Syntheses, Crystal Structures and Magnetic Properties of Four Cu^{II}-Hg^{II} Mixed-Metal Halide Oligomers

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Keywords: Copper / Mercury / Magnetic properties / Cluster compounds

Four heteronuclear Cu^{II}–Hg^{II} halides containing 2,2-bipyridine (bipy) ligands have been synthesized and structurally characterised by single-crystal X-ray diffraction studies. The dinuclear complex $[Cu(bipy)_2HgCl_2Br_2]$ (**1**) contains a five-coordinate copper(II) ion and a four-coordinate Hg^{II} ion, in which the two different types of metal ions are bridged by a pair of chloride anions. $[Cu_2(bipy)_4HgBr_4][Hg_2Br_6]$ (**2**) contains a trinuclear $[Cu_2(bipy)_4HgBr_4]^{2+}$ cation in which the two copper(II) ions are bridged by an $[HgBr_4]^{2-}$ tetrahedron via two Cu–Br bonds, and an edge-sharing tetrahedral $[Hg_2Br_6]^{2-}$ anion. The structure of $[Cu_2(bipy)_4Hg_2Br_6]$-$[Hg_4Br_{10}]$ (**3**) features a 1-D chain along the diagonal of the *a* and *c* axes constructed from tetranuclear $[Cu_2(bipy)_4Hg_2Br_6]^{2+}$ cations interconnected by $[Hg_4Br_{10}]^{2-}$ tetramers via elongated Hg–Br contacts (3.185 Å). Within the tetranuclear cationic unit, two $[Cu(bipy)_2]^{2+}$ units are bridged by an edge-sharing dimeric tetrahedral $[Hg_2Br_6]^{2-}$ anion. In the trinuclear complex $[Cu(bipy)_2Hg_2Cl_6]$ (**4**), each $[Hg_2Cl_6]^{2-}$ dimer bridges with a $[Cu(bipy)_2]^{2+}$ ion to form a trinuclear $[Cu(bipy)_2Hg_2Cl_6]$ unit, and each pair of such units is bridged by a pair of elongated Hg–Cl bonds [3.043(5) Å] to form a dimeric unit. The magnetic properties of **1**, **2**, and **4** have also been investigated.

Introduction

For several decades there has been considerable interest in polynuclear transition-metal complexes with linear-chain structures due to their unusual optical, electronic, and magnetic properties.[1] Such compounds are also ideal systems for the study of metal−metal interactions and in the search for molecular metal wires.[2] Low dimensional metal−organic halide networks have received considerable research attention in recent years due to their potential applications as electronic materials and catalysts.[3] Extensive studies on copper complexes are largely driven by their photochemical and photophysical properties. To date, numerous mononuclear metal coordination polymers with interesting structural motifs have been successfully synthesized. In contrast, the chemistry of bimetallic coordination polymers has received considerably less attention. Bimetallic coordination polymers have the potential to exhibit interesting physical properties such as electronic conductivity or magnetic ordering that result from interactions between two distinct metal centers connected by a suitable linker.[4] Homonuclear oligomers and chains of copper or mercury halogen compounds with polyamine ligands have been reported in the literature.[5−7] Their structures can be viewed as being built from polyamine (such as bipy) coordinated copper(II) moieties connected to copper(I) or copper(II) halides. Heteronuclear metal halides can exhibit not only new structural motifs that are unseen in homo-metallic systems, but also new or enhanced physical or chemical properties. However reports on heteronuclear metal halide compounds are relatively rare.[8−10] Several copper−zinc and copper−zirconium chlorides have been reported by the Martin group and[8] a series of nickel organoamine-halocadmates were reported by Zubieta and co-workers.[9] One, two, and three-dimensional mixed metal coordination polymers have been found in the $Cu(prazinecarboxylate)_2/CdCl_2$ system[10] and several Cu−Hg halides have been reported.[11] $[Cu(2\text{-pyrazinecarboxylato})_2HgI_2]\cdot HgI_2$ consists of an open framework constructed from $Cu(2\text{-pyrazinecarboxylato})_2$ and HgI_2 building blocks, the other linear HgI_2 molecule is encapsulated in the cavity of the framework as a guest molecule.[11a] In $[Cu(en)_2][Hg_2Cl_6]$, the $[Cu(en)_2]^{2+}$ cations are bridged by dimeric Hg_2Cl_6 anions into a 1-D chain, whereas in $[Cu(en)_2][Hg_2Br_6]$, the $[Hg_2Br_6]^{2-}$ anions are interconnected through Hg−Br bonds to form an infinite chain and such chains are further bridged by $[Cu(en)_2]^{2+}$ cations into a 2-D layer. $[Cu(en)_2][HgBr_4]$ has a different chain structure in which the $[Cu(en)_2]^{2+}$ moieties are bridged by $[HgBr_4]$ tetrahedra.[11b] In $[Cu(bipy)_3]$-$[Hg_2I_6]$, the anions remain isolated due to the presence of a third chelating bipy ligand at the copper(II) ion.[11c]

