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# First Example of a 2:1 Cocrystal of Mixed Cu(I)/Cu(II) Complexes and a Novel Ferromagnetic Bis($\mu$-hydroxo)dicopper(II) Complex with a Bis(pyrazol-1-yl)methane Bidentate Ligand

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A unique 2:1 cocrystal of mixed Cu(I)/Cu(II) complexes [$Cu^I(H_2CPz_2)(MeCN)_2](ClO_4)$ (**1**) and [$Cu^{II}(H_2CPz_2)_2(ClO_4)_2$] (**4**), a novel ferromagnetic $ClO_4^-$-bridged bis($\mu$-hydroxo)dicopper(II) complex, [$Cu_2(H_2CPz_2)_2(OH)_2(ClO_4)](ClO_4)(CH_3CN)_{0.5}$ (**5**), and a bischelated copper(I) complex, [$Cu(H_2CPz_2)_2](ClO_4)$ (**2**), prepared from a one-pot reaction of [$Cu(MeCN)_4](ClO_4)$ and $H_2CPz_2$, are described. The structures of these complexes have been determined by X-ray crystallographic methods. The Cu(I)–N(acetonitrile) bond distances in complex **1** are nonequivalent (1.907(8) and 2.034(9) Å), leading to the dissociation of one MeCN to form a Y-shaped complex, [$Cu^I(H_2CPz_2)(MeCN)](ClO_4)$ (**3**), which is oxidized readily in air to form complex **5** with a butterfly $Cu_2O_2$ core.

## Introduction

The cocrystallization of metal complexes is unusual, because compounds with different geometries rarely possess similar lattice packing forces and exhibit similar crystallization kinetics.[1] To date, only a few cocrystal complexes, for example, of Cu(II),[2] Rh(I),[3] and Ln(III),[4] have been reported. The metal ions of the isomers in each of these cocrystals retain the same oxidation state. Copper complexes with different oxidation states and which are crystallized in the same unit cell are unprecedented. Herein, we report an unusual 2:1 cocrystallization phenomenon for mixed Cu(I)/Cu(II) complexes [$Cu^I(H_2CPz_2)(MeCN)_2](ClO_4)$ (**1**) and [$Cu^{II}(H_2CPz_2)_2(ClO_4)_2$] (**4**) ($H_2CPz_2$ = bis(pyrazol-1-yl)methane)[5] and a novel ferromagnetic bis($\mu$-hydroxo)dicopper(II) complex, [$Cu_2(H_2CPz_2)_2(OH)_2(ClO_4)](ClO_4)(CH_3CN)_{0.5}$ (**5**).

## Experimental Section

**Materials and Methods.** The reagents from commercial sources were used without purification. The solvents were dried and distilled under nitrogen prior to use. The ligand $H_2CPz_2$[6] and the copper(I) starting material [$Cu(MeCN)_4](ClO_4)$[7] were prepared according to literature procedures. *Warning: Perchlorate compounds are potentially explosive! Extreme care must be taken when working with perchlorate complexes, and only small quantities should be handled.*

**Formation of Compounds (1 + 4), 2, and 5.** A solution of 0.230 g (1.55 mmol) of $H_2CPz_2$ in 5 mL of acetonitrile was added to a solution of 0.327 g (1.00 mmol) of [$Cu(CH_3CN)_4](ClO_4)$ in 10 mL of acetonitrile. The solution was stirred under $N_2$ at room temperature for 2 h and then further stirred in air for ca. 4 h until the solution changed to light blue. After the slow diffusion of diethyl ether into the reaction mixture for 2 days, two apparently different forms of blue crystals were produced. The main product was **5**, and a small portion, separated manually, was the cocrystal (**1** + **4**) of crystallographic quality. Anal. Calcd for $C_{36}H_{44}C1_4Cu_3N_{20}O_{16}$ (**1** + **4**): C, 32.14; H, 3.30. Found: C, 32.13; H, 3.30. The colorless crystals **2**, suitable for X-ray analysis, were obtained by the slow diffusion of diethyl ether into half of the filtrate of the previous reaction mixture for ca. 5 days. Anal. Calcd for $CuC_{14}H_{16}N_8O_4Cl$ (**2**): C, 36.60; H, 3.49; N, 24.40. Found: C, 36.87; H, 3.52; N, 24.47. The purple-blue crystals **5**, suitable for X-ray analysis, were

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[†] National Taiwan Normal University.

