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# Formation of Dinuclear, Macrocyclic, and Chain Structures from HgI$_2$ and a Semirigid Benzimidazole-Based Bridging Ligand: An Example of Ring-Opening Supramolecular Isomerism

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The reactions of HgI$_2$ with the semirigid ditopic ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms) afforded three new complexes, [Hg$_2$($\mu$-I)$_2$I$_2$(bbimms)] (**1**), [Hg$_2$I$_4$(bbimms)$_2$] (**2**), and *catena*-poly[HgI$_2$(bbimms)] (**3**). The ligand and all complexes have been structurally characterized by single-crystal X-ray diffraction. **1** is a triply bridged dinuclear complex comprised of two Hg(II) ions, one bridging ligand, two bridging I$^-$ anions, and two terminal I$^-$ anions. **2** is a dinuclear metallamacrocycle comprised of two Hg(II) ions, two bridging ligands, and four terminal I$^-$ anions, while **3** is a helical chain with the repeating unit of HgI$_2$(bbimms). **2** and **3** can be classified as supramolecular isomers, and both are related to the triply bridged precursor **1** via the addition of one more ligand in a ring-opening process.

## Introduction

During the past decade, synthetic coordination chemistry has evolved to include supramolecular synthesis[1] for organizing molecular building blocks into supramolecular assemblies. Within this area, two exciting fields that continue to attract intense interest are coordination polymers[2] and molecular architectures.[3] The former is based on the assembly of one- to three-dimensional composite organic/inorganic frameworks, while the latter focuses on the construction of discrete supramolecular architectures with defined shape and size. The key difference between the two areas are the topologies adopted by the structures, either polymeric or discrete. Interestingly, while the structures are often treated as two distinct groups, the same synthetic strategies are, in fact, utilized in both fields. This suggests that a reactive, synthetic interconversion between these two structural classes is possible as long as the same building blocks are involved. This process and the structural relationship between discrete and polymeric constructs has recently been described as *supramolecular isomerism*,[4] which is a useful concept for thinking about the synthetic processes involved in obtaining these two structural classes and, potentially, for guiding syntheses to obtain structures with desired topologies.

The existence of supramolecular isomerism in polymeric network structures has received increasing attention[4−9] recently, which is not too surprising when one considers that there exists an ever increasing number of published structures that differ not by the building blocks but rather by the

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arrangement of the building blocks within the structure. In this context, several examples of structural isomerism,[5,10] conformational isomerism,[7] and topological isomerism[11,12] have recently appeared in the literature. In contrast, discussions of supramolecular isomers, consisting of the closed and the polymeric structural isomers, have appeared only recently. For example, Zaworotko and co-workers[10] demonstrated such isomerism for the case of a discrete molecular hexagon and a polymeric zigzag chain assembled from 5-nitro-1,3-benzenedicarboxylic acid and copper(II) ions. Another example can be found in the work of James and co-workers,[13] where the coordination polymer $[M_2L_3]_n$ was obtained from the $[M_2L_3]$ molecular precursor. In the latter case, the author used the term *ring-opening polymerization* to describe this type of interconversion. Others have used this term to describe the formation of metal−phosphorus-based polymeric structures from the corresponding metallacyclic precursors.[14,15] On the basis of these examples, it appears that the conversion from the closed structure to the polymeric one inevitably accompanies at least one ring opening. Therefore, we prefer to term this interconversion process as *ring-opening isomerism.*

Our previous investigations using linear quinoline or benzimidazole-based polydentate ligands with flexible spacers resulted in a broad range of structures including helicates,[16−18] polymeric 2D networks,[19] and metallacycles,[20] while, in contrast, *N*,*N′*-bipyridyl-based rigid ligands only resulted in multidimensional polymeric networks.[21] Interestingly, by the careful design of semirigid ligands containing aromatic cores and benzimidazolyl (Bim) ring arms, we were able to construct both rectangular or prismatic architectures[22] and two-dimensional networks.[23] This implies that synthetic fine-tuning between closed and polymeric structures is possible for this type of ligand. In this paper we report three new complexes obtained from the reaction of $HgI_2$ with the semirigid ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms), namely dinuclear $[Hg_2(\mu\text{-I})_2I_2(bbimms)]$ (**1**), metallacyclic $[Hg_2I_4(bbimms)_2]$ (**2**), and its ring-opened isomer, *catena*-poly$[HgI_2(bbimms)]$ (**3**), which has a helical chain structure. **2** and **3** are supramolecular isomers and can be regarded as having resulted from precursor **1**, via ring-opening isomerism with addition of ligand.

## Experimental Section

All chemicals were of reagent grade from commercial sources and were used without further purification: mercury(II) iodide ($HgI_2$, Alfa Aesar); benzimidazole ($C_7H_6N_2$, Avocado); 1,3-bis(chloromethyl)mesitylene (Aldrich). IR spectra were recorded on a Shimadzu FTIR-8400 spectrophotometer using KBr as reference in the 4000−500 $cm^{-1}$ region. $^1H$ NMR spectra were collected at room temperature on a Varian Mercury/VX 300 spectrometer with chemical shifts in $\delta$ relative to DMSO-$d_6$. Thermogravimetric analyses were carried out on a TA Instruments SDT 2960 simultaneous DTA−TGA under flowing helium by heating the compounds from 25 to 800 °C using a heating rate of 10 °C/min. The X-ray powder diffraction patterns were acquired on a Rigaku D\Max-2200 powder X-ray diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 0.154\,18$ nm). The data were collected from 2 to 32° in steps of 0.04° in $2\theta$. The C, H, and N analyses were performed by Desert Analytics Laboratory.

