

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231232741>

# Anion-Induced Assembly of Different Mercury Coordination Complexes and DFT Calculations To Evaluate Weak Interactions between Similar Double-Helical Chains

ARTICLE in CRYSTAL GROWTH & DESIGN · AUGUST 2009

Impact Factor: 4.89 · DOI: 10.1021/cg900520j

---

CITATIONS

23

---

READS

21

13 AUTHORS, INCLUDING:



Ping-Hong Zhou

Fudan University

169 PUBLICATIONS 1,318 CITATIONS

SEE PROFILE



Peng Wang

Peking Union Medical College Hospital

89 PUBLICATIONS 3,177 CITATIONS

SEE PROFILE



Yu-He Kan

Huaiyin Normal University

137 PUBLICATIONS 1,052 CITATIONS

SEE PROFILE

# Anion-Induced Assembly of Different Mercury Coordination Complexes and DFT Calculations To Evaluate Weak Interactions between Similar Double-Helical Chains

Hong-Ping Zhou,<sup>\*,†</sup> Jian-Hui Yin,<sup>†</sup> Ling-Xia Zheng,<sup>†</sup> Peng Wang,<sup>†</sup> Fu-Ying Hao,<sup>†</sup>  
Wen-Qian Geng,<sup>†</sup> Xiao-Ping Gan,<sup>†</sup> Guo-Yi Xu,<sup>†</sup> Jie-Ying Wu,<sup>†</sup> Yu-Peng Tian,<sup>\*,†,‡,§</sup>  
Xu-Tang Tao,<sup>‡</sup> Min-Hua Jiang,<sup>‡</sup> and Yu-He Kan<sup>||</sup>

Department of Chemistry, Anhui University, and Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province, 230039 Hefei, P. R. China, State Key Laboratory of Crystal Materials, Shandong University, 250100 Jinan, P. R. China, State Key Laboratory of Coordination Chemistry, Nanjing University, 210093 Nanjing, P. R. China, and Department of Chemistry, Huaiyin Teachers College, 223300 Huaian, P. R. China

Received May 13, 2009; Revised Manuscript Received June 15, 2009

**ABSTRACT:** Self-assembly of the flexible ligand 3,6-di-(1,2,4-triazole-1-yl)-*N*-alkylcarbazole with  $\text{HgX}_2$  ( $\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{SCN}$ ) yielded a short series of new coordination polymer complexes (**1**, **3–6**) with double-helical, “W”, and single molecular structure of complex **2**. Weak interactions, including hydrogen bonds,  $\pi$ – $\pi$  interactions,  $\text{M} \cdots \text{X}$  bonds, and counteranions play significant roles in the final crystal structures. Three different DFT calculations are performed on the weak interaction between the two helical chains from the four different coordination polymers (complexes **1**, **4**, **5** and **6**). The outcomes show a similar trend, the larger the halogen anion, the weaker the interaction between the infinite chains, which provides useful information on the thermal stable properties of the infinite double-helical polymer chains.

## Introduction

The rational design and synthesis of coordination polymers is currently of great interest in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also because of their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, molecular sensing and heterogeneous catalysis.<sup>1–3</sup> These coordination polymers can be specially designed by the careful selection of metal cations with preferred coordination geometries, the nature of the anions, the structure of the connecting ligands, and the reaction conditions.<sup>4</sup> Among those mentioned above, the selection of anions is extremely important because changing the structures of the anions can control and adjust the topologies of coordination frameworks, even for structures containing the same spacer ligand and metal cation.<sup>5</sup>

To design and prepare molecular crystals having desired and predictable structures requires an understanding of the intermolecular interactions that link molecules together in the solid state. Generally it is through observing how these interactions are manifested in multiple known crystal structures that sufficient insight is gained to allow at least some predictability at the design stage of how they may be manifested in, and used to prepare, new molecular solids.<sup>6</sup> Successful noncovalent assembly of individual entities into complex structures with predetermined connectivities and stoichiometries, which normally relies on a tool-box containing intermolecular interactions such as hydrogen bonds,<sup>7</sup> metal halogen bonds,<sup>8</sup> and  $\pi$ – $\pi$  interactions,<sup>9</sup> are observed frequently in the solid state.