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[||] National Central University.

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(5) For the structures of the ligands, see Scheme 2.

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10.1021/ic048854y CCC: $30.25

**Table 1.** Crystal Structure and Refinement Data for (**1** + **4**), **2**, and **5**

| | **1** + **4** | **2** | **5** |
|---|---|---|---|
| empirical formula | $C_{36}H_{44}Cl_4Cu_3N_{20}O_{16}$ | $C_{14}H_{16}ClCuN_8O_4$ | $C_{15}H_{19.5}Cl_2Cu_2N_{8.5}O_{10}$ |
| fw | 1345.33 | 459.34 | 676.87 |
| temp (K) | 293(2) | 294(2) | 295(2) |
| wavelength (Å) | 0.70930 | 0.71073 | 0.71073 |
| cryst syst | triclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ |
| $a$ (Å) | 9.3397(19) | 8.5825(7) | 10.3563(7) |
| $b$ (Å) | 12.4097(16) | 19.8344(17) | 10.6986(7) |
| $c$ (Å) | 13.2366(14) | 11.8480(10) | 12.6420(9) |
| $\alpha$ (deg) | 93.078(9) | 90 | 72.424(1) |
| $\beta$ (deg) | 104.314(11) | 98.583(2) | 80.679(1) |
| $\gamma$ (deg) | 110.510(11) | 90 | 68.004(1) |
| $V$ (Å$^3$) | 1375.6(4) | 1994.3(3) | 1236.23(15) |
| $Z$ | 1 | 4 | 2 |
| $D_{calcd}$ (Mg/m$^3$) | 1.624 | 1.530 | 1.818 |
| abs coeff (mm$^{-1}$) | 1.425 | 1.267 | 2.005 |
| $\theta$ range for data collection (deg) | 1.60-25.91 | 2.05-28.29 | 1.69-28.25 |
| no. of reflns collected | 5651 | 6261 | 12060 |
| no. of independent reflns | 5403 [$R$(int) = 0.0402] | 2370 [$R$(int) = 0.0398] | 5417 [$R$(int) = 0.0409] |
| no. of data/restraints/params | 5403/0/355 | 2370/0/128 | 5417/0/369 |
| GOF on $F^2$ | 1.001 | 1.114 | 1.058 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0546, wR2 = 0.1392 | R1 = 0.0902, wR2 = 0.2469 | R1 = 0.0414, wR2 = 0.1196 |
| $R$ indices (all data) | R1 = 0.1683, wR2 = 0.1823 | R1 = 0.1173, wR2 = 0.2670 | R1 = 0.0511, wR2 = 0.1257 |
| largest diff peak and hole (e Å$^{-3}$) | 0.633 and −0.491 | 0.834 and −0.436 | 1.075 and −0.559 |

formed by the slow diffusion of *n*-hexane into the other half of the filtrate for ca. 1 week. UV−vis (diffuse reflectance) for **5**: $\lambda_{max}$ 346 nm, 621 nm. IR (Nujol): 3565 cm$^{-1}$ (OH), 1096 cm$^{-1}$ ($ClO_4$). Anal. Calcd for $C_{15}H_{19.5}Cl_2Cu_2N_{8.5}O_{10}$ (**5**): C, 26.62; H, 2.90; N, 17.59. Found: C, 26.39; H, 2.93; N, 17.52.

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls on a Jasco FT/IR 700 spectrophotometer. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer. Diffuse reflectance measurements from 200 to 800 nm were recorded as polycrystalline samples using a Hitachi U-3501 spectrophotometer equipped with an integrating sphere attachment. Cyclic voltammetric measurements were carried out on a potentiostat (EG&G Potentiostat/Galvan model 273) at room temperature in acetonitrile solutions (10$^{-3}$ M). The supporting electrolyte was tetraethylammonium perchlorate (0.1 M). A three-electrode assembly composed of a glassy carbon working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode was used. Elemental analyses were performed on a Heraeus CHN-OS rapid elemental analyzer by the microanalysis laboratories of National Chung Hsin University. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS7 SQUID magnetometer (measurements at 10000 G) performed at the National Taiwan University. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constant.