**Preparation of the Ligand.** The ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms) was prepared as described previously.[16] Single crystals suitable for X-ray diffraction analysis were grown in a dilute MeOH−$CH_2Cl_2$ (5:1 v/v) mixed solution.

**Preparation of the Complexes. $[Hg_2(\mu\text{-I})_2I_2(bbimms)]$ (1).** $HgI_2$ (0.068 g, 0.15 mmol) in 25 mL of MeOH−$CH_3CN$ (1:2 v/v) was slowly added to a solution of bbimms (0.019 g, 0.05 mmol) in 10 mL of $CH_2Cl_2$−MeOH (1:1 v/v). The colorless crystalline product appeared within a few hours and was collected by filtration. Yield: 89%. Anal. Calcd for $C_{25}H_{24}N_4I_4Hg_2$: C, 23.29; H, 1.88; N, 4.35. Found: C, 23.57; H, 1.68; N, 4.57. $^1H$ NMR (DMSO-$d_6$): $\delta$ 7.850 (s, 2H, $H_2$), 7.750 (ddd, 2H, $H_4$), 7.457 (ddd, 2H, $H_7$), 7.204−7.260 (m, 4H, $H_{5,6}$), 7.125 (s, 1H, $H_9$), 5.488 (s, 4H, $H_8$), 2.260 (s, 6H, $H_{11}$), 2.098 (s, 3H, $H_{10}$). IR (KBr): 3074 (w), 2968 (w), 1612 (m), 1585 (w), 1499 (s), 1456 (s), 1379 (m), 1290 (m), 1267 (w), 1184 (s), 914 (m), 745(s), 615 (w), 461 (w) $cm^{-1}$. Single crystals suitable for X-ray analyses were obtained by letting the reaction mixture sit for several days to obtain large block-shaped crystals.

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**Table 1.** Crystal Data and Structure Refinement

| | bbimms | **1** | **2** | **3** |
|---|---|---|---|---|
| emp formula | $C_{25}H_{24}N_4$ | $C_{25}H_{24}Hg_2I_4N_4$ | $C_{50}H_{48}Hg_2I_4N_8$ | $C_{25}H_{24}HgI_2N_4$ |
| fw | 380.48 | 1289.26 | 1669.74 | 834.87 |
| cryst system | orthorhombic | monoclinic | triclinic | monoclinic |
| space group | $P2_12_12_1$ | $P2_1/m$ | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 9.3790(6) | 8.0385(8) | 11.3823(7) | 17.8199(8) |
| $b$ (Å) | 9.5923(6) | 19.1301(18) | 11.5255(7) | 9.9749(5) |
| $c$ (Å) | 21.8575(13) | 9.8324(9) | 20.4802(13) | 29.2120(13) |
| α (deg) | 90 | 90 | 79.9780(10) | 90 |
| $\beta$ (deg) | 90 | 90.910(2) | 80.6890(10) | 97.8670(10) |
| $\gamma$ (deg) | 90 | 90 | 71.7790(10) | 90 |
| $V$ (Å$^3$) | 1966.4(2) | 1511.8(2) | 2496.5(3) | 5143.6(4) |
| $Z$ | 4 | 2 | 2 | 8 |
| $\rho_{calcd}$ (g/cm$^3$) | 1.285 | 2.832 | 2.221 | 2.156 |
| $\mu$ (mm$^{-1}$) | 0.077 | 1.4248 | 0.866 | 0.841 |
| cryst size (mm) | 0.36 × 0.18 × 0.12 | 0.26 × 0.24 × 0.08 | 0.24 × 0.18 × 0.04 | 0.18 × 0.08 × 0.06 |
| unique reflcns | 3130 | 3194 | 8804 | 9100 |
| GOF on $F^2$ | 0.987 | 1.003 | 1.009 | 1.043 |
| $R^a$ [$I > 2\sigma(I)$] | 0.0390 | 0.0296 | 0.0372 | 0.0525 |
| $R_w{}^b$ [$I > 2\sigma(I)$] | 0.0487 | 0.0333 | 0.0452 | 0.0606 |

$^a$ $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b$ $R_w = [(\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2)^{1/2}$.

