C. H. W.; Jones, T.; Sharma, R. D. *Inorg. Chem.* **1983**, *22*, 3924. (b) Brodersen, K.; Hummel, Hans-Ulrich. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 5, Chapter 56.2. (c) Burgess, J. *Ibid.*, Vol. 2, Chapter 15.1.

**Table VIII.** Positional and Thermal Parameters for **4**[a]

| atom | *x* | *y* | *z* | *B*(eq),[a] Å$^2$ |
|---|---|---|---|---|
| Cu(1) | 0.2735 (2) | 0.4060 (2) | 0.1558 (3) | 3.1 (2) |
| Cu(2) | 0.0440 (2) | 0.3041 (2) | 0.1390 (3) | 3.1 (2) |
| Cu(3) | −0.1024 (2) | 0.5237 (2) | 0.1578 (3) | 3.1 (2) |
| Cu(4) | 0.1362 (2) | 0.6255 (2) | 0.2001 (2) | 2.8 (2) |
| Cl(1) | 0.385 (1) | −0.069 (1) | 0.179 (1) | 14 (1) |
| Cl(2) | 0.371 (1) | 0.015 (2) | 0.431 (1) | 23 (2) |
| P | 0.7238 (7) | 0.0254 (7) | 0.2299 (8) | 5.9 (5) |
| F(1) | 0.700 (2) | 0.059 (2) | 0.120 (2) | 14 (2) |
| F(2) | 0.671 (2) | 0.133 (2) | 0.318 (2) | 17 (2) |
| F(3) | 0.823 (2) | 0.053 (3) | 0.250 (3) | 19 (3) |
| F(4) | 0.634 (2) | −0.020 (3) | 0.206 (3) | 23 (3) |
| F(5) | 0.784 (2) | −0.088 (1) | 0.139 (2) | 11 (2) |
| F(6) | 0.752 (2) | −0.015 (2) | 0.338 (2) | 14 (2) |
| O(1) | −0.015 (1) | 0.631 (1) | 0.203 (1) | 2.6 (3) |
| O(2) | 0.192 (1) | 0.308 (1) | 0.159 (1) | 3.2 (3) |
| O(3) | −0.197 (1) | 0.427 (1) | 0.124 (1) | 3.4 (3) |
| O(4) | −0.090 (1) | 0.267 (1) | 0.095 (1) | 3.6 (3) |
| O(5) | 0.275 (1) | 0.643 (1) | 0.178 (1) | 3.9 (3) |
| O(6) | 0.374 (1) | 0.479 (1) | 0.136 (1) | 4.1 (3) |
| O(7) | 0.165 (1) | 0.482 (1) | 0.080 (1) | 2.4 (3) |
| O(8) | 0.0079 (9) | 0.408 (1) | 0.061 (1) | 2.2 (3) |
| O(9) | 0.218 (1) | 0.555 (1) | 0.356 (1) | 5.2 (4) |
| O(10) | 0.121 (1) | 0.540 (1) | 0.483 (2) | 6.3 (4) |
| O(11) | −0.022 (1) | 0.456 (1) | 0.322 (1) | 3.2 (3) |
| N(1) | 0.091 (1) | 0.781 (1) | 0.305 (2) | 3.5 (4) |
| N(2) | −0.214 (1) | 0.649 (1) | 0.258 (1) | 2.9 (4) |
| N(3) | 0.086 (1) | 0.189 (1) | 0.208 (2) | 4.4 (4) |
| N(4) | 0.392 (1) | 0.305 (1) | 0.204 (2) | 4.1 (4) |
| C(1) | −0.006 (2) | 0.799 (2) | 0.362 (3) | 6.4 (7) |
| C(2) | −0.072 (2) | 0.731 (2) | 0.273 (2) | 3.6 (5) |
| C(3) | −0.161 (2) | 0.729 (2) | 0.338 (2) | 5.7 (6) |
| C(4) | 0.077 (2) | 0.851 (2) | 0.233 (3) | 8.0 (8) |
| C(5) | 0.163 (2) | 0.823 (2) | 0.406 (3) | 8.3 (8) |
| C(6) | −0.273 (2) | 0.630 (2) | 0.343 (2) | 6.2 (7) |
| C(7) | −0.286 (2) | 0.688 (2) | 0.175 (2) | 5.4 (6) |
| C(8) | 0.185 (2) | 0.203 (2) | 0.269 (2) | 5.3 (6) |
| C(9) | 0.253 (2) | 0.224 (2) | 0.193 (2) | 3.3 (5) |
| C(10) | 0.347 (2) | 0.259 (2) | 0.265 (2) | 5.0 (6) |
| C(11) | 0.009 (2) | 0.202 (2) | 0.299 (2) | 5.5 (6) |
| C(12) | 0.096 (2) | 0.087 (2) | 0.106 (2) | 5.7 (7) |
| C(13) | 0.465 (2) | 0.359 (2) | 0.294 (3) | 6.9 (7) |
| C(14) | 0.447 (2) | 0.230 (2) | 0.092 (3) | 7.1 (7) |
| C(15) | −0.172 (2) | 0.327 (2) | 0.096 (2) | 3.8 (5) |
| C(16) | −0.269 (2) | 0.282 (2) | 0.071 (2) | 5.1 (6) |
| C(17) | 0.356 (2) | 0.575 (2) | 0.159 (2) | 3.4 (5) |
| C(18) | 0.451 (2) | 0.616 (2) | 0.157 (2) | 6.5 (7) |
| C(19) | 0.195 (2) | 0.563 (2) | 0.459 (2) | 3.7 (5) |
| C(20) | 0.268 (2) | 0.606 (2) | 0.565 (3) | 6.9 (7) |
| C(21) | 0.451 (3) | −0.050 (3) | 0.321 (4) | 10 (1) |