**X-ray Crystallography.** Crystal data and collection parameters are listed in Table 1. Data collections were carried out on an Enraf Nonius TurboCAD4 diffractometer for (**1** + **4**), and on a Bruker SMART CCD diffractometer for **2** and **5**, using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods using SHELXL-97,[8] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All of the non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were located geometrically and refined in riding mode except those of the bridging hydroxyl groups for **5**. Additional crystallographic data as CIF files are available as Supporting Information.

## Results and Discussion

The light blue cocrystal of **1** and **4**, the purple-blue **5**, and the colorless [Cu($H_2CPz_2$)$_2$]($ClO_4$) (**2**) were prepared by the reaction of a 2:3 molar ratio of [Cu(MeCN)$_4$]($ClO_4$) and $H_2CPz_2$ in MeCN under $N_2$ for 2 h, which was then stirred in air for ca. 4 h. The colorless solution gradually turned a light blue color. After the slow diffusion of diethyl ether into the reaction mixture for 2 days, two apparently different forms of blue crystals were produced. The main product was **5**, and the minor portion, separated manually, was the cocrystal of **1** and **4**. From the filtrate, the colorless crystals of **2** were obtained by the slow diffusion of diethyl ether, indicating that **2** was adequately stable under aerobic conditions in MeCN solution, whereas only a small amount of **2** accompanied by **1** was oxidized to form the cocrystal of **1** and **4**. Finally, the purple-blue crystals of **5** were formed by the slow diffusion of *n*-hexane. The tentative overall reactions are presented in Scheme 1.

The molecular structures of the cocrystal complexes **1** and **4** are shown in Figure 1. The cocrystal is composed of discrete complex cations [Cu$^{I}$($H_2CPz_2$)(MeCN)$_2$]$^+$, complex molecules [Cu$^{II}$($H_2CPz_2$)$_2$($ClO_4$)$_2$], and perchlorate anions. The Cu$^{I}$ cation binds a bidentate $H_2CPz_2$ ligand, where the Cu(N−N)$_2$C fragment has an imposed boat conformation, and two unequally coordinated MeCN molecules, with a difference of 0.13 Å in the Cu−N(MeCN) distances. Being somewhat distorted from tetrahedral geometry, the [Cu$^{I}$($H_2CPz_2$)(MeCN)$_2$]$^+$ may be described as a trigonal pyramid with a Y-shaped basal plane of Cu(2)N(5)N(8)N(10) and an apex of N(9). Compared with the bond distances of the four nearly identical Cu−N bonds in [Cu(MeCN)$_4$]$^+$ (1.98 ± 0.01 Å),[9] it is likely that the elongated apical MeCN (Cu−N = 2.034(9) Å) is prone to dissociate to form a planar Y-shaped tricoordinate complex, **3**. To diagnose the formation of **3**,

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[8] Sheldrick, G. M. *SHELXL97*, version 97-2; University of Gottingen: Gottingen, Germany, 1997.

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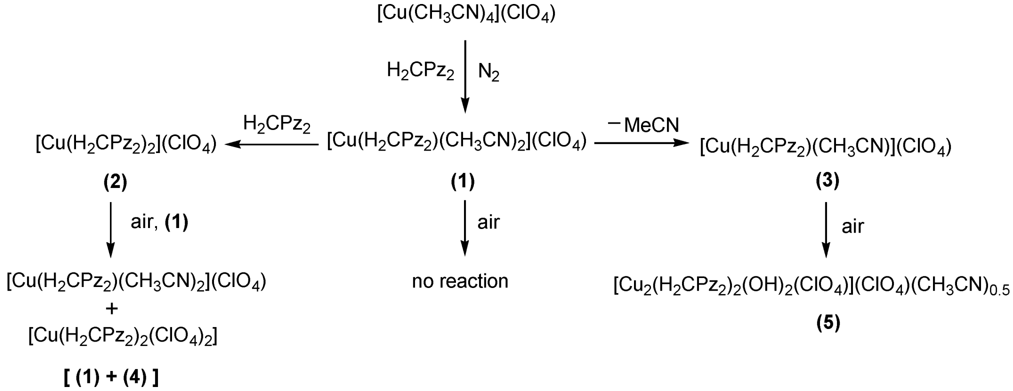
**Scheme 1.** Formation of Complexes **1**−**5**