**[$Hg_2I_4$(bbimms)$_2$] (2).** $HgI_2$ (0.023 g, 0.05 mmol) in 10 mL of MeOH−$CH_3CN$ (1:2 v/v) was added to a solution of bbimms (0.019 g, 0.05 mmol) in 5 mL of $CH_2Cl_2$−MeOH (1:1 v/v). A 10 mL volume of DMF was added, and the resulting mixture was heated to produce a clear solution. After several days colorless plate crystals appeared at the bottom of the beaker and were collected by filtration. Yield: 90%. Anal. Calcd for $C_{50}H_{48}N_8I_4Hg_2$: C, 35.97; H, 2.90; N, 6.71. Found: C, 35.87; H, 2.65; N, 6.71. $^1$H NMR (DMSO-$d_6$): $\delta$ 7.868 (s, 2H, $H_2$), 7.769 (ddd, 2H, $H_4$), 7.445 (ddd, 2H, $H_7$), 7.214−7.245 (m, 4H, $H_{5,6}$), 7.112 (s, 1H, $H_9$), 5.490 (s, 4H, $H_8$), 2.244 (s, 6H, $H_{11}$), 2.084 (s, 3H, $H_{10}$). IR (KBr): 3074 (w), 2968 (w), 1612 (m), 1585 (w), 1499 (s), 1456 (s), 1379 (m), 1290 (m), 1267 (w), 1184 (s), 914 (m), 745(s), 610 (w), 463 (w) cm$^{-1}$.

***catena*-[$HgI_2$(bbimms)]$_n$ (3).** $HgI_2$ (0.045 g, 0.1 mmol) in 10 mL of MeOH−$CH_3CN$ (1:2 v/v) was added to a solution of bbimms (0.019 g, 0.05 mmol) in 5 mL of $CH_2Cl_2$−MeOH (1:1 v/v). An additional 15 mL of $CH_3CN$ was added, and the resulting mixture was left standing at room temperature for several days to produce colorless needle-shaped crystals that were collected by filtration. Yield: 93%. Anal. Calcd for $C_{25}H_{24}N_4I_2Hg$: C, 35.97; H, 2.90; N, 6.71. Found: C, 36.30; H, 2.80; N, 6.49. $^1$H NMR (DMSO-$d_6$): $\delta$ 7.783 (s, 2H, $H_2$), 7.679 (ddd, 2H, $H_4$), 7.444 (ddd, 2H, $H_7$), 7.190−7.234 (m, 4H, $H_{5,6}$), 7.125 (s, 1H, $H_9$), 5.454 (s, 4H, $H_8$), 2.268 (s, 6H, $H_{11}$), 2.102 (s, 3H, $H_{10}$). IR (KBr): 3074 (w), 2968 (w), 1612 (m), 1585 (w), 1504 (s), 1456 (s), 1396 (m), 1292 (m), 1229 (m), 1190 (s), 906 (m), 746(s), 574 (w), 511 (w) cm$^{-1}$.

**Crystallography.** The crystals were mounted on the end of a thin glass fiber using an inert oil. X-ray intensity data covering the full sphere of reciprocal space were measured at 150.0(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å).[24] The raw data frames were integrated with SAINT+,[24] which also applied corrections for Lorentz and polarization effects. The final unit cell parameters are based on the least-squares refinement of 3130, 9135, 6755, and 9200 reflections from the data sets of bbimms, **1**, **2**, and **3**, respectively, with $I > 5\sigma(I)$. Analysis of the data showed negligible crystal decay during collection. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with SADABS.[24] The structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares against $F^2$, using SHELXTL.[25] Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. A summary of the crystal data is given in Table 1. Selected bond distances and bond angles are listed in Table 2.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**−**3**$^a$

| | | | |
|---|---|---|---|
| Compound **1** | | | |
| Hg−N(1) | 2.234(5) | Hg−I(2) | 2.8957(5) |
| Hg−I(1) | 2.6372(5) | I(2)−Hg$^{\#1}$ | 2.8957(5) |
| Hg−I(3) | 2.8434(5) | I(3)−Hg$^{\#1}$ | 2.8434(5) |
| N(1)−Hg−I(1) | 124.72(13) | I(1)−Hg−I(2) | 110.935(18) |
| N(1)−Hg−I(3) | 99.77(12) | I(3)−Hg−I(2) | 97.404(15) |
| I(1)−Hg−I(3) | 120.891(18) | Hg$^{\#1}$−I(2)−Hg | 80.116(19) |
| N(1)−Hg−I(2) | 97.74(13) | Hg−I(3)−Hg$^{\#1}$ | 81.899(19) |
| Compound **2** | | | |
| Hg(1)−N(3)$^{\#1}$ | 2.352(6) | Hg(2)−N(5) | 2.385(6) |
| Hg(1)−N(1) | 2.452(7) | Hg(2)−N(7)$^{\#2}$ | 2.392(6) |
| Hg(1)−I(2) | 2.6443(6) | Hg(2)−I(4) | 2.6408(6) |
| Hg(1)−I(1) | 2.6843(7) | Hg(2)−I(3) | 2.6848(6) |
| N(3)−Hg(1)$^{\#1}$ | 2.352(6) | N(7)−Hg(2)$^{\#2}$ | 87.4(2) |
| N(3)$^{\#1}$−Hg(1)−N(1) | 83.7(2) | N(5)−Hg(2)−N(7)$^{\#2}$ | 87.4(2) |
| N(3)$^{\#1}$−Hg(1)−I(2) | 114.86(17) | N(5)−Hg(2)−I(4) | 97.55(14) |
| N(1)−Hg(1)−I(2) | 100.19(15) | N(7)$^{\#2}$−Hg(2)−I(4) | 115.30(15) |
| N(3)$^{\#1}$−Hg(1)−I(1) | 99.54(16) | N(5)−Hg(2)−I(3) | 109.86(14) |
| N(1)−Hg(1)−I(1) | 104.32(15) | N(7)$^{\#2}$−Hg(2)−I(3) | 96.43(15) |
| I(2)−Hg(1)−I(1) | 139.52(2) | I(4)−Hg(2)−I(3) | 138.94(2) |
| Compound **3** | | | |
| Hg(1)−N(7)$^{\#1}$ | 2.311(8) | Hg(2)−N(5) | 2.300(10) |
| Hg(1)−N(1) | 2.416(9) | Hg(2)−N(3) | 2.391(10) |
| Hg(1)−I(2) | 2.6546(9) | Hg(2)−I(3) | 2.6693(9) |
| Hg(1)−I(1) | 2.6827(9) | Hg(2)−I(4) | 2.6726(10) |
| N(7)$^{\#1}$−Hg(1)−N(1) | 83.9(3) | N(5)−Hg(2)−N(3) | 95.8(3) |
| N(7)$^{\#1}$−Hg(1)−I(2) | 106.8(2) | N(5)−Hg(2)−I(3) | 115.2(2) |
| N(1)−Hg(1)−I(2) | 109.4(2) | N(3)−Hg(2)−I(3) | 103.0(2) |
| N(7)$^{\#1}$−Hg(1)−I(1) | 113.8(2) | N(5)−Hg(2)−I(4) | 106.8(2) |
| N(1)−Hg(1)−I(1) | 99.5(2) | N(3)−Hg(2)−I(4) | 98.6(2) |
| I(2)−Hg(1)−I(1) | 132.03(3) | I(3)−Hg(2)−I(4) | 129.90(4) |

