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New Coordination Motifs of Melamine Directed by N–H···X (X = Cl or Br) Hydrogen Bonds

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Unusual μ_2- and μ_3-coordination modes of melamine are found in two organic–inorganic hybrid copper halides, $[Cu_2Br_2(MA)]_n$ (**1**) and $[Cu_3Cl_3(MA)]_n$ (**2**) (MA = melamine), in which the MA ligand affords two N-heterocycle N atoms to link $(Cu_2Br_2)_\infty$ stairs and serves as a novel μ_3 bridge to give a 3D framework, respectively.

Melamine has been an important industrial raw material since 1834, when it was first obtained by Liebig. Recently, its application in the construction of supramolecular networks has attracted more and more attention because it has three ring N atoms and three amidos, enabling it to be the hydrogen-bond donor and acceptor to form very extensive hydrogen bonds.[1] Moreover, its three ring N atoms can also be potential coordinate points to construct metal–organic frameworks (MOFs). As far as we are aware, the coordination chemistry of melamine remains rarely explored and only several metal complexes with melamine have been reported since 1999,[2] whose structures are very simple except the only 1D complex.[3] In these complexes, the melamine molecule mostly affords only one ring N as the coordinating atom, and this may be due to the following restrictive factors: (i) the trend to form hydrogen bonds between melamine molecules; (ii) the space block between adjacent amine groups; (iii) the strong rigidity of the N-heterocycle. Here we report two types of unusual coordination modes of melamine that are directed by N–H···X (X = Cl or Br) hydrogen bonds. The melamine (MA) ligand adopts two N-heterocycle N atoms to link $(Cu_2Br_2)_\infty$ stairs in $[Cu_2Br_2(MA)]_n$ (**1**) and acts as a μ_3 bridge to give a 3D framework $[Cu_3Cl_3(MA)]_n$ (**2**). To our knowledge, such a μ_3-bridging mode, which overcomes the forenamed restrictive factors, has never been reported before, giving a new motif of the coordination chemistry of melamine.

The reaction of CuBr with melamine and 5-aminoisophthalate in a molar ratio of 2:1:1 under hydrothermal conditions at 160 °C for 60 h produced colorless crystals of **1** in 60% yield. When $CuCl_2 \cdot 2H_2O$ was used instead of CuBr, compound **2** was obtained.[4] Compounds **1** and **2** are completely different from each other. The diversity of the van der Waals radii between Br and Cl is maybe the main reason,[5] and the formation of different CuX (X = Cl^- or Br^-) skeletons also gives rise to different frameworks. Both of them are characterized by elemental and single-crystal X-ray diffraction (XRD) analysis.[6]

The structure of **1** consists of neutral coordination layers of $(Cu_2Br_2)_\infty$ stairs linked by MA ligands (Figure 1). All Cu^I atoms in the $(Cu_2Br_2)_\infty$ stairs are 3-fold-coordinated to Br, and all Br atoms also bridge to three Cu centers, giving Cu–

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(4) Synthesis: A mixture of MA (0.124 g, 1 mmol), aluminum isopropoxide (0.187 g, 1 mmol), CuBr (0.445 g, 2 mmol), and H_2O (15 mL) was heated in a stainless steel reactor with a Teflon liner at 160 °C for 60 h. After cooling within 60 h, colorless crystals of **1** were obtained in about 60% yield (based on Cu). Anal. Calcd for $C_3N_6H_6Br_2Cu_2$: C, 8.72; H, 1.47; N, 20.35. Found: C, 8.68; H, 1.44; N, 20.44. IR (solid KBr pellet, ν/cm^{-1}) for complex **1**: 3434 (vs), 3335 (vs), 3176 (s), 1660 (m), 1619 (s), 1542 (w), 1462 (m), 1399 (s), 1152 (w), 790 (w), 612 (w). Compound **2** was obtained similarly to **1** except that CuBr was replaced by $CuCl_2 \cdot 2H_2O$ (0.343 g, 2 mmol). White crystals of **2** were obtained in about 50% yield (based on Cu). Anal. Calcd for $C_3N_6H_6Cl_3Cu_3$: C, 8.51; H, 1.43; N, 19.87. Found: C, 8.47; H, 1.41; N, 19.95. IR (solid KBr pellet, ν/cm^{-1}) for complex **1**: 3434 (m), 3346 (m), 3137 (s), 1663 (m), 1621 (m), 1399 (vs), 1158 (w), 779 (w), 634 (w), 612 (w).