On the other hand, 1,2,4-triazole and its derivatives are very interesting ligands not only because they combine the coordination geometry of both pyrazoles and imidazoles with regard to

the arrangement of their three heteroatoms but also because they can be used as spin crossover materials, which has potential application in information storage.<sup>10</sup> Recently using the functional flexible ligand **L**<sup>1</sup>, 3,6-di-(1,2,4-triazol-1-yl)-*N*-ethylcarbazole, we reported Co(II) complexes with interesting framework structures and supramolecular architectures.<sup>11</sup> Therefore, in this work, we also designed and synthesized the other new functional flexible triazole ligand **L**<sup>2</sup>, 3,6-di-(1,2,4-triazol-1-yl)-*N*-hexylcarbazole, and considered the spherical  $d^{10}$  configuration and softness of mercury(II) that is particularly suited for the construction of coordination polymers and networks.<sup>12–14</sup> A flexible coordination environment associated with  $d^{10}$  configuration can lead to mercury complexes with variable geometries from tetrahedral through trigonal bipyramidal and tetragonal pyramidal to octahedral and often leads to severe distortion from the ideal polyhedron. This coupled with the general lability of the mercury complexes can lead to coordination polymers of varieties of architectures, ranging from one-, two-, to three-dimensional (1D, 2D, to 3D) networks.

In this paper, a short series of new coordination polymer complexes (**1**, **3–6**) with double-helical, “W”, and single molecular structure of complex **2** based on the reaction of **L**<sup>1</sup>, **L**<sup>2</sup> and mercury(II) ions were obtained by self-assembled under room temperature. Mindful of the similar double-helical structure of four different coordination polymers (complexes **1**, **4**, **5** and **6**), we calculated the weak interactions between the two helical chains through density functional theory (DFT) calculations (ADF). Although the interaction between the chains is different from one to another, the outcomes show the weak interaction between the infinite chains quite depends on the  $\text{C–H} \cdots \text{X}$ .

## Experimental Section

**Materials and Physical Measurements.** The reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded with a Nicolet FT-IR Nexus 870 instrument (KBr disks) in the 400–4000  $\text{cm}^{-1}$  region.

\* Corresponding authors. E-mail: zhpzhp@263.net.

<sup>†</sup> Department of Chemistry, Anhui University, and Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province.

<sup>‡</sup> Shandong University.

<sup>§</sup> Nanjing University.

<sup>||</sup> Huaiyin Teachers College.

Table 1. Crystallographic Data for L<sup>1</sup>, L<sup>2</sup> and 1–6

complex	L <sup>1</sup>	L <sup>2</sup>	1	2	3	4	5	6
empirical formula	C <sub>18</sub> H <sub>15</sub> N <sub>7</sub>	C <sub>22</sub> H <sub>23</sub> N <sub>7</sub>	C <sub>20</sub> H <sub>15</sub> HgN <sub>9</sub> S <sub>2</sub>	C <sub>36</sub> H <sub>30</sub> HgI <sub>2</sub> N <sub>14</sub>	2(C <sub>24</sub> H <sub>23</sub> HgN <sub>9</sub> S <sub>2</sub> )•0.5(C <sub>2</sub> H <sub>8</sub> O <sub>2</sub> )	C <sub>22</sub> H <sub>23</sub> HgI <sub>2</sub> N <sub>7</sub>	C <sub>22</sub> H <sub>23</sub> Br <sub>2</sub> HgN <sub>7</sub>	C <sub>22</sub> H <sub>23</sub> Cl <sub>2</sub> HgN <sub>7</sub>
formula mass	329.37	385.47	646.12	1113.13	1436.53	839.86	745.88	656.96
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 21	<i>P</i> 1	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> [Å]	14.822(3)	16.573(5)	8.4300(17)	4.3396(17)	7.3832(12)	10.635(5)	10.769(5)	10.8306(8)
<i>b</i> [Å]	12.118(2)	12.057(5)	22.100(4)	15.280(6)	12.720(2)	14.016(5)	13.245(5)	12.8699(9)
<i>c</i> [Å]	8.8580(18)	10.417(5)	13.357(4)	27.243(11)	14.480(2)	17.117(5)	17.086(5)	17.0548(13)
α [deg]	90	90	90	90	100.387(3)	90	90	90
β [deg]	100.00(3)	107.518(5)	122.80(2)	91.070(5)	92.247(3)	90.453(5)	90.876(5)	91.4380(10)
γ [deg]	90	90	90	90	96.202(3)	90	90	90
<i>V</i> [Å <sup>3</sup> ]	1566.8(5)	1985.0(14)	2091.7(8)	1806.2(12)	1327.4(4)	2551.4(17)	2436.8(16)	2376.5(3)
<i>Z</i>	4	4	4	2	1	4	4	4
<i>D</i> <sub>calcd</sub> [g·cm <sup>−3</sup> ]	1.396	1.29	2.052	2.047	1.797	2.186	2.033	1.836
θ <sub>range</sub> [deg]	2.18–25.00	2.12–25.00	1.84–25.00	0.75–26.00	1.64–25.50	1.88–25.00	1.89–25.00	1.88–26.00
total no. of data	2717	3494	3677	6882	4872	4493	4290	4641
no. of unique data	1376	1927	2903	5468	4064	3428	3237	3750
no. of params refined	227	294	290	481	371	290	290	290
<i>R</i> <sub>1</sub>	0.0813	0.0782	0.0319	0.0438	0.0375	0.0323	0.0323	0.0230
<i>wR</i> <sub>2</sub>	0.2375	0.2103	0.1054	0.1122	0.0853	0.0491	0.0515	0.0608
GOF	1.043	1.214	0.903	0.997	1.079	1.251	1.206	0.981