the ESI/MS spectrum of the vacuum-dried solids of the reaction mixture prior to exposing them to air was acquired. The resulting two significant peaks at 252 (100%) and 458.2 (20%) indicate the presence of $[Cu(H_2CPz_2)(MeCN)]^+$ and $[\mathbf{2} - H]^+$, respectively. Moreover, the absence of the molecular ion peak $[Cu(H_2CPz_2)(MeCN)_2]^+$ suggests that one of the coordinated MeCN groups is readily dissociated from complex **2**. In addition, an analogous Y-shaped tricoordinate complex, $[Cu(H_2CPz'_2)(MeCN)](ClO_4)$[10] ($H_2CPz'_2$ = bis(3,5-dimethylpyrazol-1-yl)methane) has been prepared and structurally characterized. To our knowledge, complex **1** is the first structurally characterized tetracoordinated bisacetonitrile copper(I) complex with a bidentate ligand.

The molecular structure of the central symmetric $[Cu^{II}(H_2CPz_2)_2(ClO_4)_2]$ (**4**) features a rigorously planar $CuN_4$ chromophore, and two elongated, slightly tilted axial Cu−O bonds reside on the opposite sides of the $CuN_4$ plane due to the Jahn−Teller distortion. The two boat fragments $Cu(N-N)_2C$ are oriented in opposite directions. The mean Cu(II)−N distance of 1.998 ± 0.006 Å and the $H_2CPz_2$ ligand bite angle of 88.9° are within the normal ranges.

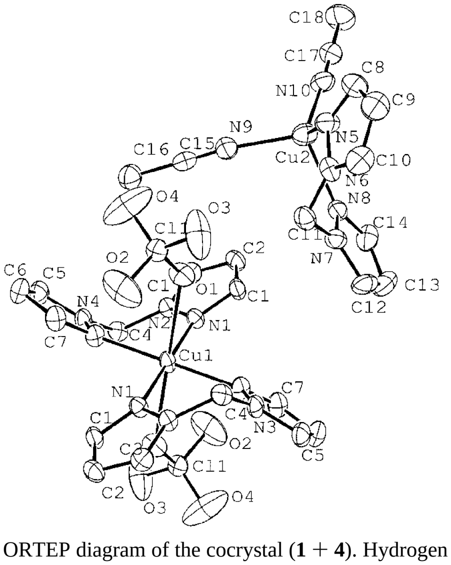


**Figure 1.** ORTEP diagram of the cocrystal (**1** + **4**). Hydrogen atoms and discrete perchlorates are omitted for clarity. Selected distances (Å) and angles (deg): Cu1−N1 1.992(6), Cu1−N4 2.004(6), Cu2−N5 2.006(8), Cu2−N8 2.083(7), Cu2−N9 2.034(9), Cu2−N10 1.907(8), Cu1−O1 2.609(8); N1−Cu1−N4 88.9(3), N1−Cu1−N4a 91.1(3), N5−Cu2−N8 91.3(3), N5−Cu2−N9 109.8(3), N5−Cu2−N10 118.9(3), N8−Cu2−N9 103.8(3), N8−Cu2−N10 122.7(3), N9−Cu2−N10 108.5(3).