$^a$ Symmetry transformations used to generate equivalent atoms are as follows. **1**: #1, $x$, $-y + 3/2$, $z$. **2**: #1, $-x + 1$, $-y$, $-z + 1$; #2, $-x$, $-y + 1$, $-z + 2$. **3**: #1, $-x + 1$, $y + 1/2$, $-z + 1/2$.

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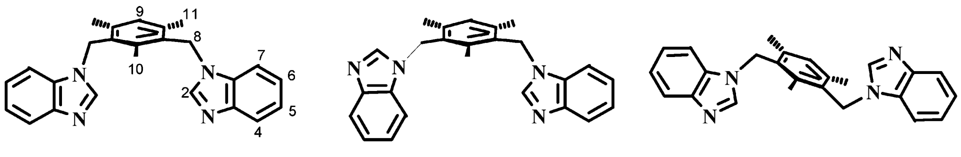
**Chart 1**



***syn*-conformation** **intermediate conformation** ***anti*-conformation**

## Results and Discussion

**Syntheses and Characterization.** As shown in Figure S1, the ligand bbimms has two Bim ring arms and one mesitylene spacer, both of which are rigid. However, the joints between the arms and the core are methylene groups ($-CH_2-$) which allow the two arms to rotate freely. This type of semirigidity endows the ligand with the flexibility to take on a variety of conformations. The solid structure of bbimms exhibits a *syn*-conformation, i.e., the two Bim rings are located on the same side of the core and are pointing in the same direction. In contrast, if one of the two Bim rings is rotated by 180°, the *anti*-conformation, i.e., two Bim rings positioned on opposite sides of the core pointing in opposite directions, will be obtained, as shown in Chart 1. Other intermediate conformations are also possible, and in solution, it is expected that fast conformational exchange will take place because of the low rotational energy barriers between the *anti*- and *syn*-conformations. Therefore, reaction of this ligand with the same metal ions may result in different structures on the basis of the conformation adopted by the ligand, which should sensitively depend on the solution environment. Indeed, three different complexes were obtained from the reaction of $HgI_2$ and bbimms: dinuclear $[Hg_2(\mu\text{-}I)_2I_2(\text{bbimms})]$ (**1**); macrocyclic $[Hg_2I_4(\text{bbimms})_2]$ (**2**); and polymeric *catena*-poly[$HgI_2$(bbimms)] (**3**).

The resulting structures were closely tied to the reaction conditions employed, especially to the solvent and the metal-to-ligand ratio. Under carefully controlled conditions, both the dinuclear complex **1** and the polymeric complex **3** can be obtained as pure compounds from a $MeOH-CH_3CN$ mixed-solvent system when using an excess of $HgI_2$ ($CH_2Cl_2$ is added to facilitate dissolution of the ligand bbimms but does not exert any noticeable influence on the formation of the complexes). The former requires no less than a 3-fold excess of $HgI_2$ over bbimms, while the latter requires a larger amount of acetonitrile in the solvent. By contrast, to prepare pure complex **2** it is necessary to use DMF as one of the solvents and the metal-to-ligand ratio is best kept at 1:1. When pure MeOH was used as the solvent for the synthesis, the fast precipitation of the product made it difficult to identify the precipitate, which presumably was just a mixture of different kinetic products. The addition of acetonitrile significantly slowed the crystallization process which enabled the isolation of a relatively pure product **3**. Warm DMF, which turns out to be a good solvent for the precipitate that appears in the $MeOH-CH_3CN$ reaction mixture, slows down the crystallization and leads to the formation of pure macrocyclic **2**. When using the $MeOH-CH_3CN-DMF$ solvent system with an excess of $HgI_2$, all three complexes cocrystallize and can be identified and distinguished on the basis of their crystal morphology under an optical microscope. However, increasing the amount of DMF in this mixture while decreasing the molar ratio of $HgI_2$ leads to the macrocyclic **2** becoming the dominant product and eventually the sole product. In general, excess $HgI_2$ leads to the formation of dinuclear **1**, while the addition of a large amount of acetonitrile with the concomitant reduction of the metal-to-ligand ratio to less than 2:1 leads to an increased yield of polymeric **3**. Regardless, **2** was always present in the product mixture if DMF was used to prevent rapid crystallization, no matter which metal to ligand molar ratio was used. These findings support the notion that **1** and **3** are probably kinetic products while **2** is more thermodynamically stable.