Table 2. Selected Intra- and Intermolecular Bond Lengths (Å) and Angles (deg) for 1–6

Complex 1			
Hg1–N1	2.353(4)	N1–Hg1–S1	111.35(13)
Hg1–N7	2.365(5)	N7–Hg1–S1	102.81(14)
Hg1–S1	2.408(2)	N1–Hg1–S3	101.29(13)
Hg1–S3	2.411(2)	N7–Hg1–S3	108.88(13)
N1–Hg1–N7	92.53(17)	S1–Hg1–S3	132.86(8)
Complex 2			
Hg1–N3	2.391(11)	I2–Hg1–I1	154.16(4)
Hg1–I2	2.6124(13)	N3–Hg1–I1	87.7(3)
Hg1–I1	2.6516(11)	I2A–Hg1A–I1	95.91(4)
I1–Hg2	3.3144(14)	I1–Hg1A–I1A	92.66(4)
N3–Hg1–I2	108.2(3)	Hg1–I1–Hg1A	92.66(4)
N3–Hg1–I1	96.5(3)		
Complex 3			
Hg1–N3	2.239(5)	N7–Hg1–S1	99.60(13)
Hg1–N7	2.435(5)	N3–Hg1–S2	111.7(4)
Hg1–S1	2.4472(17)	N7–Hg1–S2	106.9(3)
Hg1–S2	2.467(17)	S1–Hg1–S2	111.9(3)
Hg1–S2'	2.515(17)	N3–Hg1–S2'	107.1(4)
N7–Hg1	2.435(5)	N7–Hg1–S2'	100.1(3)
N3–Hg1–N7	90.95(17)	S1–Hg1–S2'	119.0(3)
N3–Hg1–S1	129.60(14)	S2–Hg1–S2'	8.6(3)
Complex 4			
Hg1–N6	2.409(5)	I2–Hg1–N6	74.0(5)
Hg1–N4	2.430(4)	I1–Hg1–N6	83.7(5)
Hg1–I2	2.6351(10)	N4–Hg1–N6	18.0(5)
Hg1–I1	2.6456(9)	I2–Hg1–N6	121.8(5)
N4–Hg1–N6	177.8(5)	I1–Hg1–N6	80.5(5)
Complex 5			
Hg1–N5	2.381(4)	N5–Hg1–N2	86.61(15)
Hg1–N	2.2402(4)	N5–Hg1–Br2	110.03(11)
Hg1–Br2	2.4744(11)	N2–Hg1–Br2	104.06(11)
Hg1–Br1	2.4885(10)	N5–Hg1–Br1	104.93(11)
Br2–Hg1–Br1	139.29(3)	N2–Hg1–Br1	98.09(11)
Complex 6			
Cl–Hg1	2.3665(11)	Cl2–Hg1–Cl1	140.68(5)
Cl2–Hg1	2.3463(11)	Cl2–Hg1–N7	110.35(9)
Hg1–N7	2.375(3)	Cl1–Hg1–N7	103.90(9)
Hg1–N3	2.400(3)	Cl2–Hg1–N3	103.74(7)
N7–Hg1–N3	86.32(10)	Cl1–Hg1–N3	97.04(7)

<sup>1</sup>H spectra were performed on Bruker 400 MHz Ultrashield spectrometer and are reported as parts per million (ppm) from TMS (δ).

