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Chemical Rearrangement under Hydrothermal Conditions: Formation of Polymeric Chains $(CuX)_2$(dpiz) and $(CuX)_3$(dpiz) (X = Cl, Br; dpiz = Dipyrido[1,2-*a*:2′,3′-*d*]imidazole) and Crystal Structures of $_{\infty}^{1}[(CuCl)_2(C_{10}H_7N_3)]$ and $_{\infty}^{1}[(CuBr)_3(C_{10}H_7N_3)]$

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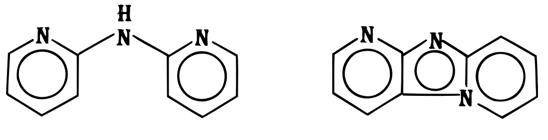
There is much interest being currently paid to the incorporation of metal ions into organic polymers and to the design of coordination frameworks with specific geometrical arrangements and specified properties.[1−6] The preparations of these coordination compounds are, however, limited largely to nonaqueous solution methods. Although the hydrothermal method[7] has been widely applied in the synthesis and crystal growth of many inorganic compounds, use of this technique for the metal−organic systems is limited.[5a,b,8] To explore the applicability of hydrothermal routes toward the synthesis of coordination frameworks, we have recently investigated several group 11−12 metal systems.[9] Our interest in 2,2′-dipyridylamine (dpa) metal complexes is mainly due to their excellent redox catalytic abilities.[10] In this Communication, we report the synthesis of novel one-dimensional polymeric compounds $(CuX)_2$(dpiz) and $(CuX)_3$(dpiz), the chemical rearrangement products via hydrothermal reactions, and the crystal structures of $_{\infty}^{1}[(CuCl)_2(C_{10}H_7N_3)]$ (**I**) and $_{\infty}^{1}[(CuBr)_3(C_{10}H_7N_3)]$ (**II**).

Chart 1



2,2′-dipyridylamine dipyrido[1,2-a:2′,3′-d]imidazole

Reactions of $CuCl_2{\cdot}2H_2O$(0.1705 g), dpa (0.1712 g), and H_2O (5 mL) in the mole ratio 1:1:278 and of $CuBr_2$ (0.2234 g), dpa (0.0856 g), and H_2O (6 mL) in the mole ratio 2:1:334 in 23 mL acid digestion bombs at 170 °C afforded orange crystals of $_{\infty}^{1}[(CuCl)_2(C_{10}H_7N_3)]$ (**I**) and $_{\infty}^{1}[(CuBr)_3(C_{10}H_7N_3)]$ (**II**), respectively ($C_{10}H_7N_3$ = dpiz = dipyrido[1,2-a:2′,3′-d]imidazole). Both dpa and dpiz are shown in Chart 1. Similar reactions also produced $(CuBr)_2$(dpiz) and $(CuCl)_3$(dpiz), whose structures were identified by powder X-ray diffraction analysis and are isotypic to **I** and **II**, respectively. Subsequent reactions using a $CuCl_2$:dpa:H_2O ratio of 2:1:278 gave a higher yield of **I** (ca. 70%), in accordance with the overall reaction for the formation of this compound: $2CuCl_2 + \text{dpa} \rightarrow (CuCl)_2(\text{dpiz}) + 2HCl$. This was also supported by the pH value of the solution, which changed from ∼4 to ∼1 during the reaction. Using CuX_2:CuX:dpa:H_2O = 2:1:1:334 (X = Cl, Br) also gave higher yields for compounds $[(CuX)_3(C_{10}H_7N_3)]$ (ca. 60% for X = Cl and 70% for X = Br). The balanced equations may be written as $2CuX_2 + CuX + \text{dpa} \rightarrow (CuX)_2(\text{dpiz}) + 2HX$.

The single-crystal X-ray analysis on **I** and **II** revealed that dpa underwent a chemical rearrangement during the hydrothermal self-assembly process in forming copper dipyrido[1,2-*a*:2′,3′-*d*]imidazole halide polymers. The molecular dpiz can be prepared by photolysis of [chloro(hetero)arylamino]pyridine.[11] The crystal structures of **I** and **II** have a common motif, displayed in Figure 1.[12] There are two crystallographically independent copper sites in this common motif. Cu(1), the Cu atom in the tetrahedral site, is coordinated to three halide ions X^- (X = Cl, Br) and the N atom in the five-membered ring of the dpiz molecule. Cu(2), the Cu atom with a slightly distorted triangular planar geometry,

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(1) See, for example: (a) Mukherjee, A.; Biswas, M. *J. Appl. Polym. Sci*. **1993**, *50*, 1485. (b) Gatteschi, D. *Adv. Mater*. **1994**, *6*, 635. (c) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 385. (d) Miller, J. S.; Epstein, A. J. *Adv. Chem. Ser.* **1995**, *245*, 161. (e) Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc*. **1996**, *118*, 1803.