[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 IX.** Bond Lengths (Å) and Angles (deg) for **4**[a]

| | | | |
|---|---|---|---|
| (a) Lengths | | | |
| Cu(1)–Cu(4) | 2.998 (5) | C(8)–C(9) | 1.50 (3) |
| Cu(1)–O(2) | 1.98 (1) | C(9)–C(10) | 1.52 (3) |
| Cu(1)–O(6) | 1.98 (1) | C(15)–C(16) | 1.54 (3) |
| Cu(1)–O(7) | 1.92 (1) | C(17)–C(18) | 1.54 (3) |
| Cu(1)–O(9) | 2.45 (2) | O(1)–C(2) | 1.36 (2) |
| Cu(1)–N(4) | 2.03 (2) | O(2)–C(9) | 1.41 (2) |
| Cu(2)–Cu(3) | 3.109 (5) | O(3)–C(15) | 1.25 (2) |
| Cu(2)–O(2) | 1.99 (1) | O(4)–C(15) | 1.19 (2) |
| Cu(2)–O(4) | 1.97 (1) | O(5)–C(17) | 1.20 (2) |
| Cu(2)–O(8) | 1.94 (1) | O(6)–C(17) | 1.22 (2) |
| Cu(2)–O(11) | 2.37 (1) | O(9)–C(19) | 1.23 (2) |
| Cu(2)–N(3) | 2.00 (2) | O(10)–C(19) | 1.22 (2) |
| Cu(3)–O(1) | 2.02 (1) | N(1)–C(1) | 1.44 (3) |
| Cu(3)–O(3) | 2.00 (1) | N(1)–C(4) | 1.50 (3) |
| Cu(3)–O(8) | 1.92 (1) | N(1)–C(5) | 1.49 (3) |
| Cu(3)–O(11) | 2.50 (1) | N(2)–C(3) | 1.44 (3) |
| Cu(3)–N(2) | 1.99 (2) | N(2)–C(6) | 1.46 (3) |
| Cu(4)–O(1) | 2.01 (1) | N(2)–C(7) | 1.47 (3) |
| Cu(4)–O(5) | 1.99 (1) | N(3)–C(8) | 1.46 (3) |
| Cu(4)–O(7) | 1.90 (1) | N(3)–C(11) | 1.49 (3) |
| Cu(4)–O(9) | 2.44 (2) | N(3)–C(12) | 1.44 (3) |
| Cu(4)–N(1) | 1.98 (2) | N(4)–C(10) | 1.41 (2) |
| | | N(4)–C(13) | 1.47 (3) |
| | | N(4)–C(14) | 1.43 (3) |
| C(19)–C(20) | 1.52 (3) | C(1)–C(2) | 1.49 (3) |
| | | C(2)–C(3) | 1.50 (3) |
| (b) Angles | | | |
| Cu(4)–Cu(1)–O(2) | 110.9 (4) | Cu(1)–Cu(4)–O(1) | 112.9 (4) |
| Cu(4)–Cu(1)–O(6) | 79.2 (5) | Cu(1)–Cu(4)–O(5) | 77.5 (4) |
| Cu(4)–Cu(1)–O(7) | 37.9 (4) | Cu(1)–Cu(4)–O(7) | 38.6 (4) |
| Cu(4)–Cu(1)–O(9) | 52.1 (4) | Cu(1)–Cu(4)–O(9) | 52.4 (4) |
| Cu(4)–Cu(1)–N(4) | 151.8 (5) | Cu(1)–Cu(4)–N(1) | 150.7 (5) |
| O(2)–Cu(1)–O(6) | 169.4 (6) | O(1)–Cu(4)–O(5) | 167.1 (5) |
| O(2)–Cu(1)–O(7) | 94.5 (5) | O(1)–Cu(4)–O(7) | 91.9 (5) |
| O(2)–Cu(1)–O(9) | 99.2 (5) | O(1)–Cu(4)–O(9) | 105.9 (5) |
| O(2)–Cu(1)–N(4) | 83.7 (6) | O(1)–Cu(4)–N(1) | 83.6 (6) |
| O(6)–Cu(1)–O(7) | 91.7 (6) | O(5)–Cu(4)–O(7) | 92.4 (6) |