**Synthesis. Preparation of the Ligand L<sup>1</sup>.** L<sup>1</sup> was synthesized by a two-step reaction according to the method of our previous paper.<sup>11</sup>

**Preparation of the Ligand L<sup>2</sup>.** 0.24 g (1.20 mmol) of CuI, 0.54 g (2.70 mmol) of 1,10-phenanthroline and 6 mL of DMF were added to a three-necked flask equipped with a magnetic stirrer and a reflux

condenser. This mixture was refluxed for 5 min in an oil bath at 140 °C and cooled to room temperature, and then 5.04 g (70 mmol) of 1,2,4-triazole, 8.06 g (72 mmol) of *t*-BuOK and 9 mL of DMF were added and heated to 140 °C for 0.5 h; 3.02 g (6 mmol) of 3,6-diiodo-9-hexylcarbazole and 18-crown-6 (little) were added and heated to 190 °C for 4 h, and cooled to room temperature. The residue was extracted with 500 mL of dichloromethane, washed three times with distilled water, and dried with anhydrous magnesium sulfate. Then it was filtered and concentrated; the recrystallization from ethyl acetate produced gray solids. Yield: 1.25 g (54%). IR (KBr cm<sup>−1</sup>): 3119 w, 2955 w, 2927 w, 2825 w, 1513 s, 1485 m, 1452 m, 1276 m, 1147 w, 985 w, 871 w, 805 w, 673 m. <sup>1</sup>H NMR (DMSO, 400 MHz) δ/ppm: 0.81 (t, 3H, CH<sub>3</sub>), 1.31 (m, 6H, CH<sub>2</sub>), 1.82 (t, 2H, CH<sub>2</sub>), 4.54 (t, 2H, CH<sub>2</sub>), 7.98 (d, 2H, CH), 7.85 (d, 2H, CH), 8.27 (s, 2H, CH), 8.74 (s, 2H, CH), 9.28 (s, 2H, CH). MS, *m/z*: 385.19 (M<sup>+</sup>), 314.10 [ (M − *n*-C<sub>5</sub>H<sub>11</sub>)<sup>+</sup> ]. Anal. Calcd (%) for C<sub>22</sub>H<sub>23</sub>N<sub>7</sub> (385.47): C, 68.55; H, 6.01; N, 25.44. Found: C, 68.41; H, 5.90; N, 25.89%.

