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[9] The plate was prepared with a solution of *rac*-**4a** at 4.7 M in *rac*-1,2-hexanediol in wells A1-H1; 4.3 M in A2; 3.7 M in B2; 3.3 M in C2; 2.7 M in D2; 2.3 M in E2; 1.7 M in F2; 1.3 M in G2, and 0.7 M in H2 and with (*R*,*R*)-**5** at 5.8 μM in A2-H2 and A1; 4.9 μM in B1; 4.1 μM in C1; 3.3 μM in D1; 2.5 μM in E1; 1.7 μM in F1; 0.8 μM in G1; and 0 μM in B1. Reaction was initiated by the addition of water.

[Cu(2-pyrazinecarboxylato)$_2$HgI$_2$] · HgI$_2$: An Open Noninterpenetrating Cu^{II}–Hg^{II} Mixed-Metal Cuboidal Framework Encapsulating Nearly Linear HgI$_2$ Guest Molecules[**]

Yu-Bin Dong, Mark D. Smith, and
Hans-Conrad zur Loye[*]

Self-assembly of organic ligands and inorganic metal ions is one of the most efficient and widely utilized approaches for the construction of organic/inorganic coordination polymers. During the past decades unimetallic coordination polymers, which contain only one kind of metal center, have been the predominant synthetic target in this rapidly expanding area of research.[1] To date, numerous unimetallic coordination polymers with impressive structural motifs have been successfully synthesized. In contrast, the chemistry of bimetallic coordination polymers has received considerably less attention, although bimetallic extended structures based on inorganic counterions such as cyanide (Prussian blue phases) and thiocyanate have been reported.[2]

Bimetallic coordination polymers have the potential to exhibit interesting physical properties such as electrical conductivity or magnetic ordering that result from interactions between two distinct metal centers connected by a suitable linker. For example, complex magnetic behavior in Cu^{II}–Mn^{II} mixed-metal coordination polymers was reported by Kahn et al.[3] Likewise, a series of mixed-metal molecular magnets [Cp$_2^*$Z^{III}][M^{II}M^{III}(ox)$_3$] (Z^{III} = Co, Fe; M^{III} = Cr, Fe; M^{II} = Mn, Fe, Co, Cu, Zn; Cp* = η^5-C$_5$Me$_5$) based on bridging oxalato (ox) ligands was reported by Coronado et al.[4] Of course, novel physical properties are not the only reason for pursuing the synthesis of bimetallic coordination polymers; propagation of the structural preferences (influenced by oxidation state and coordination predisposition) of two different metal centers in mixed-metal systems should result in a broader palette of polymer structural motifs than is achievable in unimetallic systems, and this may in turn lead to better understanding of composition–structure relationships.

We have initiated a synthetic program for the preparation of mixed-metal coordination polymers, in which the concepts of self-assembly and metal-containing building block ligands were combined to yield a series of novel bimetallic framework structures. These materials are based on [M(2-pyrazinecarboxylato)$_2$] · nH$_2$O and [M(methylpyrazine-5-carboxylato)$_2$] · nH$_2$O (M = Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}; n = 0, 2, 3) and were synthesized by treating these metal-containing ligands with a variety of metal salts.[5] Here we report on the first hydrothermally synthesized Cu^{II}–Hg^{II} mixed-metal framework material, namely, [Cu(2-pyrazinecarboxylato)$_2$HgI$_2$] · HgI$_2$ (**1**), which is constructed from [Cu(2-pyrazinecarboxylato)$_2$] building blocks and HgI$_2$ linkers. This neutral, cuboidal framework structure possesses regular square channels (dimensions 7.24 × 7.24 Å)[6] in which, surprisingly, uncoordinated, nearly linear HgI$_2$ molecules are encapsulated. While it is quite common to find solvated species in the void spaces of coordination polymers, we believe the presence of a free inorganic salt to be quite novel.