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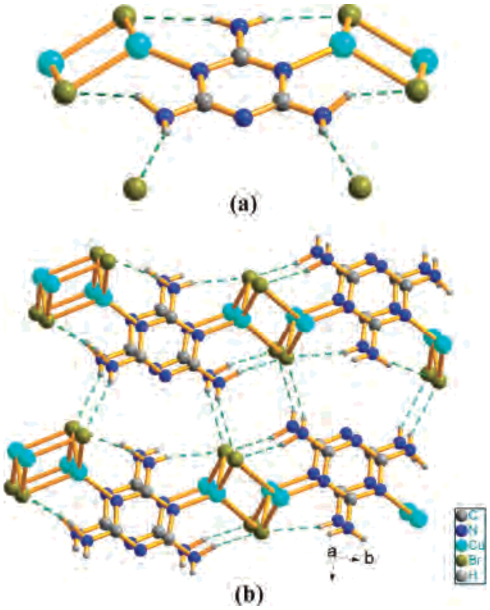

Figure 1. (a) Coordination mode and hydrogen-bonding interactions of melamine. Hydrogen bonds are shown as dashed lines. (b) Packing structure of the layers of **1** showing the intra- and interlayer hydrogen bonds (dashed lines).

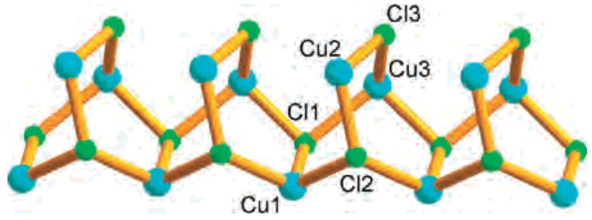

Figure 2. $(Cu_3Cl_3)_\infty$ stairs presenting a novel skeleton motif for copper(I) halides.

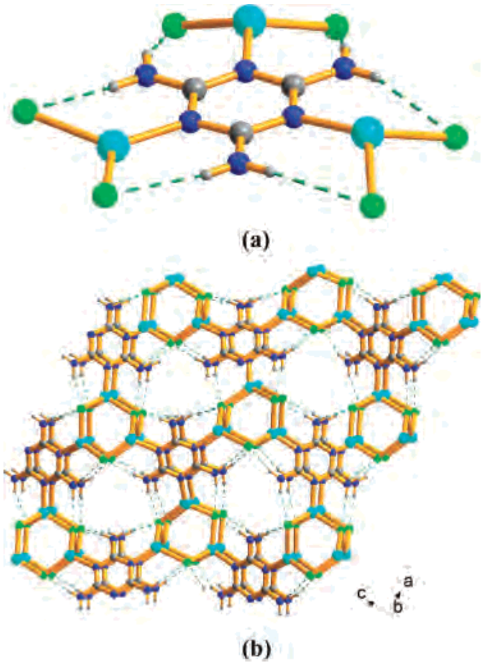

Figure 3. (a) Coordination mode and hydrogen-bonding interactions of melamine. Hydrogen bonds are shown as dashed lines. (b) 3D framework of **2** showing the N−H⋯Cl hydrogen-bonding interactions (dashed lines).

Br distances varying from 2.520(9) to 2.587(2) Å. The shortest Cu⋯Cu distance is 2.994(6) Å, which is greater than the sum of the van der Waals radii (2.80 Å). Each MA ligand affords two N-heterocycle N atoms as the fourth coordination of Cu, with a Cu−N distance of 2.004(3) Å. In each layer, the melamine molecules in a row are parallel to each other, with the centroid-to-centroid distance being about 3.872 Å. It is interesting to note that there are abundant N−H⋯Br hydrogen bonds between amine groups of melamine and Br atoms (H⋯Br = 2.79−2.95 Å; ∠N−H⋯Br = 135.6−165.4°). Hydrogen-bonding interactions are found not only within the layers but also between the layers, causing the compound to have remarkable thermal stability. Although the μ_2-bridging mode of melamine has been reported in complex $[Ag(NO_3)(MA)]_3$,[3] compound **1** is the first species that possesses an extended 2D structure via μ_2-melamine.

The structure of **2** possesses a 3D architecture that contains μ_3-bridging melamine and $(Cu_3Cl_3)_\infty$ stairs. It is worth noting here that the $(Cu_3Cl_3)_\infty$ stairs present a novel skeleton motif for copper(I) halides.[7] As shown in Figure 2, the μ_3-Cl atoms connect four-coordinate Cu centers to form stairs, and the bonds of the μ_2-Cl atoms and three-coordinate Cu centers that locate at the same side act as "sticks" to reinforce the stairs. Such an unusual skeleton motif can also be described as parallel Cu_3Cl_3 hexagons arranged along the *b* axis, with each hexagon being connected to its two neighbors through Cu−Cl contacts. Different from the structure of **1**, there are two kinds of coordination patterns of Cu cations in **2**. Cu2 is located at the core of a distorted triangle and coordinated by two Cl anions and one N atom from the melamine molecule, while Cu1 and Cu3 are coordinated by three Cl anions and one N atom with distorted tetrahedral geometry.

The most interesting feature of **2** is that each MA ligand has overcome different kinds of forenamed restrictive factors and adopted all of the three aromatic ring N atoms to connect three parallel $(Cu_3Cl_3)_\infty$ stairs through Cu−N bonds (Figure 3). The Cu−N distances are 1.988(4), 2.029(5), and 2.035(4) Å. At the same time, the amine groups of the MA ligand form abundant N−H⋯Cl hydrogen bonds with the $(Cu_3Cl_3)_\infty$ stairs (H⋯Cl = 2.47−2.60 Å; ∠N−H⋯Cl = 158.00−170.80°), which further stabilize the 3D framework.