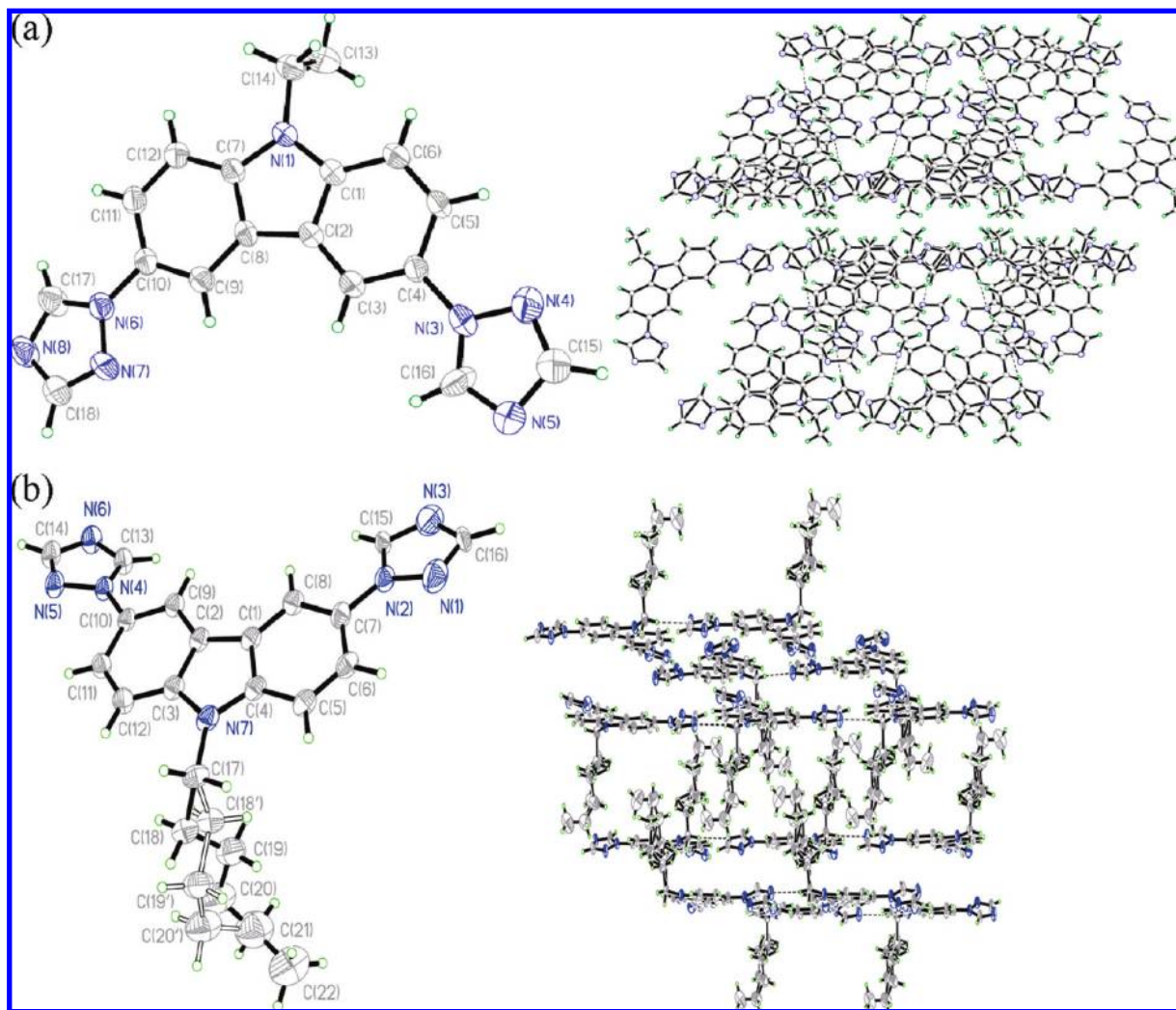
**Preparation of Complexes 1–6.** [Hg(L<sup>1</sup>(SCN)<sub>2</sub>)<sub>∞</sub>] (1). Hg(SCN)<sub>2</sub> (9.50 mg, 0.03 mmol) in 10 mL of MeOH was layered onto a solution of L<sup>1</sup> (9.88 mg, 0.03 mmol) in 5 mL of CHCl<sub>3</sub> and stood for ten days to give colorless block single crystals. Yield: 15.89 mg, 82%. IR (KBr cm<sup>−1</sup>): 3114 w, 2981 w, 2123 vs, 1513 s, 1485 m, 1278 m, 1247 w, 1163 w, 1142 s, 975 m. Anal. Calcd (%) for C<sub>20</sub>H<sub>15</sub>HgN<sub>9</sub>S<sub>2</sub> (646.12): C, 37.18; H, 2.34; N, 19.51. Found: C, 37.32; H, 2.56; N, 19.36%.

[Hg(L<sup>1</sup>I<sub>2</sub>)L<sup>1</sup>] (2). L<sup>1</sup> (19.74 mg, 0.06 mmol) and HgI<sub>2</sub> (13.62 mg, 0.03 mmol) were dissolved in 25 mL of acetone (10 mL) and refluxed for 2 h at 70 °C. The solution was cooled and filtered, and it stood for several days to give white needle single crystals. Yield: 25.05 mg, 75%. IR (KBr cm<sup>−1</sup>): 3125 w, 2972 w, 3067 w, 1509 s, 1488 s, 1278 s, 1147 s, 989 w, 844 w, 671 s. Anal. Calcd for C<sub>36</sub>H<sub>30</sub>HgN<sub>14</sub>I<sub>2</sub> (1113.13): C, 38.84; H, 2.72; N, 17.62. Found: C, 38.30; H, 2.96; N, 17.27%.