We utilized the 2,2′-bipyridine ligand as a template to form the $[Cu(2,2'\text{-pyridine})_2]^{2+}$ cation. Reactions of the latter with Hg^{II} halides under different conditions (such as

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DOI: 10.1002/ejic.200300554

different Cu/Hg ratios and solvents) led to four new $Cu^{II}-Hg^{II}$ mixed-metal oligomers, namely binuclear $[Cu(bipy)_2HgCl_2Br_2]$ (**1**), $[Cu_2(bipy)_4HgBr_4][Hg_2Br_6]$ (**2**) containing a trinuclear $[Cu_2(bipy)_4HgBr_4]^{2+}$ cation and an isolated $[Hg_2Br_6]^{2-}$ anion, $[Cu_2(bipy)_4Hg_2Br_6][Hg_4Br_{10}]$ (**3**) featuring a 1-D chain built from tetranuclear $[Cu_2(bipy)_4Hg_2Br_6]^{2+}$ cations interconnected by $[Hg_4Br_{10}]^{2-}$ tetramers and the trinuclear $[Cu(bipy)_2Hg_2Cl_6]$ (**4**), in which two $[Cu(bipy)_2]^{2+}$ cations are bridged by an $[Hg_4Cl_{12}]^{2-}$ tetramer. Herein we report their syntheses, crystal structures, and characterization.

Results and Discussion

The structures of **1−4** feature linear heteronuclear $Cu^{II}-Hg^{II}$ halogen oligomers in which the two different types of metal ions are bridged by the halide anions.

As shown in Figure 1, the Hg^{II} ion in dinuclear $[Cu(bipy)_2HgCl_2Br_2]$ (**1**) is tetrahedrally coordinated by two chloride anions and two bromide anions, whereas the copper(II) ion is six-coordinate with two bidentate chelating bipy ligands and two chloride anions in a distorted octahedral geometry. The Cu−N distances range from 2.00(1) to 2.08(1) Å. The Hg−Cl, Hg−Br, and Cu−Cl distances are 2.670(3), 2.488(2), and 2.750(4) Å, respectively and these bond lengths are similar to those reported in other copper(II) and Hg^{II} halogen complexes.[5,6,11] Unlike in $[Cu(en)_2]HgBr_4$,[11b] the Cu^{II} and Hg^{II} ions in **1** are bridged by a pair of μ^2-chloride anions to form a dinuclear molecular unit. $[Cu(en)_2]HgBr_4$ has a 1-D chain structure in which the two metal centers are bridged by only one bromide anion.[11b] We suggest that the difference is mainly due to the much larger steric hindrance of the bipy ligand than that of ethylene diamine. The structure of **1** is also significantly different from that of binuclear $[Ni(bipy)_2CdCl_2I_2]$ in that the cadmium(II) ion has a square planar coordination geometry instead of a tetrahedral one for the Hg^{II} ion.[9] The Cu···Hg separation is 3.881(1) Å, indicating that there is no metal−metal bonding between the two metal centers.