The purity of the complexes can be convincingly established by X-ray powder diffraction measurements. Figure S2 shows the observed powder diffraction pattern acquired from a typical batch of complex **3** together with its simulated pattern generated from single-crystal diffraction data. (Patterns for complexes **1** and **2** can be found in the Supporting Information as Figures S3 and S4.) It is clear that the observed patterns closely match the simulated ones, confirming that a single phase (greater than ~95% purity) is formed for each complex under the appropriate reaction conditions. The IR spectra of all three complexes are quite similar and comparable to that of the free ligand. By contrast, the $^1H$ NMR spectra of the complexes show more resolved proton signals compared to those of the ligand and exhibit a general downfield shift.[12,14]

**Thermogravimetric Analysis.** Thermogravimetric analysis was performed by heating the complexes from 26 to 800 °C under flowing helium. The TGA for all three complexes showed similar weight loss patterns: the first major weight loss occurred between 200 and 310 °C and is immediately followed by a second weight loss in the temperature range 310 to 350 °C. Similar decomposition processes are typical for complexes that are compositionally and structurally closely related.

**Crystal Structures.** The molecular structure of the ligand is depicted in Figure S1. It adopts a *syn*-conformation in the solid state. The two Bim rings are positioned on the same side of the central mesitylene group with a dihedral angle of 63.1° between them, making them both nearly perpendicular to the central mesitylene group with dihedral angles of 84.6 and 87.5°, respectively. This conformation is virtually retained in complex **1**, where two Bim rings are bound to two Hg(II) ions through two imino nitrogen atoms as shown in Figure 1. In addition, the two Hg(II) ions are symmetrically bridged by two $I^-$ anions, thus forming a triply bridged dinuclear complex. The remaining fourth coordina-

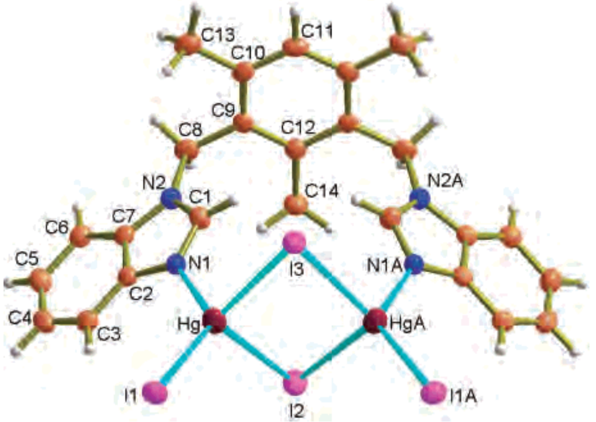


**Figure 1.** Molecular structure of the complex **1** viewing parallel to the mirror plane.

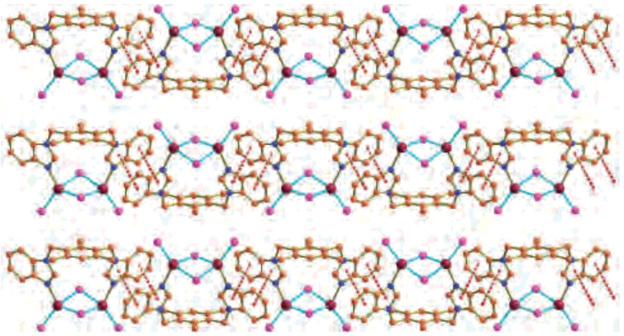


**Figure 2.** View of parallel chains formed via $\pi-\pi$ interactions along the *b* axis in **1**.

tion site of each Hg(II) ion is occupied by a terminal $I^-$ anion, resulting in an overall distorted tetrahedral geometry. A crystallographically imposed mirror plane that contains the two $\mu_2$-bridging $I^-$ anions and carbon atoms C11, C12, and C14 of the mesitylene group bisects the molecule. As a result, the dinuclear complex contains two identical Hg(II) ions that have the same coordination environment. The bridging Hg−I bonds are almost equivalent and are significantly longer than the terminal Hg−I bonds (Table 2). The formation of a four-membered $[Hg_2I_2]^{2+}$ ring is common in mercury complexes;[26] however, a triply bridged dinuclear mercury complex based on an $[Hg_2I_2]^{2+}$ motif has not been observed previously. The $[Hg_2I_2]^{2+}$ ring causes a large deviation from the ideal tetrahedral geometry around the Hg(II) ions and includes an I−Hg−I angle of 97.404(15)° and small Hg−I−Hg angles of 80.116(19) and 81.899(19)°. This arrangement creates significant ring strain, which may account for the ease with which the ring-opening isomerization occurs. Vide infra. A crystal packing analysis by the program PLATON[27] identifies weak intermolecular $\pi-\pi$ interactions between the Bim rings, as shown in Figure 2. Each Bim ring of the complex is nearly parallel and inverted relative to the one in the adjacent complex. The centroid-to-centroid distance between the five-membered and six-membered rings of the two neighboring Bim rings is 3.732 Å, and the dihedral angle between them is only 0.36°. The connectivity between the $\pi-\pi$ coupled dinuclear complexes is such that the ring orientation alternates up and down, thereby generating a one-dimensional chain that runs along the *b* direction. Adjacent chains are in registry with respect to the orientation of the $[Hg_2I_2]^{2+}$ ring, as shown in Figure 2.