[2(Hg(L<sup>2</sup>(SCN)<sub>2</sub>)•CH<sub>3</sub>OH)]<sub>∞</sub> (3). L<sup>2</sup> (11.56 mg, 0.03 mmol) and Hg(SCN)<sub>2</sub> (9.50 mg, 0.03 mmol) were dissolved in 25 mL of methanol and refluxed for 2 h at 70 °C. The solution was cooled and filtered, and it stood for several days to give light yellow cube single crystals. Yield: 34.91 mg, 81%. IR (KBr cm<sup>−1</sup>): 3091 m, 2926 s, 2859 w, 2113 vs, 1513 s, 1486 s, 1278 m, 1139 s, 976 s, 807 m, 671 s. Anal. Calcd for C<sub>49</sub>H<sub>50</sub>Hg<sub>2</sub>N<sub>18</sub>OS<sub>4</sub> (1436.53): C, 40.97; H, 3.51; N, 17.55. Found: C, 40.48; H, 3.69; N, 17.78%.

[Hg(L<sup>2</sup>I<sub>2</sub>)<sub>∞</sub>] (4). L<sup>2</sup> (11.56 mg, 0.03 mmol) and HgI<sub>2</sub> (13.62 mg, 0.03 mmol) were dissolved in 25 mL of ethyl acetate and refluxed for 2 h at 70 °C. The solution was cooled and filtered, and it stood for several days to give yellow cube single crystals. Yield: 19.65 mg, 78%. IR (KBr cm<sup>−1</sup>): 3131 m, 3107 m, 2950 s, 2921 s, 2850 s, 1509 vs, 1487 s, 1280 vs, 1285 m, 1141 s, 1070 w, 1046 m, 975 s, 854 m, 670 s, 587 w. Anal. Calcd for C<sub>22</sub>H<sub>23</sub>HgI<sub>2</sub>N<sub>7</sub> (839.86): C, 31.46; H, 2.76; N, 11.67. Found: C, 31.79; H, 2.58; N, 12.03%.

[Hg(L<sup>2</sup>Br<sub>2</sub>)<sub>∞</sub>] (5). L<sup>2</sup> (11.56 mg, 0.03 mmol) and HgBr<sub>2</sub> (10.08 mg, 0.03 mmol) were dissolved in 25 mL of CH<sub>3</sub>CN and refluxed for 2 h at 70 °C. The solution was cooled and filtered, and it stood for three weeks to give yellow grain single crystals. Yield: 19.02 mg, 85%. IR (KBr cm<sup>−1</sup>): 3135 m, 3103 m, 2949 m, 2923 m, 2853 m, 1512 s, 1488 s, 1358 m, 1281 s, 976 s, 856 m, 670 s, 587 w. Anal. Calcd for



**Figure 1.** (a) ORTEP diagram showing the structure of compound  $L^1$  and  $L^2$  with thermal ellipsoids at the 30% probability level and the atom-labeling scheme. (b) Molecular packing of compound  $L^1$  and  $L^2$ .

$C_{22}H_{23}HgBr_2N_7$  (745.88): C, 35.43; H, 3.11; N, 13.15. Found: C, 35.98; H, 3.36; N, 13.40%.

$[HgL^2Cl_2]_n$  (6).  $L^2$  (11.56 mg, 0.03 mmol) and  $HgCl_2$  (8.13 mg, 0.03 mmol) were dissolved in 25 mL of THF refluxed for 2 h at 70 °C. The solution was cooled and filtered, and it stood for several days to give yellow grain single crystals. Yield: 15.96 mg, 81%. IR (KBr  $cm^{-1}$ ): 3102 m, 2948 m, 2922 m, 2852 m, 1511 m, 1487 s, 1280 m, 1241 w, 1142 s, 975 s, 855 s, 670 s. Anal. Calcd for  $C_{22}H_{23}HgCl_2N_7$  (656.96): C, 40.22; H, 3.53; N, 14.92. Found: C, 40.03; H, 3.65; N, 14.68%.