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(6) (a) Crystal data for **1**: $C_3N_6H_6Br_2Cu_2$, fw = 413.04, monoclinic, *P*2(1)/*m*; $a = 3.872(3)$ Å, $b = 16.647(10)$ Å, $c = 7.377(5)$ Å, $\beta = 99.074(8)$°; $V = 469.6(5)$ Å^3, $Z = 2$, $D_c = 2.921$ g cm^{-3}, $F(000) = 388$, crystal size = 0.21 × 0.08 × 0.04 mm. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The final R1 = 0.0284, wR2 = 0.0661, and $S = 1.057$ for 963 observed reflections with $I > 2.0\sigma(I)$. (b) Crystal data for **2**: $C_3N_6H_6Cl_3Cu_3$, fw = 423.14, orthorhombic, *Pna*2(1); $a = 17.8255(18)$ Å, $b = 3.6689(4)$ Å, $c = 15.9805(18)$ Å; $V = 1045.12(19)$ Å^3, $Z = 4$, $D_c = 2.689$ g cm^{-3}, $F(000) = 816$, crystal size = 0.15 × 0.07 × 0.05 mm. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The final R1 = 0.0285, wR2 = 0.0544, and $S = 1.022$ for 1860 observed reflections with $I > 2.0\sigma(I)$.

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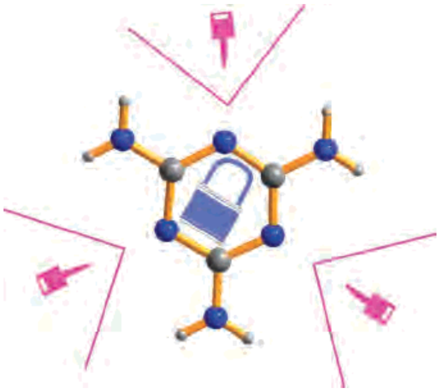

Figure 4. Schematic representation of the relationship of a lock and key between melamine and CuX.

The adjacent N-heterocycles are almost parallel with a centroid-to-centroid distance of 3.668(9) Å, indicating the existence of $\pi\cdots\pi$ stacking interactions. To the best of our knowledge, compound **2** presents the first 3D metal−melamine complex containing novel μ_3-bridging melamine.

According to the above structural descriptions, we notice that the N−H···X (X = Cl or Br) interactions play important roles in the formation of the coordination fashions of the MA ligand. The first unusual aspect is that no hydrogen-bonding interactions are found between MA ligands in the two complexes. The second unusual aspect is just like the relationship of a lock and key: the planar melamine molecule looks like a lock with three "V"-type windows, into which can be inserted arrowlike CuX_2 groups (Figure 4). The N−H···X hydrogen bonds just ensure the parallel embedding (Figures 1a and 3a).

Compounds **1** and **2** were analyzed by thermogravimetric analysis (TGA) under N_2 with a heating rate of 15 °C min^{-1}. Both of the two structures remain stable up to ~350 °C, comparable with ~200 °C of the most previously reported organic−inorganic hybrid copper halides with nitrogenous donor ligands.[8] Powder XRD patterns confirm that polycrystalline **1** and **2** are stable upon heating at 350 °C for 30 min. For both **1** and **2**, the powder XRD patterns after treatment at 350 °C are similar to the calculational patterns and the patterns at room temperature, which indicates that the two frameworks do not collapse (Figures S3 and S4 in the Supporting Information). This is in agreement with the results of TGA measurements.

The photoluminescent properties of compounds **1** and **2** in the solid state at room temperature have also been studied. Upon excitation at 290 and 355 nm, **1** and **2** exhibit strong photoluminescence with emission maxima at 529 and 485 nm, respectively (Figure S5 in the Supporting Information). The emission spectra of **1** is similar to the reported complexes [CuBr(pyridine)] (λ_{em} = 509 nm) and [Cu_2Br_2(bpe)$_2$] (λ_{em} = 529 nm).[9] Therefore, the emission of **1** can be similarly assigned to both cluster-centered transition and halide (X)-to-ligand charge transfer (XLCT). The emission band of **2** in the blue-green region is similar to the typical isolated Cu^I emission in inorganic solids,[10] which may be due to the relatively long Cu···Cu distance [2.994(6) Å] in **2**. So, the possible assignment of this transition is considered as a Cu^I d−s transition and XLCT.

In summary, we have presented here two unusual coordination modes of melamine in two organic−inorganic hybrid copper halides, $[Cu_2Br_2(MA)]_n$ (**1**) and $[Cu_3Cl_3(MA)]_n$ (**2**). The important N−H···X (X = Cl or Br) hydrogen bonds directed the μ_2- and μ_3-bridging coordination of melamine. The strong coordination ability of melamine also makes the frameworks highly thermally stable. Our research results here reveal a brand new future for the coordination chemistry of melamine.

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Supporting Information Available: X-ray crystallographic files in CIF format and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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