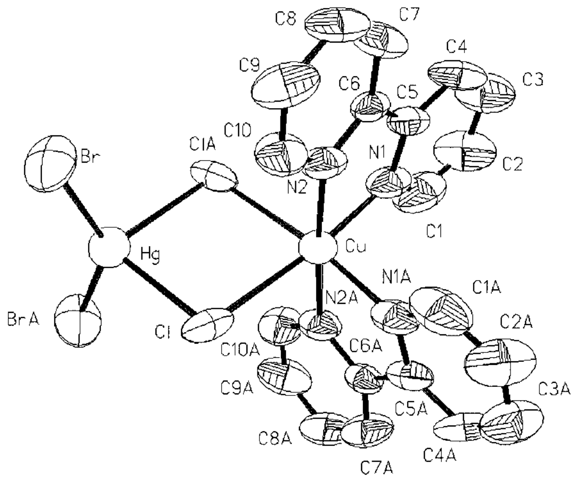

Figure 1. ORTEP representation of the asymmetric unit of $[Cu(bipy)_2HgCl_2Br_2]$ (**1**). Thermal ellipsoids are drawn at the 50% probability level. Symmetry code for the generated atoms: 1 − *x*, *y*, 3/2 − *z*

These dinuclear molecular units in **1** are further interlinked via weak π-π interactions between neighboring pyridine rings to form a 1-D chain along the diagonal of the *a* and *c* axes (Figure 2). The distance between the centers of two such rings is 3.949 Å, and the dihedral angle between the two rings is 4.4°. Similar π-π interactions between pyridine rings have been reported in many phen-containing copper(II) complexes.[12] Such chains are held together via weak van der Waals forces.

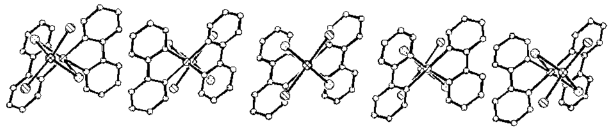

Figure 2. A 1-D chain formed from molecular units of complex **1** via π-π interactions between the pyridine rings

The copper(II) ions in **2**, **3**, and **4** are five-coordinate with two chelating bipy ligands and a halide anion. The coordination geometries around the Cu^{II} ions can be described as a slightly distorted square pyramidal with the square plane formed by 4 N atoms and the halogen atom occupying the axial position.

The structure of $[Cu_2(bipy)_4HgBr_4][Hg_2Br_6]$ (**2**) contains a trinuclear $[Cu_2(bipy)_4HgBr_4]^{2+}$ cation and a $[Hg_2Br_6]^{2-}$ anion (Figure 3). Within the trinuclear cationic unit, a pair of $[Cu(bipy)_2]^{2+}$ cations are bridged by an $HgBr_4$ tetrahedron. Hg(2) in the $[Hg_2Br_6]^{2-}$ anion is also four-coordinate and two $HgBr_4$ tetrahedra share an edge (Br5−Br5A) to form a dimeric unit. Such an $[Hg_2Br_6]^{2-}$ anion has been reported in other Hg^{II} bromide complexes.[11] The Cu−N, Cu−Br, and Hg−Br distances are similar to those in **1** (Table 1). The shortest Hg−Hg and Hg−Cu distances are 3.838(1) and 4.698(1) Å, respectively, thus there is no metal−metal interaction. The distance from Cu(1) in $[Cu_2(bipy)_4HgBr_4]^{2+}$ to the bromide of the nearest $[Hg_2Br_6]^{2-}$ anion is 3.838(2) Å, indicating that there are only electrostatic interactions between the two different building units. Similar to **1**, the neighboring $[HgCu_2(bipy)_4Br_4]^{2+}$ cations are further interlinked via weak π-π interactions between pyridine rings to form a 1-D double chain along the diagonal of the *a* and *c* axes. The

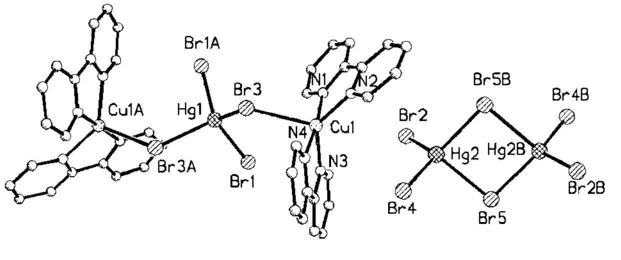

Figure 3. The structure of $[Cu_2(bipy)_4HgBr_4][Hg_2Br_6]$ (**2**). Symmetry codes for the generated atoms: a. −*x*, *y*, 1/2 − *z*; b. −1/2 − *x*, 3/2 − *y*, −1 − *z*