The molecular structure of **2**, shown in Figure 2, is depicted with the $C_2$ axis nearly perpendicular to the plane of the paper. The dihedral angle of the two chelating planes (N1N3ACu1 and N1AN3Cu1) is 74.5°, which is somewhat off the 90° of a tetrahedral geometry. The mean Cu−N distance of 2.065 ± 0.065 Å and the $H_2CPz_2$ ligand bite angle of 94.1° are larger than those of the corresponding $Cu^{II}$ complex **4** and are reasonably normal. It is obvious that complex **4** is the oxidized product of complex **2**. The cyclic voltammogram of **2** (Figure 3) exhibited a very large $\Delta E$ ($E_{pa} - E_{pc}$) of 520 mV, indicating that a large structural reorganization energy was required for the redox processes between the distorted tetrahedral $Cu^I$ complex **2** and the tetragonal $Cu^{II}$ complex **4**.

Similar to the closely related complex $[Cu(HCPz'_3)(MeCN)](PF_6)$,[11] ($HCPz'_3$ = tris(3,5-dimethylpyrazol-1-yl)methane, as shown in Scheme 2), which reacts with dioxygen to give a $\mu$-$\eta^2$:$\eta^2$-peroxo complex, $[Cu_2(HCPz'_3)_2(\mu\text{-}O_2)](PF_6)_2$, at −80° to +7° and then gradually decomposes to a bis($\mu$-hydroxo) complex, $[Cu_2(HCPz'_3)_2(\mu\text{-}OH)_2](PF_6)_2$, it is likely that the reaction of the tricoordinate complex $[Cu(H_2CPz_2)(NCCH_3)](ClO_4)$ (**3**) with dioxygen to yield the bis($\mu$-hydroxo) complex **5** may proceed via a similar dioxygen-adduct intermediate, $[Cu_2(H_2CPz_2)_2(O_2)](ClO_4)_2$ in the present case.

The molecular structure of **5**, as shown in Figure 4, is composed of $[Cu_2(H_2CPz_2)_2(\mu\text{-}OH)_2(ClO_4)]^+$ complex cations and discrete $CH_3CN$ and perchlorates. The complex cation exists in a type I conformer (Scheme 3) with the two Cu−(N−N)$_2$−C boat fragments oriented in the same direction and one bridging bidentate $ClO_4^-$ anion weakly coordinated to the two copper atoms having a Cu−O($ClO_4^-$) mean distance of 2.593 ± 0.079 Å. The Cu(II) ions exhibit a distorted square pyramidal coordination with $\tau = 0.051$ and 0.060, respectively.[12] It is noteworthy that unlike the known $[Cu_2(HB(3,5\text{-}i\text{-}Pr_2Pz)_3)_2(\mu\text{-}OH)_2]$[13] and $[Cu_2(HCPz'_3)_2(\mu$-

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(10) Chou, C.-C.; Su, C.-C. To be published.

(11) Cvetkovic, M.; Batten, S. R.; Moubaraki, B.; Murray, K. S.; Spiccia, L. *Inorg. Chim. Acta* **2001**, *324*, 131.

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(13) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.

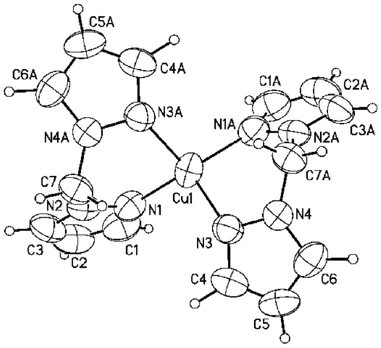


**Figure 2.** ORTEP diagram of **2**. $ClO_4^-$ is omitted for clarity. Selected distances (Å) and angles (deg): Cu1−N1 2.009(5), Cu1−N3 2.120(4); N1−Cu1−N3A 94.1(2), N1−Cu1−N1A 144.3(3), N1−Cu1−N3 105.1(2).