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(12) Crystal data for $[(CuCl)_2(C_{10}H_7N_3)]$ (**I**): orthorhombic, $Pna2_1$ (No. 33), $a = 30.485(6)$ Å, $b = 9.071(2)$ Å, $c = 3.838(8)$ Å, $V = 1061.3(4)$ Å^3, $Z = 4$, $F(000) = 720$, $D_{calc} = 2.298$ g/cm^3. Crystal data for $[(CuBr)_3(C_{10}H_7N_3)]$ (**II**): monoclinic, $P2_1/c$ (No. 14), $a = 16.883(3)$ Å, $b = 4.052(1)$ Å, $c = 20.481(4)$ Å, $\beta = 108.84(3)^{\circ}$, $V = 1326.0(5)$ Å^3, $Z = 4$, $D_{calc} = 3.003$ g/cm^3. Data for both **I** and **II** were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) with the ω-scan method within the limits $5° \le 2\theta \le 50°$ (**I**) and $7° \le 2\theta \le 50°$ (**II**). Raw data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied to all data. The structures were solved by direct methods with the SHELX-97 program[21] (Unix version). The non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The final full-matrix least-squares refinement on F^2 converged with R1 = 0.0357, wR2 = 0.0520 for 857 reflections ($I > 4\sigma$) for **I** and R1 = 0.0861, wR2 = 0.1347 for 1179 reflections ($I > 4\sigma$) for **II**. All structure plots were produced with ORTEP and SCHAKAL 92 software.[22]

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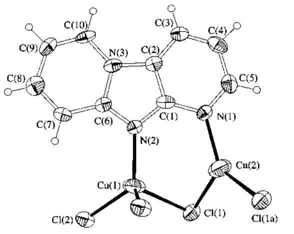

Figure 1. ORTEP representation of the basic and common structural motif in **I** and **II** with labeling schemes (50% probability ellipsoids).

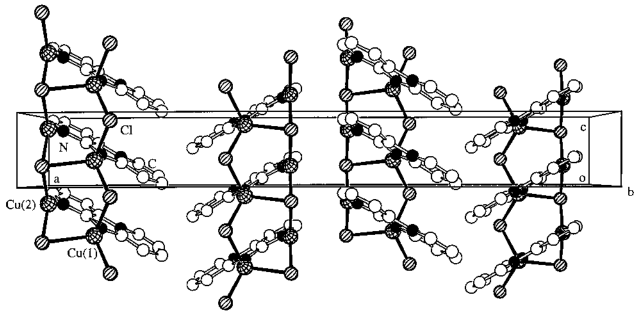

Figure 2. Perspective view of the one-dimensional chain structure of $^{1}_{\infty}[(\mathrm{CuCl})_2(\mathrm{C}_{10}\mathrm{H}_7\mathrm{N}_3)]$ (**I**) along the *b*-axis.

is coordinated to two X^- and the N in the six-membered ring of the dpiz molecule. In compound **I**, these Cu atoms share corners via μ_2-Cl and μ_3-Cl to form an extended one-dimensional chain along the *c*-axis, as shown in Figure 2. The Cu(1)−Cl distances, 2.291(2)-2.629(2) Å, and the average Cu(2)−Cl distance, 2.314(2) Å, are comparable with those found in [CuCl(bpy)] (2.415(6)−2.475(6) Å).[5c] The Cu(2)−N distance, 1.969(5) Å, is slightly shorter than the Cu(1)−N distance, 2.003(5) Å. Both are comparable with those found in bis(dipyridylamine) copper(I) complex (2.003(2) to 2.022(2) Å)[13] and Cu(dpa)(CO)Cl (2.027(3)−2.035(3) Å).[14] The tetrahedrally coordinated copper is quite distorted, with Cl−Cu−Cl angles ranging from 99.88(7)° to 109.91(7)° and Cl−Cu−N angles of 105.5(2)° and 121.292°. The Cl−Cu−Cl and Cl−Cu−N angles for the triangular copper are 112.1(1)° and 121.1(1)°, 125.9(2)°, respectively.