Table 1. Selected bond lengths [Å] and angles [°] for **1**−**4**

1			
Hg−Br#1[a]	2.4882(16)	Hg−Br	2.4882(16)
Hg−Cl	2.670(3)	Hg−Cl#1	2.670(3)
Cu−N(2)#1	2.000(11)	Cu−N(2)	2.000(11)
Cu−N(1)#1	2.077(13)	Cu−N(1)	2.077(13)
Cu−Cl#1	2.750(4)	Cu−Cl	2.750(4)
2			
Hg(1)−Br(1)#1	2.539(3)	Hg(1)−Br(1)	2.539(3)
Hg(1)−Br(3)#1	2.707(2)	Hg(1)−Br(3)	2.707(2)
Hg(2)−Br(2)	2.520(3)	Hg(2)−Br(4)	2.525(3)
Hg(2)−Br(5)#2	2.663(3)	Hg(2)−Br(5)	2.814(3)
Br(3)−Cu(1)	2.778(4)	Cu(1)−N(1)	1.961(17)
Cu(1)−N(4)	1.987(17)	Cu(1)−N(3)	2.035(16)
Cu(1)−N(2)	2.058(17)		
3			
Hg(1)−Br(3)	2.514(2)	Hg(1)−Br(2)	2.526(2)
Hg(1)−Br(1)	2.626(2)	Hg(1)−Br(2)#1	3.108(2)
Hg(2)−Br(5)	2.403(3)	Hg(2)−Br(4)	2.411(3)
Hg(2)−Br(6)	3.043(3)	Hg(3)−Br(7)	2.528(2)
Hg(3)−Br(6)	2.531(3)	Hg(3)−Br(8)	2.653(2)
Hg(3)−Br(8)#2	2.802(2)	Cu−N(2)	1.972(15)
Cu−N(3)	1.990(14)	Cu−N(1)	2.000(15)
Cu−N(4)	2.025(15)	Cu−Br(1)	2.791(4)
4			
Hg(1)−Cl(3)	2.333(5)	Hg(1)−Cl(2)	2.334(5)
Hg(1)−Cl(1)	2.734(4)	Hg(1)−Cl(4)	2.889(5)
Hg(2)−Cl(6)	2.359(5)	Hg(2)−Cl(5)	2.386(5)
Hg(2)−Cl(4)	2.534(4)	Cu−N(2)	1.982(13)
Cu−N(3)	1.992(13)	Cu−N(1)	2.057(13)
Cu−N(4)	2.139(13)	Cu−Cl(1)	2.319(5)

[a] Symmetry transformations used to generate equivalent atoms: For **1**: #1 $-x + 1, y, -z + 3/2$. For **2**: #1 $-x, y, -z + 1/2$ #2 $-x - 1/2, -y + 3/2, -z - 1$. For **3**: #1 $-x, -y, -z + 2$ #2 $-x - 1, -y, -z + 1$.

distance between the centers of two such rings is 3.771 Å, and the dihedral angle between the two rings is 6.2°.

The structure of $[Cu_2(bipy)_4Hg_2Br_6][Hg_4Br_{10}]$ (**3**) features a novel one-dimensional chain along the diagonal of the *a* and *c* axes (Figure 4). The chain is built from tetranuclear $[Cu_2Hg_2(bipy)_4Br_6]^{2+}$ cations interconnected by $[Hg_4Br_{10}]^{2-}$ tetramers via elongated Hg−Br bonds [3.185(2) Å]. Within the tetranuclear $[Cu_2Hg_2(bipy)_4Br_6]^{2+}$ cation, the edge-sharing tetrahedral dimeric $Hg(1)_2Br_6$ unit bridges with two $[Cu(bipy)_2]^{2+}$ units via two Br(1) atoms. The $[Hg_4Br_{10}]^{2-}$ tetramer is composed of an edge-sharing $Hg(3)_2Br_6$ dimeric unit and two $Hg(2)Br_2$ units [Br−Hg−Br 160.7(1)°] that are interconnected via Hg−Br bonds [Hg(2)−Br(6) 3.043(3) Å]. The coordination geometries around Hg(1) and Hg(3) can be described as slightly distorted tetrahedral. The distortion of the $Hg(2)Br_4$ tetrahedron is even more severe, two of the Hg-Br distances are longer than the remaining two Hg−Br bonds by more than 0.64 Å (Table 1). Similar to the situation in **1** and **2**, there is no metal−metal bonding between the metal centers, the shortest Hg−Cu and Hg−Hg distances are 4.435(2) and 3.823(2) Å, respectively. The 1-D chains of $[Cu_2(bipy)_4Hg_2Br_6][Hg_4Br_{10}]$ (**3**) are further interconnected via weak π-π interactions between neighboring pyridine rings to form a <010> 2-D layer (Figure 5). The distance between the centers of two such rings is 4.153 Å, and the dihedral angle between the two rings is 1.9°.