| O(6)–Cu(1)–O(9) | 89.7 (6) | O(5)–Cu(4)–O(9) | 86.3 (5) |
| O(6)–Cu(1)–N(4) | 88.7 (7) | O(5)–Cu(4)–N(1) | 90.3 (6) |
| O(7)–Cu(1)–O(9) | 87.4 (5) | O(7)–Cu(4)–O(9) | 88.2 (5) |
| O(7)–Cu(1)–N(4) | 169.6 (7) | O(7)–Cu(4)–N(1) | 170.7 (6) |
| O(9)–Cu(1)–N(4) | 103.0 (7) | O(9)–Cu(4)–N(1) | 100.8 (6) |
| Cu(3)–Cu(2)–O(2) | 112.7 (4) | Cu(3)–O(1)–Cu(4) | 136.6 (7) |
| Cu(3)–Cu(2)–O(4) | 78.3 (4) | Cu(3)–O(1)–C(2) | 110 (1) |
| Cu(3)–Cu(2)–O(8) | 36.2 (3) | Cu(4)–O(1)–C(2) | 112 (1) |
| Cu(3)–Cu(2)–O(11) | 52.1 (3) | Cu(1)–N(4)–C(10) | 106 (1) |
| Cu(3)–Cu(2)–N(3) | 147.8 (5) | Cu(1)–N(4)–C(13) | 115 (2) |
| O(2)–Cu(2)–O(4) | 167.2 (6) | Cu(1)–N(4)–C(14) | 107 (2) |
| O(2)–Cu(2)–O(8) | 94.0 (5) | Cu(3)–N(2)–C(3) | 105 (1) |
| O(2)–Cu(2)–O(11) | 98.3 (5) | Cu(3)–N(2)–C(6) | 117 (1) |
| O(2)–Cu(2)–N(3) | 84.9 (6) | Cu(3)–N(2)–C(7) | 110 (1) |
| O(4)–Cu(2)–O(8) | 91.7 (6) | Cu(2)–N(3)–C(11) | 112 (1) |
| O(4)–Cu(2)–O(11) | 93.6 (5) | Cu(2)–N(3)–C(12) | 108 (1) |
| O(4)–Cu(2)–N(3) | 88.6 (7) | Cu(1)–O(2)–Cu(2) | 135.6 (7) |
| O(8)–Cu(2)–O(11) | 83.9 (5) | Cu(1)–O(2)–C(9) | 112 (1) |
| O(8)–Cu(2)–N(3) | 175.7 (7) | Cu(2)–O(2)–C(9) | 112 (1) |
| O(11)–Cu(2)–N(3) | 100.3 (6) | Cu(3)–O(3)–C(15) | 127 (1) |
| Cu(2)–Cu(3)–O(1) | 107.7 (4) | Cu(2)–O(4)–C(15) | 127 (2) |
| Cu(2)–Cu(3)–O(3) | 75.8 (4) | Cu(4)–O(5)–C(17) | 127 (1) |
| Cu(2)–Cu(3)–O(8) | 36.7 (3) | Cu(1)–O(6)–C(17) | 125 (1) |
| Cu(2)–Cu(3)–O(11) | 48.5 (3) | Cu(1)–O(7)–Cu(4) | 103.5 (6) |
| Cu(2)–Cu(3)–N(2) | 145.1 (5) | Cu(2)–O(8)–Cu(3) | 107.1 (5) |
| O(1)–Cu(3)–O(3) | 175.1 (6) | Cu(1)–O(9)–Cu(4) | 75.5 (5) |
| O(1)–Cu(3)–O(8) | 92.2 (5) | Cu(1)–O(9)–C(19) | 135 (2) |
| O(1)–Cu(3)–O(11) | 92.8 (5) | Cu(4)–O(9)–C(19) | 137 (2) |
| O(1)–Cu(3)–N(2) | 85.5 (6) | Cu(2)–O(11)–Cu(3) | 79.3 (4) |
| O(3)–Cu(3)–O(8) | 92.6 (5) | Cu(4)–N(1)–C(1) | 108 (1) |
| O(3)–Cu(3)–O(11) | 87.0 (5) | Cu(4)–N(1)–C(4) | 113 (2) |
| O(3)–Cu(3)–N(2) | 89.7 (6) | Cu(4)–N(1)–C(5) | 115 (2) |
| O(8)–Cu(3)–O(11) | 80.9 (5) | Cu(2)–N(3)–C(8) | 105 (1) |
| O(8)–Cu(3)–N(2) | 177.6 (6) | | |
| O(11)–Cu(3)–N(2) | 100.1 (6) | | |