Reaction of [Cu(2-pyrazinecarboxylato)$_2$] (**2**) or [Cu(2-pyrazinecarboxylato)$_2$] · 2H$_2$O (**3**)[5b, 7] with HgI$_2$ (1:2 molar ratio) in water under hydrothermal conditions (130 °C, 24 h), afforded the title compound as blue-green orthorhombic plate crystals in quantitative yield. Single-crystal structure analysis[8] revealed a three-dimensional extended cuboidal framework based on [Cu(2-pyrazinecarboxylato)$_2$] and HgI$_2$ building blocks. Each Cu^{II} center has a slightly distorted {CuN$_4$O$_2$} octahedral coordination sphere, with two nitrogen donors and two oxygen donors of two 2-pyrazinecarboxylato ligands in the equatorial plane. The coordination sphere is completed by the terminal nitrogen donors of two neighboring [Cu(2-pyrazinecarboxylato)$_2$] building blocks in the axial positions. The framework Hg^{II} centers reside in a distorted {HgI$_2$O$_2$} tetrahedral coordination environment that is composed of two iodide ions (Hg–I 2.603(2), 2.633(2) Å; I-Hg-I 158.79(6)°) and two oxygen atoms of two adjacent [Cu(2-pyrazinecarboxylato)$_2$] building blocks (Hg–O 2.532(9) Å). The two copper-bound carboxylate oxygen atoms interact very weakly with the Hg^{II} centers (Hg $\cdots$ O 3.119(4) Å). The Cu^{II} and Hg^{II} centers are linked by the carboxylate moiety of 2-pyrazinecarboxylate in a bis-monodentate fashion to form linear [Cu(2-pyrazinecarboxylato)$_2$HgI$_2$] mixed-metal chains (Figure 1). Identical chains, rotated along the chain direction by 90°, are interconnected through Cu^{II} nodes into a three-dimensional cuboidal network. As shown in Figure 2, each cuboidal box consists of eight Cu^{II} atoms at the corners, which are connected by four long carboxylate-Hg-carboxylate (Cu $\cdots$ Cu 9.99(4) Å) and eight shorter pyrazine (Cu $\cdots$ Cu 7.24(4) Å) linkers that make up the 12 edges. This cuboidal Cu^{II}–Hg^{II} structural motif is clearly different from those of

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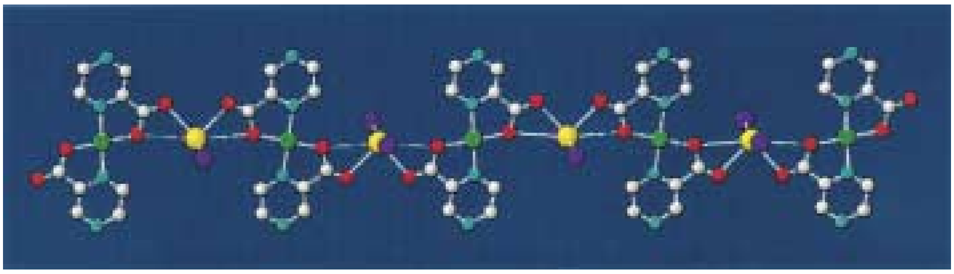

Figure 1. The [Cu(2-pyrazinecarboxylato)$_2$HgI$_2$] mixed-metal chain in **1**. Yellow spheres, Hg; purple, I; green, Cu; blue, N; red, O; white, C. Hydrogen atoms are omitted for clarity.