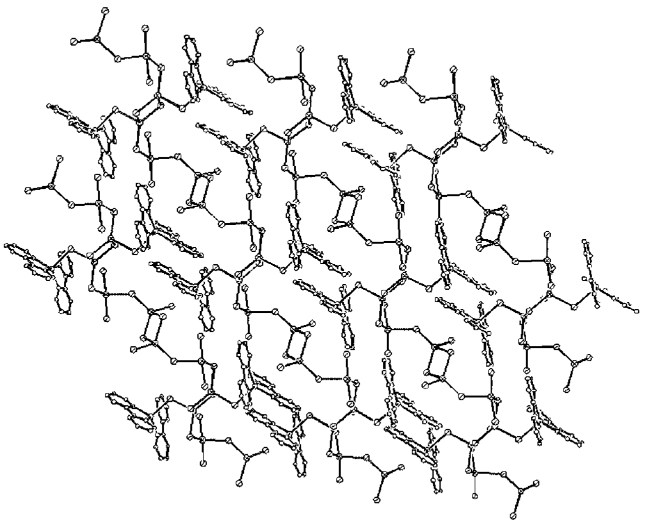

Figure 5. A <0 1 0> layer formed by 1-D chains of complex **3** through π-π interactions between the pyridine rings

In $[Cu(bipy)_2Hg_2Cl_6]$ (**4**), each $[Hg_2Cl_6]^{2-}$ dimeric unit bridges with a $[Cu(bipy)_2]^{2+}$ cation to form a trinuclear

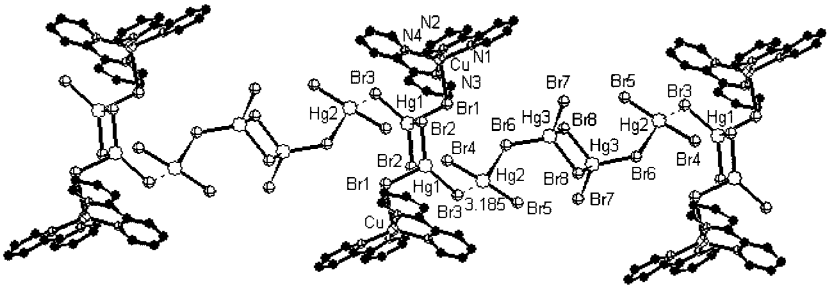

Figure 4. 1-D chain of $[Cu_2(bipy)_4Hg_2Br_6][Hg_4Br_{10}]$ (**3**) along the diagonal axis of *a* and *c.* Longer Hg−Br contacts are represented by dotted lines

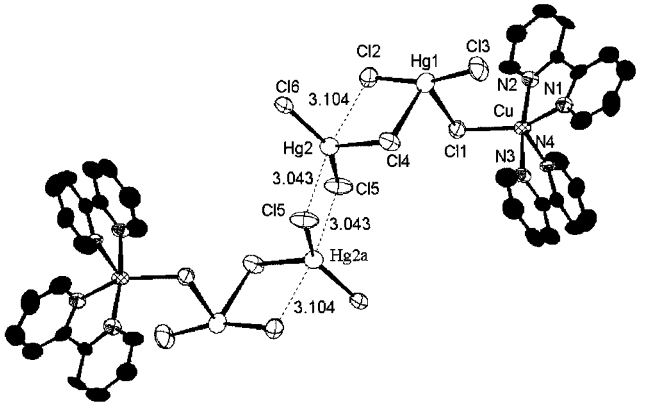

Figure 6. ORTEP representation of the structure of $[Cu(bipy)_2Hg_2Cl_6]_2$ (**4**). Thermal ellipsoids are drawn at the 50% probability level. Longer Hg−Cl contacts are represented by dotted lines. Symmetry code for the generated atoms: $1 - x$, $2 - y$, $-z$