through the formation of two long Cu–O bonds, Cu(1)–O(9) = 2.45 (2) Å, Cu(4)–O(9) = 2.44 (2) Å, Cu(2)–O(11) = 2.37 (1) Å, Cu(3)–O(11) = 2.50 (1) Å. As a result, the Cu(1)–Cu(4) distance, 2.998 (5) Å, and Cu(2)–Cu(3) distance, 3.109 (5) Å, are much shorter than the corresponding ones in **3**. The assignment of O(11) to an $H_2O$ ligand and O(8) to an OH ligand was based on the overall charge of the cation and the Cu–O bonding distances. As an anion the $OH^-$ ligand has a much stronger affinity to the Cu(II) cation and forms a shorter bond than the $H_2O$ ligand does.[12] Although a water molecule as a bridging ligand is rare in transition-metal complexes, several examples are known in alkali- and alkaline-earth-metal complexes.[14d,18c] The geometry of each copper atom is approximately square-pyramidal. The plane Cu(1)O(2)O(7)O(6)N(4) and the plane Cu(2)O(2)O(8)O(4)N(3) are nearly coplanar with a dihedral angle of 4.5°. The plane Cu(3)O(1)O(3)O(8)N(2) has a dihedral angle of 7.5° with the plane Cu(4)O(1)O(5)O(7)N(1). The dihedral angles between the Cu(1) plane and the Cu(4) plane, and the Cu(2) plane and Cu(3) plane are 60.1 and 58.0°, respectively.

The most important feature of this molecule is that the $Cu_4$ cations form a one-dimensional structure in the solid state, as shown in Figure 7. This one-dimensional structure is achieved through the formation of two intermolecular hydrogen bonds between the $H_2O$ and acetate ligands. O(10)···O(11′) = 2.73 (2) Å, C(19)–O(10)···O(11′) = 142 (2)°, two long intermolecular Cu–O bonds, Cu(3)–O(7′) = 2.81 (1) Å, and perhaps two weak