Complex **2** contains two crystallographically independent neutral $M_2L_2$ metallacycles with the same molecular formula. Both are composed of two Hg(II) ions, two bridging bbimms ligands, and four terminal $I^-$ anions. The ligand takes on an apparent *syn*-conformation to bind to two Hg(II) ions; however, it is a different arrangement from that found in **1**: one of the two Bim rings in **2** is rotated around the $CH_2$ group to point its imino nitrogen donor in a different direction from that of the other Bim ring. While such an intermediate conformation is not surprising because of the two flexible $CH_2$ groups, it is nonetheless unexpected that it leads to such a drastically different structure. Two Bim rings belonging to different ligands stay parallel and approach closely, thereby significantly reducing the cavity inside the metallacycle. The crystallographically imposed inversion center is located in the center of each macrocycle, relating two ligands and four $I^-$ anions to give two Hg(II) ions the identical distorted tetrahedral coordination geometries.

As indicated in Table 2, the Hg−I bond distances are comparable to the terminal Hg−I bond distances in **1**, while the Hg−N bonds are a little longer than those in **1**. The largest deviation from the ideal tetrahedral geometry is found in the N−Hg−N angle rather than in the I−Hg−I angle as in **1**. The two crystallographically independent metallacycles in the asymmetric unit show very similar structural topologies. However, they differ slightly in their bond distances and bond angles and in the separation between two adjacent Bim rings as shown in Figure 3. This removes any potential symmetry between these two molecules. There are, however, intermolecular $\pi-\pi$ stacking interactions between the mesitylene group of one molecule and the five-membered ring of another molecule. As shown in Figure 4, each molecule provides two mesitylene groups and two of its four five-membered rings to form four $\pi-\pi$ interactions with four crystallographically independent neighboring molecules. Thus, a two-dimensional network is generated. PLATON analysis shows that the centroid-to-centroid distances between the mesitylene groups and the five-membered rings are 3.70 and 3.66 Å, while the dihedral angles are 7.27 and 5.87°, respectively.

Complex **3** also contains two independent $HgI_2$ and ligand motifs in its asymmetric unit cell. However, these components do not connect to one another to form a macrocyclic structure but rather connect to form an extend polymeric chain structure. The ligand bbimms acts as a bidentate bridging agent and coordinates with two crystallographically independent Hg(II) ions. Each Hg(II) ion joins two different ligands and further binds to two terminal $I^-$ anions to

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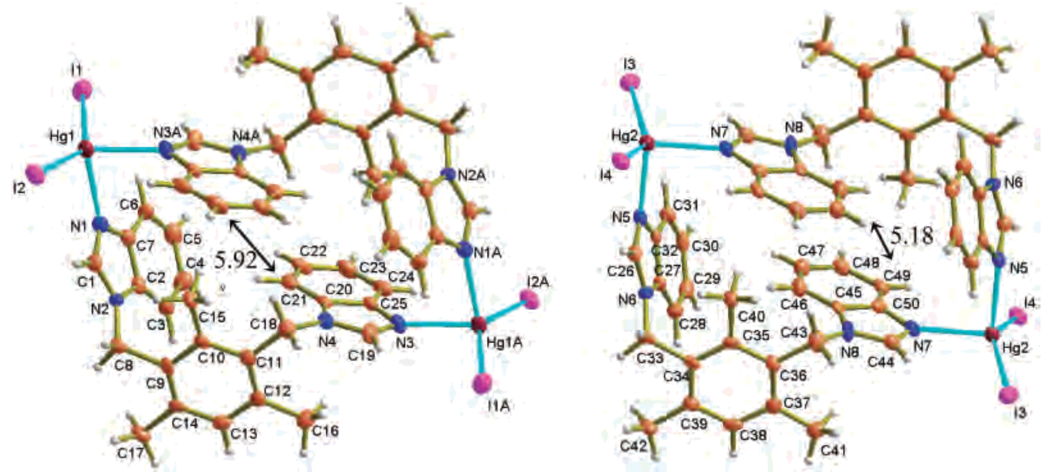

**Figure 3.** Two crystallographically independent metallacycles in **2** showing slightly different offsets of the two adjacent Bim rings.