$[Cu(bipy)_2Hg_2Cl_6]$ unit (Figure 6). Two such neighboring units are interconnected by a pair of weak Hg−Cl bonds [Hg(2)−Cl(5) Å] into a hexanuclear $[Cu(bipy)_2Hg_2Cl_6]_2$ unit. The Hg(2)−Cl(2) distance of 3.104 Å is also much longer than the remaining Hg−Cl distance (Table 1). With all Hg−Cl bonds included, the coordination geometry around Hg(2) can be described as distorted trigonal bipyramidal with the two axial Hg−Cl bonds elongated. The coordination geometry of the Hg(1) center is severely distorted tetrahedral. The shortest Cu−Hg and Hg−Hg contacts are 4.053(1) and 4.0699(1) Å, respectively. The shortest Hg−Cl distance between two neighboring $[Hg_2Cu(bipy)_2Cl_6]_2$ units is more than 3.582(5) Å, thus these dimeric units are not further condensed. The structure of **4** is different from those of $[Cu(en)_2][Hg_2Cl_6]$ and $[Cu(en)_2][Hg_2Br_6]$ although they have a similar structural formula.[11b] In $[Cu(en)_2][Hg_2Cl_6]$, each $[Hg_2Cl_6]$ anion bridges with two $[Cu(en)_2]^{2+}$ cations to form a 1-D chain, and the Cu^{II} ion has a Jahn−Teller distorted octahedral coordination geometry. In $[Cu(en)_2][Hg_2Br_6]$, the copper(II) ion is also octahedrally coordinated, however the $[Hg_2Br_6]^{2-}$ anions are interconnected into a 1-D chain, and all Hg^{II} ions are five-coordinate with trigonal bipyramidal geometries. The anionic chains of $[Hg_2Br_6]^{2-}$ are cross-linked by bridging $[Cu(en)_2]^{2+}$ cations into a 1-D layer.[11b] Again we suggest the steric effect of the bipy group plays an important role in determining the structures of the so formed Cu^{II}−Hg^{II} halide compounds. Strong steric hindrance of two bipy ligands makes the octahedral coordination geometry unfavorable for the Cu^{II} ion.

The formula units of **4** are packed via π-π interactions between the pyridine rings to form a 1-D chain along the diagonal of the *a* and *c* axes. The distance from the pyridine ring center formed by N(3), C(11), C(12), C(13), C(14), and C(15) to that formed by N(4), C(16), C(17), C(18), C(19), and C(20) in neighboring formula units is 3.888 Å. The dihedral angle between these two pyridine rings is only 5.2°.

Results of magnetic measurements for **1**, **2**, and **4** indicate that the three compounds contain one, two, and one isolated single-spin d^9 Cu^{II} ion, respectively. Magnetic measurements for **3** were not performed due to an insufficient amount of samples. The measured μ_{eff} values are 1.766(3), 2.494(2), and 1.764(1) μ_B, respectively for **1**, **2**, and **4**. These values decrease very slightly with decreasing temperature and non-linear fitting of the data according to the Cuie−Weiss law [$\chi_M = C/(T - \theta) + \chi_0$] in the temperature range of 6−300 K gives θ vlues of −0.24(3), −0.27(1), and −0.15(6), and χ_0 values of $3.1(2)\cdot10^{-4}$, $-6.5(2)\cdot10^{-4}$, and $-3.9(2)\cdot10^{-4}$ emu/mol, for **1**, **2**, and **4** respectively. Thus there is little magnetic interaction between neighboring Cu^{II} ions, which is in good agreement with results from the X-ray structural analyses in which the nearest Cu···Cu separations are 8.112(2), 7.431(2), and 7.386(2) Å, for **1**, **2**, and **4** respectively.