The crystal structure of **II** is closely related to **I** (see Figure 3). It is constructed by inserting an infinite $\mathrm{Cu(3)}_2\mathrm{Br}_2$ double chain between every pair of $(\mathrm{CuBr})_2$(dpiz) chains similar to those shown in **I**, where Cu(3) represents the third independent copper atom in **II**. The three chains connect themselves via Cu(3)−(μ_2-Br) bonds, which gives rise to a stable tetrahedral d^{10} configuration for Cu(3). The resultant structure is a one-dimensional ribbonlike polymer. The Cu(1)−N distance is 2.004 (2) Å, very similar to that found in **I** (2.003(5) Å). The Cu(2)−N distance is 1.921(1) Å, slightly shorter than that in **I** (1.969(5) Å). The tetrahedrally coordinated Cu(1) atom has Br−Cu−Br angles ranging from 95.0(1)° to 111.0(1)° and Br−Cu−N angles of 116.7(8)° and 118.8(5)°. The Br−Cu(2)−Br angle is 113.9(1)°, and the Br−Cu−N angles are 120.9(4)° and 125.1(4)°, respectively, comparing well with the corresponding ones found in **I**. Relatively short Cu...Cu contacts are found in both **I** and **II**. The Cu(1)...Cu(2) distances are 2.937(1) and 2.827(4) Å in **I** and **II**, respectively. There is also a Cu(3)...Cu(3) contact of 2.906(4) Å in **II**.

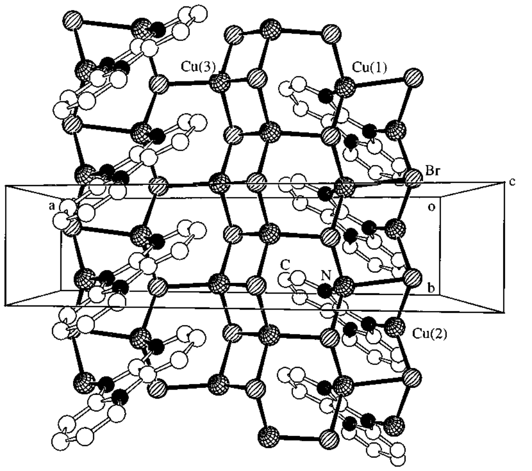

Figure 3. Perspective view of the one-dimensional ribbonlike structure of $^{1}_{\infty}[(\mathrm{CuBr})_3(\mathrm{C}_{10}\mathrm{H}_7\mathrm{N}_3)]$ (**II**) along the *c*-axis.

Thermal analysis[15] was performed on ground crystals of **I**. The measurement was carried out at 30−500 °C. The weight loss curve indicated that **I** was stable up to ~350 °C and began to decompose at higher temperatures to give an amorphous residue.

Both **I** and **II** were constructed via a self-assembly process under mild hydrothermal conditions. The molecular building block $(\mathrm{CuX})_2(\mathrm{C}_{10}\mathrm{H}_7\mathrm{N}_3)$ was formed through a redox reaction [in which Cu(II) was reduced to Cu(I)] involving oxidation and rearrangement of dpa to dpiz. The resultant compounds were stabilized upon such a ligand rearrangement. In the case of **I**, the one-dimensional $^{1}_{\infty}[(\mathrm{CuCl})_2(\mathrm{C}_{10}\mathrm{H}_7\mathrm{N}_3)]$ chains were assembled by connecting the $(\mathrm{CuCl})_2$(dpiz) building blocks via bridging chlorines (μ_2-Cl and μ_3-Cl). In formation of **II**, more copper bromide was provided. The additional copper and bromine simply incorporated into the final product as a $^{1}_{\infty}[\mathrm{Cu(3)}_2\mathrm{Br}_2]$ double chain whereas the polymeric motif $^{1}_{\infty}[(\mathrm{CuBr})_2(\mathrm{C}_{10}\mathrm{H}_7\mathrm{N}_3)]$ remains intact.

Although a large number of copper complexes containing 2,2′-dipyridylamine have been obtained from non-hydrothermal reactions,[1a,13,14,16−19] no chemical rearrangement of dpa has been observed previously. Nonaqueous solution syntheses using the same reagents have produced many molecular compounds in which dpa simply binds to the metal centers without undergoing rearrangement. Under normal, ambient conditions, Cu^+ ions are known to disproportionate in water to produce Cu^{2+} and Cu;[20] however, the Cu(I) state is stabilized under hydrothermal conditions. Such a stabilization may, at least in part, promote the redox and ligand rearrangement process.

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Supporting Information Available: Tables of crystal structural data, atomic coordinates, and anisotropic and isotropic parameters of all non-hydrogen atoms (11 pages). Ordering information is given on any current masthead page.

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