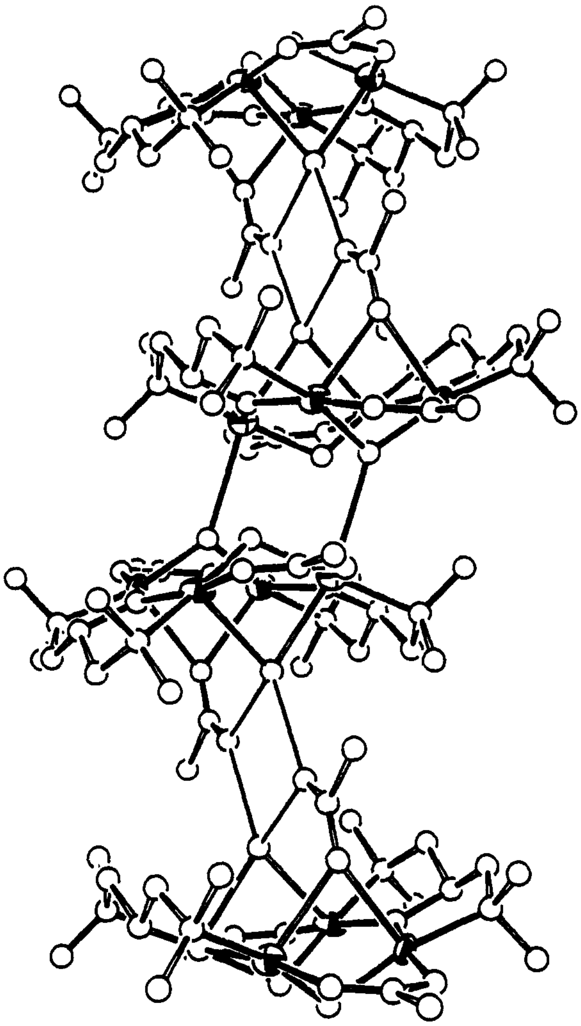

**Figure 7.** ORTEP diagram showing the polymeric structure and hydrogen bonds of **4**.

intermolecular hydrogen bonds between the hydroxy ligand O(8) and the O(1) atom of the dmap ligand, (O(1)···O(8′) = 2.92 (2) Å, C(2)–O(1)···O(8′) = 113 (1)°. O(10) also forms an intramolecular hydrogen bond with the $H_2O$ ligand, as evidenced by the O(10)···O(11) distance of 2.71 (2) Å and the C(19)–O(10)···O(11) angle of 127 (2)°. The shortest intermolecular Cu–Cu distance is 3.910 (5) Å for Cu(3)–Cu(4′), comparable to the intramolecular Cu–Cu distances of Cu(3)–Cu(4), 3.746 (6) Å, and Cu(1)–Cu(2), 3.676 (6) Å. Hydrogen bonds between a water molecule and a acetate have been observed previously in inorganic and organic hydrates such as oxalic acid dihydrate where the water molecule is the donor of two protons.[14c]

Use of hydrogen bonds to control the assembly of molecules has been one of the widely-used strategies in the synthesis of supramolecules.[19] The structure of **4** demonstrates that hydrogen bonds can also be used to assemble polynuclear metal complexes as one-dimensional arrays.

Synthesis of low-dimensional polymeric compounds, especially those containing metal atoms in one-dimensional arrays, has been a very active research area.[20] Low-dimensional materials are attractive to chemists not only because they display interesting anisotropic properties but also because they may have important applications as advanced materials. Most of the known one-dimensional inorganic compounds have a staggered, one-metal-centered chain structure in the solid state.[20,21] One-dimensional inorganic compounds which contain multiple-metal-centered units arranged along one dimension are rare. **3** and **4** represent a new class of polymeric inorganic material. Investigation of inserting yttrium and barium ions between these cyclic $Cu_4$ units is in progress.