Experimental Section

Materials and Methods: $CuCl_2\cdot2H_2O$, $CuBr_2$, $HgBr_2$, and 2,2′-bipyridine were purchased from the Fourth Factory of Shanghai Reagent and NH_4PF_6 was obtained from Acros. All chemicals and solvents were of reagent grade and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the 4000−400 cm^{-1}. Magnetic susceptibility measurements on polycrystalline samples were performed with a Quantum Design SQUID magnetometer at a field of 1 T over the range of 6 to 300 K. Raw data were corrected for the susceptibility of the container.

Synthesis of $[Cu(bipy)_2HgCl_2Br_2]$ (1): $CuCl_2\cdot2H_2O$ (0.09 g, 0.5 mmol), NH_4PF_6 (0.16 g,1.0 mmol, used for adjusting pH value of the solution), and 2,2′-bipyridine (0.16 g, 1.0 mmol) were dissolved in a solvent mixture of acetone (10.0 mL), ethanol (10.0 mL), and acetonitrile (10.0 mL) whilst stirring at room temperature. After 10 min, $HgBr_2$ (0.16 g, 0.5 mmol) was added and the solution was stirred for 20 hours. The resultant solution with a pH value close to 6.0 was filtered and allowed to evaporate slowly at room temperature. Blue crystals of **1** were obtained after five days in a yield of 40.2% (0.16 g). IR (KBr cm^{-1}): $\tilde{\nu}$ = 1601 m, 1570 w, 1495 m, 1444 s, 1317 m, 839 vs, 768 vs, 731 m, 557 m. $C_{20}H_{16}Br_2Cl_2CuHgN_4$ (807.22): found C 29.81, H 2.48, N 6.95%; calcd. C 29.76, H 2.00, N 6.94%.

Synthesis of $[Cu_2(bipy)_4HgBr_4][Hg_2Br_6]$ (2): $CuBr_2$ (0.16 g, 0.5 mmol), NH_4PF_6 (0.16 g, 1.0 mmol), and 2,2′-bipyridine (0.16 g, 1.0 mmol) were dissolved in a solvent mixture of acetone (10.0 mL), ethanol (10.0 mL), and acetonitrile (10.0 mL) at room temperature and stirred for 30 min. $HgBr_2$ (0.36 g, 1.0 mmol) was then added and the reaction was allowed to continue for a further 20 hours. The resultant solution with a pH value of 6.0 was filtered and the filtrate was allowed to evaporate slowly at room temperature. Green-blue crystals of **2** were obtained after one day in a yield of 78.1% (0.42 g). IR data (KBr cm^{-1}): $\tilde{\nu}$ = 1601s, 1495 m, 1473 s, 1444 vs, 1317 m, 1252 m, 1159 m, 1034 m, 764 vs, 732 s, 663 w. $C_{40}H_{32}Br_{10}Cu_2Hg_3N_8$ (2152.69): found C 22.54, H 3.20, N 5.12, Cu 6.26%. calcd. C 22.32, H 1.50, N 5.21, Cu 5.9%.

Synthesis of $[Cu_2(bipy)_4Hg_2Br_6][Hg_4Br_{10}]$ (3): A mixture of $CuBr_2$ (0.16 g, 0.5 mmol), NH_4PF_6 (0.08 g, 0.5 mmol), and 2,2′-bipyridine (0.16 g, 1.0 mmol) was dissolved in a solvent mixture of acetonitrile (5 mL) and methanol (5 mL) which was placed in one side of an H-shaped tube (total volume 35 mL). $HgBr_2$ (0.18 g, 0.5 mmol) dis-