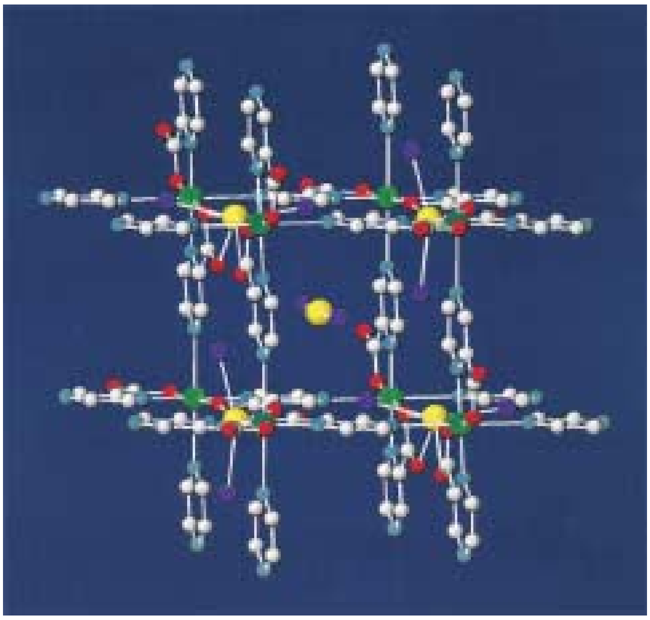

Figure 2. A single cuboid box, showing the framework around one encapsulated HgI$_2$ molecule. For color code, see Figure 1. Hydrogen atoms are omitted for clarity.

ReO$_3$, α-polonium, and Prussian blue and analogous cyanometalate phases, all of which exhibit cubic frameworks (Figure 3).[9] The cuboid form is one of the fundamental structural types, and **1** is the first example of a neutral organic/inorganic mixed-metal extended cuboidal framework generated from a metal/organic ligand and a metal salt.

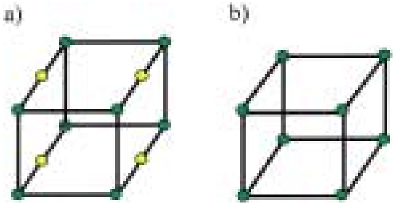

Figure 3. Comparison of the novel cuboidal unit in **1** (a) with a cubic unit (b).

Figure 4 shows a view of the full three-dimensional structure along the crystallographic *b* axis (along the chain direction). All [Cu(2-pyrazinecarboxylato)$_2$] units in the two equivalent chains are strictly coplanar and, moreover, perpendicular relative to each other. This is distinctly different from the orientations of the pyrazine ligands in [Ag(pyrazine)$_3$](SbF$_6$), which forms a cationic cubic framework in which the pyrazine ligands are alternately rotated by different angles in opposite directions.[10]

When viewed down the crystallographic *b* axis, very regular square channels (crystallographic dimensions, 7.24 × 7.24 Å) are evident in **1** (Figure 4). Remarkably, these channels encapsulate neutral HgI$_2$ guest molecules which are nearly linear (I-Hg-I 175.87(9)°), with equal Hg–I distances of 2.577(2) Å, slightly shorter than the coordinated (framework) Hg–I bonds. Interestingly, this distance is the same as the Hg–I bond length in HgI$_2$ vapor (2.57(4) Å). Both framework and guest Hg–I bonds are significantly shorter than those in the low-temperature (red) form of solid HgI$_2$ (2.78 Å), in which mercury is tetrahedrally coordinated. The HgI$_2$ molecules in the intrachannel [$\cdots$I-Hg-I$\cdots$I-Hg-I$\cdots$] columns are quite distant from one another, with intermolecular I$\cdots$I distances of about 14.2 Å, yet no other guest molecules are located in the space between these HgI$_2$ molecules. The mercury atoms of the HgI$_2$ guests are also weakly coordinated to four iodide ions in the framework, with I$\cdots$Hg distances of 3.68(4), and 3.761(4) Å, which are slightly shorter than the sum of the van der Waals radii of Hg and I.