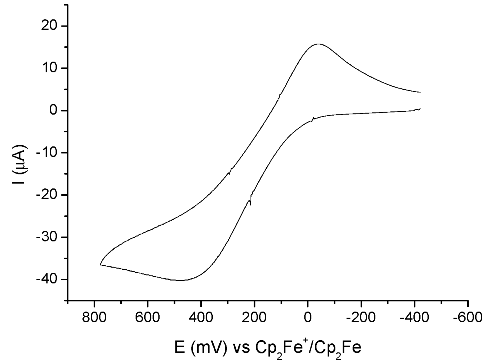
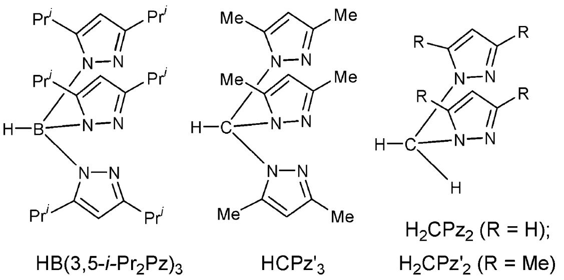


**Figure 3.** Cyclic voltammogram of **2** (1.0 mM) in MeCN with $\Delta E$ = 0.520 V ($E_{pa}$ = 0.479 V; $E_{pc}$ = − 0.041 V), scan rate 50 mV/s, electrolyte $(Bu_4N)ClO_4$ (0.1 M).

**Scheme 2.** Structural Comparison for Ligands HB(3,5-*i*-$Pr_2Pz)_3$, $HCPz'_3$, $H_2CPz_2$, and $H_2CPz'_2$



$OH)_2](PF_6)_2$[11] having a planar $Cu_2O_2$ structure, complex **5** possesses a butterfly $Cu_2O_2$ core,[14−16] presumably resulting mainly from the bridging perchlorate anion.

The molecular structure of **5** meets the requirements of Ruiz's model:[17,18] (i) a small Cu−O−Cu angle, $\theta_m = 95.8°$, (ii) large out-of-plane shifts of the hydrogen atoms of the bridging hydroxo groups, $\tau_m = 38.6°$, and (iii) hinge-distorted $Cu_2O_2$ rings, with a dihedral angle of Cu1O1O2 and Cu2O1O2 of 153.1°. Accordingly, it is expected to exhibit a ferromagnetic character. Indeed, the magnetic susceptibility follows the equation $\chi = C/(T - \Theta)$. A least-squares fit for $T > 5$ K data gave $C = 0.87$ (emu K)/mol and $\Theta = 4.4$ K (Figure 5). The positive value of $\Theta$ indicates the ferromagnetic interaction between Cu ions. Moreover, the magnetization as a function of the applied magnetic field for **5** has been recorded at 2 K. Upon applying a magnetic field, the magnetization increases progressively and reaches a value of 1.98 $N\beta$ at 7.03 T. The value corresponds to the theoretical value of ca. 2 $N\beta$ expected for an $S = 1$ ground state (Figure 6). Apparently, the identity and the conformation of the coordinated ligands play an important role in governing the $Cu_2O_2$ ring toward a puckered or a planar structure, and in turn affect the magnetic properties.[19,20]

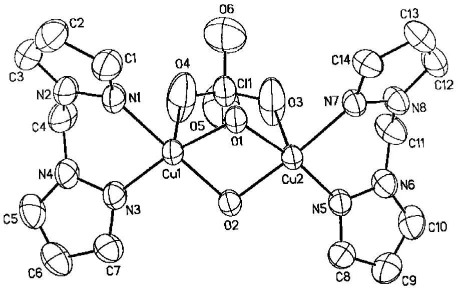


**Figure 4.** ORTEP plot of **5**. Discrete $ClO_4^-$ and $CH_3CN$ are omitted for clarity. Selected distances (Å) and angles (deg): Cu1−O1 1.949(2), Cu1−O2 1.920(2), Cu1−N1 1.986(3), Cu1−N3 2.001(3), Cu2−O1 1.950(2), Cu2−O2 1.927(2), Cu2−N7 1.990(3), Cu2−N5 1.990(3), Cu1−O4 ($ClO_4^-$) 2.513(2), Cu2−O3 ($ClO_4^-$) 2.672(2); Cu1−O1−Cu2 94.9(1), Cu1−O2−Cu2 96.6(1), O2−Cu1−O1 80.7(1), O2−Cu2−O1 80.5(1), N1−Cu1−N3 89.9(1), N7−Cu2−N5 90.7(1), O1−Cu1−N1 94.9(1), O2−Cu1−N3 93.7(1), O2−Cu2−N5 92.4(1), O1−Cu2−N7 96.5(1).