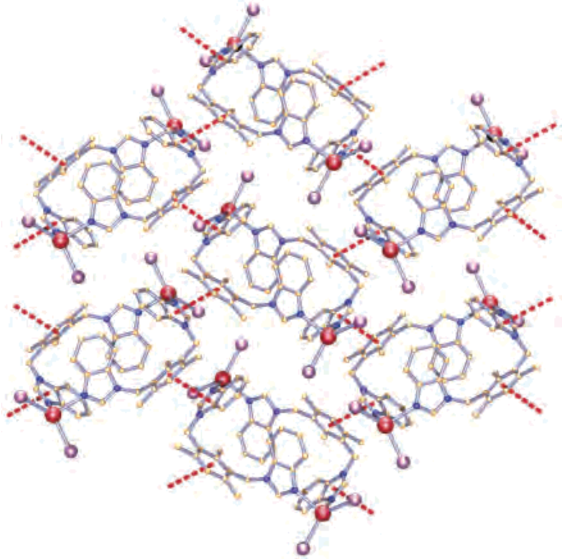

**Figure 4.** Two-dimensional network generated by $\pi-\pi$ interactions in **2**.

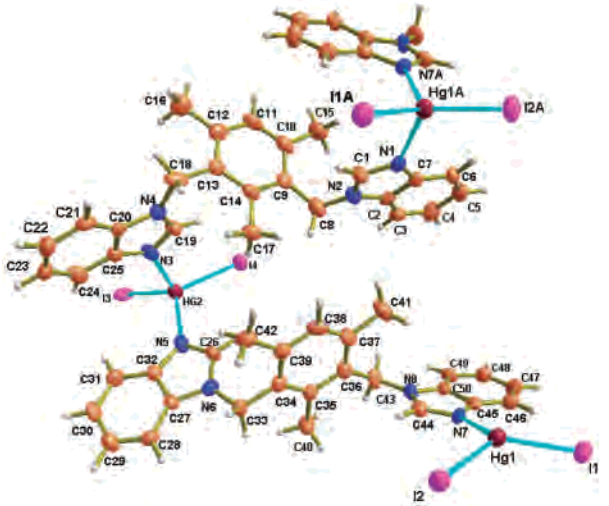

**Figure 5.** Molecular structure of **3** showing different coordination environments of the two structurally independent Hg(II) ions.

complete a distorted tetrahedral geometry. It is clearly shown in Figure 5 that the ligand takes on the *anti*-conformation in this structure to connect two crystallographically different

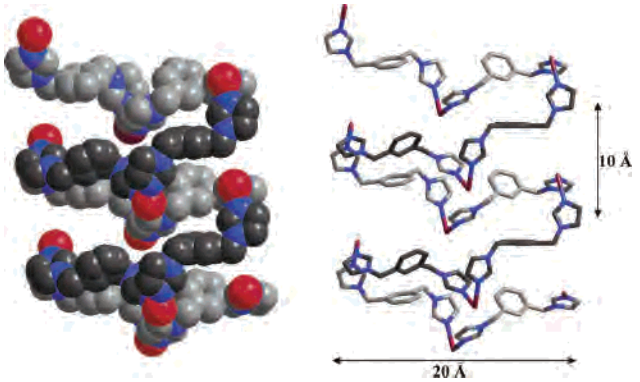

**Figure 6.** Helical structure in **3** shown in (a) space-filling mode and (b) wire mode with the screw diameter and pitch. For clarity only the skeleton atoms are retained.

Hg(II) ions. Two Bim rings are connected by Hg2 to adopt the same orientation, while those connected by Hg1 take on the opposite orientation. This connectivity has the effect that while Hg1 simply extends the span of the two ligands, Hg2 forces a turn in the chain. Such an arrangement endows the chain structure with an intrinsic helical sense. The repeating unit in this single-stranded helix consists of a pair of $HgI_2$ units and two bbimms ligands. As depicted in Figure 6, a fairly flattened, loose helix runs along the *b* axis with a pitch of about 10 Å; at the widest point the diameter of the helix equals 20 Å. Both left-handed and right-handed helicates coexist in the crystal to form a racemate, which is typical for synthetic single-stranded helicates derived from achiral starting materials[17,28] and different from *meso*-helical single-stranded structures found by us[16] and others.[14,16,29] It is worth noting that the coordination geometries of the two Hg(II) ions are quite similar to those in **2**, with all Hg−N and Hg−I bond distances and angles being almost identical (see Table

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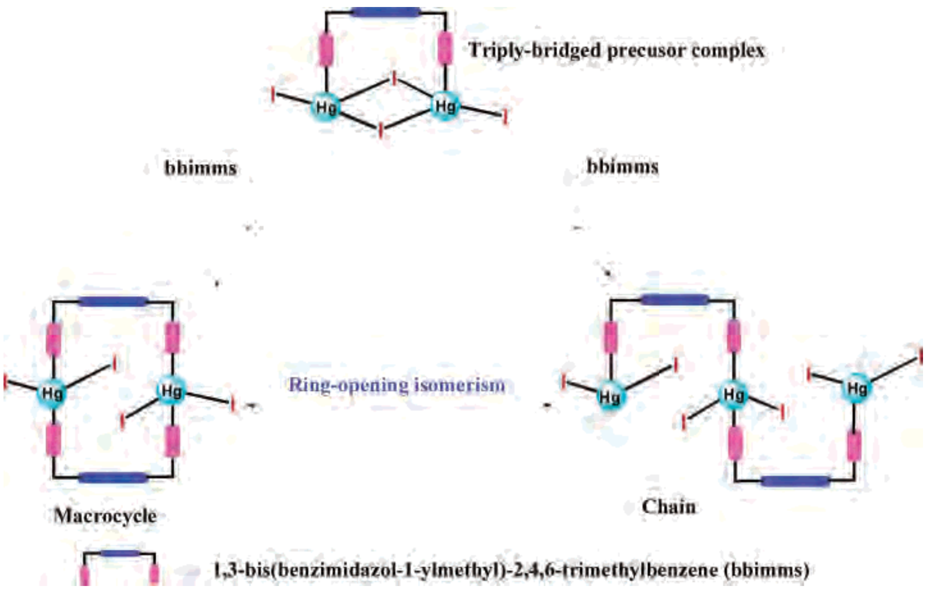
**Scheme 1**