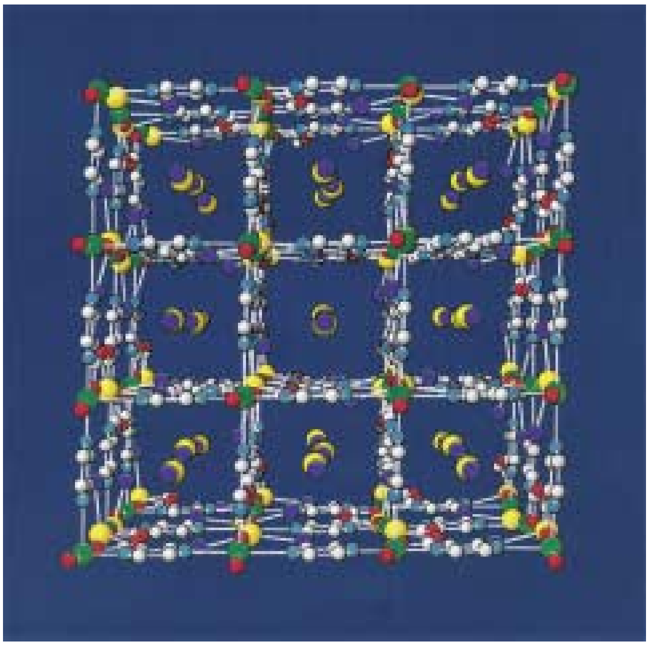

Figure 4. The extended cuboidal framework in **1**, viewed down the crystallographic *b* axis. For color code, see Figure 1. Hydrogen atoms are omitted for clarity.

A remarkable feature of **1** is the inclusion of HgI$_2$ guest molecules instead of the organic ligands, solvent or water molecules, or inorganic counterions commonly observed in coordination polymer voids.[11] In addition, to the best of our knowledge, **1** is the first bimetallic coordination polymer obtained by hydrothermal synthesis,[12] a method which has proven to be expedient for growing crystals of numerous metal/organic compounds.[1a]

All of the free (uncoordinated) donor atoms (two nitrogen and two oxygen donors) in the metal-containing building blocks **2** or **3** are fully utilized in the extended structure of **1** to bind the two kinds of metal ions into a polymeric structure, while retaining the original geometry of the molecular building block. In fact, both **2** and **3** can be regarded as fourfold rigid connectors for incorporation into bimetallic polymeric frameworks. The separations between the two terminal nitrogen atoms in **2** and **3** are 9.48(3) and 9.50(3) Å, respectively,[5a, 7] significantly longer than the N···N distance (7.12(3) Å)[13] in 4,4′-bipyridine but comparable to those of 1,2-bis(4-pyridyl)ethene (9.385(4) Å)[14] and 1,2-bis(4-pyridyl)-ethyne (9.685(4) Å).[15] The free O···O separations in **2** and **3** are 7.86(3) and 7.96(3) Å, respectively, also slightly longer than the N···N distance in 4,4′-bipyridine.

Compound **1** is air-stable and is insoluble in water or common organic solvents. To create an open framework with an accessible void space, we examined the possibility of removing the HgI_2 guest molecules by heating a sample and monitoring the process by thermogravimetric analysis (TGA).[16] Unfortunately, this results in the collapse of the framework structure. The TGA showed that the framework of **1** is stable up to 180 °C, and both HgI_2 moieties per formula unit (cavity and framework) were released in the temperature range 180–261 °C (observed weight loss 75.0%, calculated 74.6%).

This study again demonstrates the utility of a pre-synthesized metal-containing ligand as a precursor for constructing mixed-metal framework structures. We expect this approach to be viable for the construction of many more new and interesting mixed-metal coordination polymers, and studies toward the preparation of new mixed-metal systems containing other transition metals and/or ligands are underway.

Experimental Section

1: Either **2** or **3** (0.12 mmol), HgI_2 (0.24 mmol), and water (4 mL) were placed in an acid digestion bomb. The mixture was heated at 130 °C for 24 h, cooled to 70 °C at 1 °C min^{-1}, and held at this temperature for an additional 7 h, after which the mixture was allowed to cool to room temperature. Blue-green crystals were isolated from the bomb in quantitative yield. IR (KBr pellet): $\tilde{\nu} = 1651$ (s), 1644 (s), 1634 (s), 1614 (s), 1593 (s), 1557 (s), 1538 (s), 1504 (s), 1468 (s), 1416 (s), 1346 (s), 1285 (s), 1181 (s), 1158 (s), 1058 (s), 1047 (s), 862 (s), 792 (s), 738 (s), 718 (s), 667 cm^{-1} (s); elemental analysis calcd for $C_{10}H_6O_4N_4I_4CuHg_2$ (%): C 9.84, H 0.49, N 4.59; found: C 9.88, H 0.50, N 4.45.

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