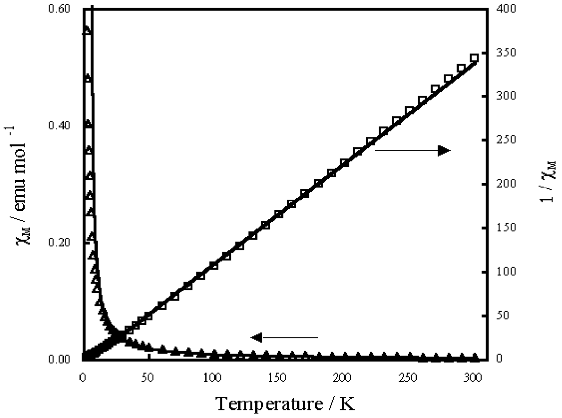
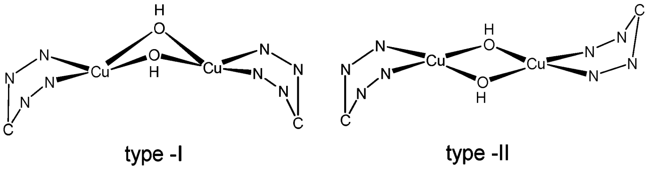


**Figure 5.** $\chi_M$ versus $T$ (K) plot for **5** to the left axis: (△) experimental data; (−) best fit and $1/\chi_M$ versus $T$ (K) plot for **5** to the right axis: (□) experimental data; (−) best fit.

**Scheme 3.** Two Possible Conformations of the Bis(*μ*-hydroxo)copper(II) Complex



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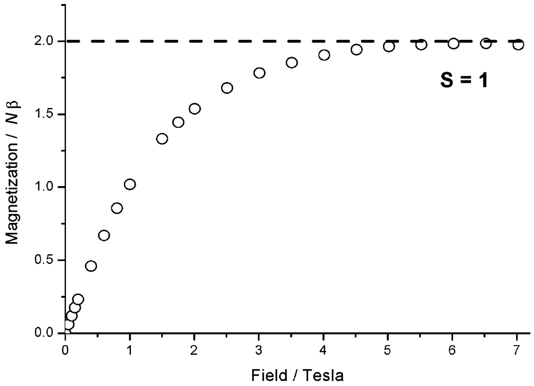

**Figure 6.** Field dependence of magnetization **M**/$N\beta$ at 2 K for **5**.

In conclusion, we present the first example of a 2:1 cocrystal of discrete $Cu^I$/$Cu^{II}$ complexes. The cocrystallization may be the result of the coexistence of the $Cu^I$ complex **1** and the $Cu^{II}$ complex **4** in $CH_3CN$ solution. While the tetracoordinate complex **1** is stable enough to cocrystallize with **4** in air, the Y-shaped complex **3** is readily oxidized by dioxygen to yield the end product **5** at room temperature. Studies on puckered bis($\mu$-hydroxo)dicopper(II) complexes by varying the bridging anions are currently in progress.

**Acknowledgment.** Financial support of the National Science Council of the Republic of China is highly appreciated. We thank Mr. C.-M. Wang for dealing with the magnetic data. Our gratitude also goes to the Academic Paper Edition Clinic, National Taiwan Normal University.

**Supporting Information Available:** X-ray crystallographic data in CIF format for cocrystal {$[Cu^I(H_2CPz_2)(MeCN)_2](ClO_4)$ and $Cu^{II}(H_2CPz_2)_2(ClO_4)_2$}, compounds $[Cu^I(H_2CPz_2)_2](ClO_4)$ and $[Cu_2(H_2CPz_2)_2(\mu\text{-}OH)_2(ClO_4)](ClO_4)(CH_3CN)_{0.5}$. This material is available free of charge via the Internet at http://pubs.asc.org.

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