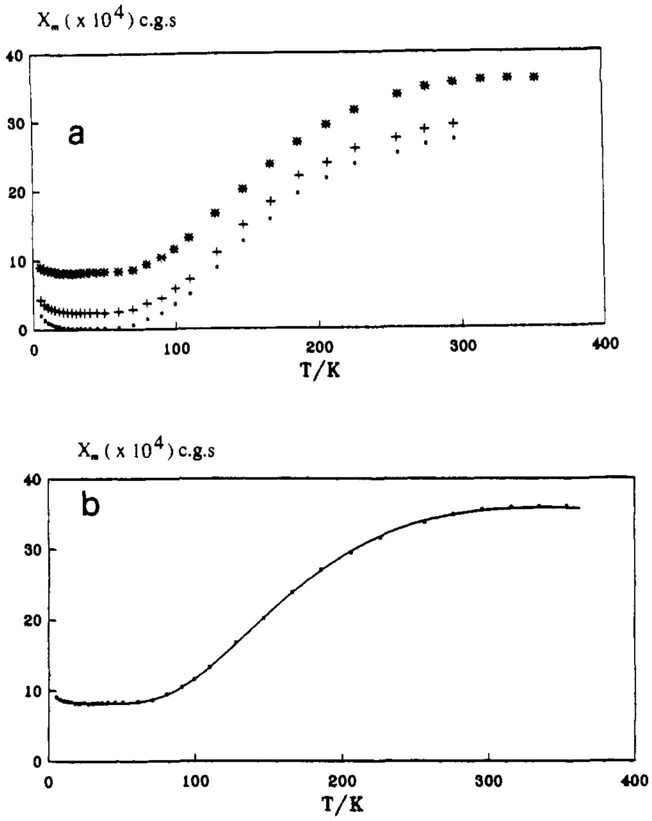

**Figure 8.** (a) Magnetic susceptibility of **3**: (*) data at 0.5 kG; (+) data at 3 kG; (●) data at 7 kG. (b) Theoretical fitting for the data at 0.5 kG: (dotted line) experimental data; (solid line) theoretical fitting.

The common feature of the structures **1**–**4** is the presence of the cyclic unit composed of four copper(II) ions, two acetate ligands, and two dmap ligands. The structures of **1**–**4** illustrate that the cyclic $Cu_4$ unit is capable of accommodating a variety of ligands. We believe that the ligand environments on the ring can be modified such that heterometal ions such as $Y^{3+}$ or $Ba^{2+}$ can be readily incorporated into the $Cu_4$ complexes. Such an investigation is in progress.

**Magnetic Properties and Bondings of 3.** It has been suggested that superconductivity is magnetic in origin.[22] Magnetic interactions of Cu ions in the high-temperature superconductors appear to play an important role in the superconductivity. Studies of magnetic properties of molecular complexes with structures resembling those of superconductors might provide valuable information on superconductivity. For these reasons, we conducted the study of the magnetic properties of the $Cu_4$ complexes. Because compounds **1**, **2**, and **4** are often contaminated by impurities, we used compound **3** for the study.

The molar magnetic susceptibility data, after diamagnetic corrections, in the temperature range 5–352 K at three different magnetic fields are given in Figure 8a. The magnetic susceptibility of **3** appears field-dependent. It decreases with the increase of the field strength. Such peculiar field-dependent behavior in

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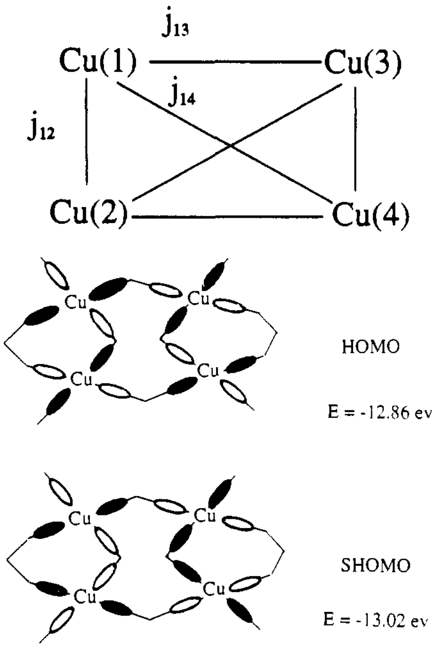

**Figure 9**. (a, Top) theoretical fitting model. (b, Bottom) d orbitals of Cu atoms in the HOMO and SHOMO.

this system has not been understood. The magnetic susceptibility has a minimum at about 27 K. After this temperature it steadily increases. The magnetic susceptibility at a low temperature range appears to be dominated by antiferromagnetism. A rectangular model (Figure 9a) with three $j$ coupling constants, $j_{12} = j_{34}$, $j_{23} = j_{14}$, $j_{13} = j_{24}$, was used to fit the experimental data. The general magnetic susceptibility expression derived by Hatfield and coworkers from the Van Vleck equation for a tetranuclear Cu(II) complex[23] was used for the theoretical fitting. The data were corrected for temperature-independent paramagnetism (TIP), the presence of paramagnetic monomer impurity, and diamagnetism according to eq 4. The best fitting for the data at 0.5 kG (Figure 8b) yielded the values $g = 2.19$, $j_{12} = -186.5$ cm$^{-1}$, $j_{23} = 39.7$ cm$^{-1}$ and $j_{13} = -4.4$ cm$^{-1}$. These results suggest that the electron-spin exchange in this system appears to be dominated by this coupling. The large antiferromagnetic exchange constant $j_{12}$ could be attributed to the spin exchange between Cu(1) and Cu(2) bridged by an acetate ligand and a hydroxy ligand, since the Cu(1)–Cu(2) separation is the shortest compared with other Cu–Cu distances in **3** and antiferromagnetic couplings of electron spins are most common among dinuclear Cu(II) complexes with similar ligand environments.[12,24] The smallest exchange constant $j_{13}$ can be assigned to the spin exchange of Cu(1) and Cu(1′), since this pair of Cu(II) ions is more than 4 Å apart. As a result of such assignment, the spin exchange between Cu(1) and Cu(2′) is ferromagnetic. Ferromagnetic exchanges between dimers in dimer–dimer types of tetranuclear copper(II) complexes have been observed previously.[23,24]