2). This suggests that there is only a minor energy difference between **2** and **3** although they have completely different structural topologies.

**Supramolecular Isomerism.** Complexes **2** and **3** have the same stoichiometry with a 1:1 metal-to-ligand ratio that is different from the 2:1 metal-to-ligand ratio found in **1**. The transformation of dinuclear **1** into either the macrocyclic **2** or the polymeric **3**, therefore, requires the addition of one more ligand as well as changes in the structural topology involving the breaking and forming of bonds. Scheme 1 illustrates the potential structural interconversion between the three complexes. Since two Hg(II) ions in **1** are triply bridged (one ligand and two $I^-$ anions), the conversion into **2** or **3** has to involve the breaking of two Hg−I bonds and the subsequent formation of two Hg−N bonds in order for the two ring-openings and, in the case of **2**, the subsequent ring closure to proceed. In the transformation from **1** to **2**, the breaking of the two Hg−I bonds is compensated for by the formation of two Hg−N bonds, while in the transformation from **1** to **3** the breaking of the two Hg−I bonds will only approach full compensation with the formation of two Hg−N bonds in the limit of achieving an infinite polymeric structure. Therefore, for short chain lengths of **3**, there will exist a small energy difference between **2** and **3** and a structural interconversion between them may be affected by the adjustment of various factors that include the solvent and the temperature of the reaction (in addition to enthalpic considerations). This is apparent from the results of a crystal structure analysis: **2** and **3** exhibit very similar coordination geometries and bond parameters as discussed above. By contrast, complex **1** exhibits a different coordination environment. However, the fact that two longer bridging Hg−I bonds in **1** were replaced by one shorter terminal Hg−I and one Hg−N bond might account for the observation that **2** and **3** form readily at low metal-to-ligand ratios in the more soluble solvents. Since the formation of either oligomer or polymer can always be considered to start from the ring opened dinuclear **1** with addition of a ligand, **1** can reasonably be thought of as the precursor to macrocyclic **2** and polymeric **3**.

Complexes **2** and **3** can be described as supramolecular isomers: two structures containing the common building block [$HgI_2$(bbimms)] with almost the same structural parameters of the metal ions. The only difference is the conformation of the ligands, which leads to the closed structure of **2** and the extended structure of **3**. This is analogous to the supramolecular isomers described by Zaworotko[10] (molecular hexagon and zigzag chain) and by James[13] ([$M_2L_3$] cage and [$M_2L_3$]$_n$ polymer). This type of isomerism can be described in general terms as consisting of a closed discrete structure that is related to an extended structure by a ring-opening process. For example, a macrocyclic structure may open the ring to form either a larger macrocylce by insertion of a metal−ligand unit or an extended polymer by the repeated addition of a metal−ligand unit. For that reason, we feel that the term *ring-opening isomerism* provides a general description of such phenomena.[14,15]

We believe that consideration of this ring-opening isomerism concept helps to understand (and plan for) some of the structural diversity achievable in the field of supramolecular chemistry. One can of course argue that the closed and the extended complexes are actually different structures according to their stoichiometry; this however should not distract us from the potential usefulness of this concept[30,31] in the exploration of coordination polymers[2] and molecular architectures.[3] Clearly, we still have a lot to learn about the mechanisms by which closed metallacycles and extended coordination polymers form and potentially interconvert, but

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all this notwithstanding, this simple concept may well enhance our ability to predict and synthetically influence[8,11,32] the resulting structures.

## Conclusion

This work showed that three different but inherently related complexes, the dinuclear $[Hg_2(\mu\text{-}I)_2I_2(bbimms)]$ (**1**), the macrocyclic $[Hg_2I_4(bbimms)_2]$ (**2**), and the polymeric *catena*-$[HgI_2(bbimms)]_n$ (**3**), can be formed from the reaction of the semirigid ligand bbimms with $HgI_2$. Under carefully controlled conditions, single-phase products can be obtained and identified by XRD measurements. Complexes **2** and **3** are supramolecular isomers and can be considered to have been reactively derived from the precursor **1**. Structural exchange among these three complexes involves a ring-opening process, and consequently, the term ring-opening isomerism was used by us to describe this system and, in general, systems that contain both a closed and an extended structure based on the same building block. It is likely that the application of this concept to synthesis can enhance our ability to predict and synthetically influence the formation of potential supramolecular isomers.

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**Supporting Information Available:** Molecular structure of the ligand bbimms, powder X-ray diffraction patterns of complex **1**−**3** and their single-crystal diffraction simulations, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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