Table 2. Summary of crystal data and details of intensity collection and refinement for **1**−**4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{20}H_{16}Br_2Cl_2CuHgN_4$	$C_{40}H_{32}Br_{10}Cu_2Hg_3N_8$	$C_{40}H_{32}Br_{16}Cu_2Hg_6N_8$	$C_{20}H_{16}Cl_6CuHg_2N_4$
Molecular mass	807.22	2152.69	3233.92	989.79
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$C2/c$	$P2_1/c$	$P\bar{1}$
Crystal size [mm]	0.30 × 0.18 × 0.14	0.32 × 0.24 × 0.06	1.00 × 0.10 × 0.08	0.46 × 0.40 × 0.24
a [Å]	21.7605(12)	25.5990(9)	13.904(3)	9.8091(2)
b [Å]	9.3851(5)	14.3303(4)	16.723(3)	11.5407(3)
c [Å]	15.6452(8)	15.2380(6)	14.272(3)	12.4901(2)
α [deg]	90	90	90	82.140(1)
β [deg]	132.187(2)	109.3850(10)	101.90(3)	71.099(1)
γ [deg]	90	90	90	85.734(1)
V [Å^3]	2367.5(2)	5273.0(3)	3247.3(11)	1324.45(5)
Z	4	4	4	2
Dc [gcm^{-3}]	2.2652.265	2.712	3.307	2.482
μ [cm^{-1}]	10.991	17.113	24.648	12.981
$F(000)$	1508	3904	2852	910
Reflections, total	3914	9306	6619	6805
Reflections, unique	2049(R_{int} = 5.63%)	4605(R_{int} = 7.15%)	6351(R_{int} = 8.41%)	4583(R_{int} = 4.74%)
No. of parameters refined	137	286	325	299
GOF on F^2	0.911	1.135	0.935	1.130
R[a] $(I > 2.00\sigma(I))$	0.0537	0.0808	0.0681	0.0707
R_w[b] $(I > 2.00\sigma(I))$	0.1125	0.1538	0.1472	0.1713
Residual extremes [e·Å^{-3}]	1.171, −1.188	1.615, −2.350 (1.02 and 1.33 Å from Hg2)	1.859 (1.20 Å from Hg2), −1.341	2.045, −2.964 (2.04 and 1.05 Å from Hg1)

[a] $R1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$ and $wR2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$. [b] Data with $I > 4\sigma(I)$ for **3**.

solved in acetonitrile (10 mL) was added to the other side of the H-shaped tube. A solvent mixture of CH_2Cl_2 (5 mL) and hexane (5 mL) was then layered on the top of both ends of the H-shaped tube. The tube was sealed and the reaction allowed to proceed through diffusion of the two solutions over a period of six days. Air-stable green-blue crystals of **3** were collected from the $HgBr_2$-containing side of the H-tube in a very low yield of 5.6% (0.045 g). IR (KBr cm^{-1}): $\tilde{\nu}$ = 1601 s, 1568 m, 1477 m, 1444 vs, 1317 m, 1159 m, 1034 m, 764 vs, 729 s, 663 m. $C_{40}H_{32}Br_{16}Cu_2Hg_6N_8$ (3233.92): found C 14.92, H 2.60, N 3.34%; calcd. C 14.86, H 2.30, N 3.47%.

Synthesis of [Cu(bipy)$_2$Hg$_2$Cl$_6$]$_2$ (4): Compound **4** was synthesized by a similar procedure to that of **1** by reacting $CuCl_2{\cdot}2H_2O$ (0.09 g, 0.5 mmol), NH_4PF_6 (0.16 g, 1.0 mmol), 2,2′-bipyridine (0.16 g, 1.0 mmol), and $HgBr_2$ (0.27 g, 1.0 mmol) in a solvent mixture of acetone (10.0 mL) and methanol (10.0 mL) at room temperature. Yield 50.0%. IR (KBr): $\tilde{\nu}$ = 1599 cm^{-1} s, 1493 m, 1473 s, 1443 vs, 1317 m, 1250 m, 1157 m, 1028 m, 769 vs, 729 s, 650 w. $C_{20}H_{16}Cl_6CuHg_2N_4$ (989.79): found C 24.36, H 1.06, N 5.52%; calcd. C 24.25, H 1.62, N 5.65%.

Crystallography: Single crystals of **1**, **2**, and **4** were mounted on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for Lorentz polarization as well as for absorption using the SADABS program.[13] Data collection for **3** was performed on an Enraf−Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K using ω-2θ scan methods. The data set for **3** was corrected for Lorentz polarization and an empirical absorption correction was applied based on the ψ scan technique. All four structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 using SHELX-97.[13] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in geometrically calculated positions. Crystallographic data and structural refinements for **1** to **4** are summarized in Table 2. Important bond lengths and angles are listed in Table 1.

CCDC-209447 to -209450 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Innovative Project, the Introduction of Overseas Elitists Program by the Chinese Academy of Sciences and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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Received August 10, 2003
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