$$\chi_{\mathrm{calc}} = (1 - \rho)\chi + \chi_{\mathrm{TIP}} + \rho\chi_{\mathrm{mono}} + \chi_{\mathrm{diam}} \qquad (4)$$

$$\rho = 1.067 \times 10^{-3}$$

$$\chi_{\mathrm{TIP}} = 9.181 \times 10^{-4}$$

$$\chi_{\mathrm{mono}} = \text{molar susceptibility of monomeric cupric impurity}$$

$$R = 0.777 \times 10^{-2}$$

The results of MO calculations indicate that about 20% of the contributions are from copper atomic orbitals in the HOMO and second HOMO which are mainly $d_{x^2-y^2}$ in character, as shown in Figure 9b. The HOMO and SHOMO are close in energy. The electron-spin couplings in this molecule are probably through these $\sigma$ orbitals.

**Conclusion.** A new class of cyclic tetranuclear Cu(II) complexes has been synthesized. These complexes are capable of forming one-dimensional arrays in the solid state if appropriate ligands and metal ions are present. They are potential precursors for the syntheses of heteronuclear metal complexes with compositions and structures resembling those of high-$T_c$ superconductors. Compound **3** displays interesting field-dependent behavior in magnetic susceptibility. Further investigation on this behavior is necessary in order to have a full understanding of the magnetic property in this system.

**Acknowledgment.** We thank the University of Windsor and the Natural Science and Engineering Research Council for financial support.

**Supplementary Material Available:** Table S1, listing crystallographic data for **1**–**4**, Tables S2–S7 and S10–S12, giving H atom parameters, anisotropic temperature factors, and bond lengths and angles of the $PF_6$ anions for **1**, **2**, and **4**, Tables S8 and S9, giving H atom parameters and anisotropic temperature factors for **3**, Tables S21–S22, listing bond lengths and angles for the dmap ligand and $CH_2Cl_2$ molecule in **1** and **4**, and Figures S17–S20, showing the structures of the $CH_2Cl_2$ solvent molecule and the $PF_6$ anion in **1** and **4** (24 pages); Tables S13–S16, listing observed and calculated structure factors for **1**–**4** (61 pages). Ordering information is given on any current masthead page.

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# Solid-State Metathesis as a Quick Route to Transition-Metal Mixed Dichalcogenides

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Solid-solution transition-metal dichalcogenides, traditionally synthesized from the elements at elevated temperatures over long periods of time, can now be prepared from rapid self-propagating reactions between transition-metal halides and alkali-metal mixed chalcogenides such as $Na_2(S,Se)$. The transition-metal dichalcogenide solid solution is isolated by simply washing away the byproduct salt. Powder X-ray diffraction and thermogravimetric analyses of the solid solutions $Mo(S,Se)_2$ and $W(S,Se)_2$ are presented. Although any composition can theoretically be prepared, the stoichiometry of the product is influenced by the temperatures attained during the course of the reaction. The products are characteristically enriched in the more volatile non-metal component relative to the alkali-metal mixed-chalcogenide precursor. The observed kinetic products and selective enrichment suggest that elemental intermediates may be involved in these reactions.

## Introduction

Precursor reactions are an effective synthetic route for the preparation of a large number of materials. One type of precursor method involves an exchange of two or more species during a reaction. Reactions of this type can, in principle, be carried out in the liquid, gas, or solid state.[1-5] The approach, however, has

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