**X-ray Crystallography.** Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of unit cell parameters and data collections were performed with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods using SHELXL-97.<sup>15</sup> The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on  $F^2$ . The hydrogen atoms were added theoretically and riding on the concerned atoms. Crystallographic crystal data and processing parameters for  $L^1$ ,  $L^2$  and complexes 1–6 are shown in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC-727518, 721583 (for  $L^1$  and  $L^2$ ) and CCDC-721584, 726904, 726903, 721581, 721582, 726905 (1, 2, 3, 4, 5, 6 for the metal complexes) contain the supplementary crystallographic data for this

paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Computational Details.** DFT is a simple, widely applicable, and high efficient vs time-consuming method. One better DFT even reproduces the results better than MP2 calculation. Our calculations<sup>16</sup> were carried out with the Amsterdam Density Functional (ADF-2008) program. The weak interaction between two infinite one-dimensional chains can be simply thought to be the sum of the weak interaction between repeat units cut from the infinite ones, and the more the repeat units used, the more accurate outcomes obtained. In our previous work, the outcomes show that correlation energy between two repeat units could stand for the energy between infinite chains, but we must make sure that the repeat units contain all the interaction between the two chains.<sup>17</sup> Five units are selected to interact with another five units nearby. Three different functionals, BPW91,<sup>18</sup> BP86<sup>19</sup> and BLYP,<sup>20</sup> respectively, are used to ensure the validity of the functional itself. The selected two fragments (Figure 8) were cut out directly from the CIF data without optimization. Fragment analysis is performed on two relative fragments for investigation on the attractive energy between them. Large atom basis sets TZP are used to ascribe all the atoms here. A frozen core approximation was used to treat the core electrons: (1s) for C and N, (4p) for I, (3p) for Br and (2p) for Cl, (4d) for Hg. Relativistic effects were accounted with the ZORA approximation.<sup>21</sup>

## Results and Discussion

**Structure of Ligands. Structure of  $L^1$ .** The X-ray crystallographic analysis revealed that ligand  $L^1$  crystallizes in the

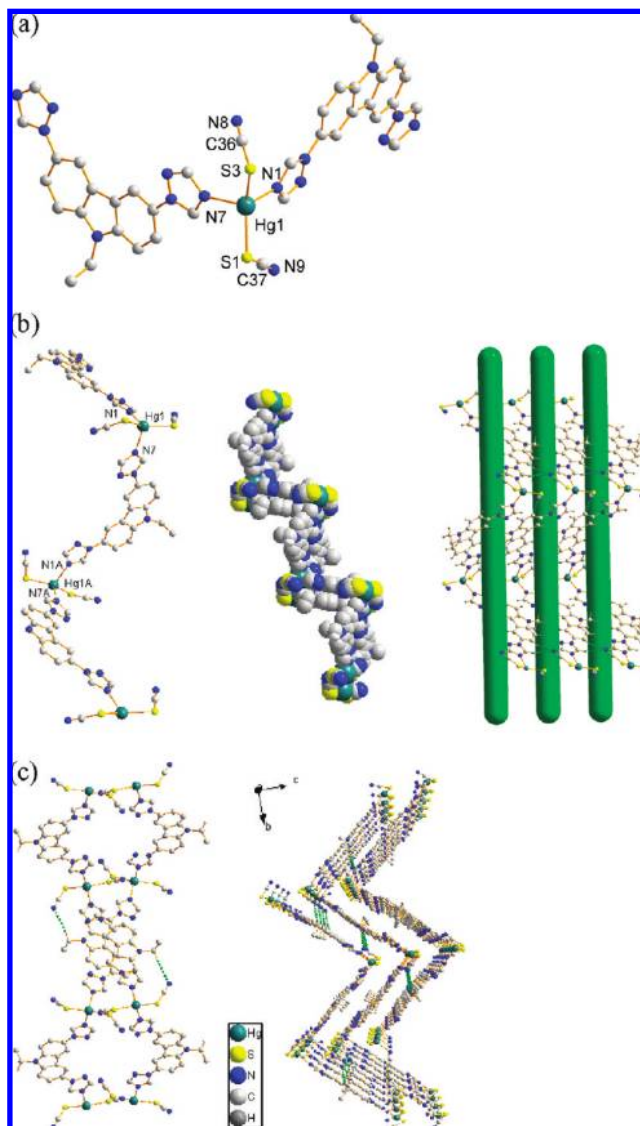


monoclinic form with space group  $P2(1)/c$ . The structure of ligand  $L^1$ , including two triazole rings and an ethyl-carbazole unit, possesses perfect planarity. The dihedral angles between the two triazole rings and the central carbazole unit range from  $3.87^\circ$  to  $12.25^\circ$ . The adjacent molecules are stacked through strong  $C-H\cdots N$  interactions between ethyl  $C-H$  and triazole  $N$  ( $C-H\cdots N$  is  $3.583\text{ \AA}$  and the angle is  $169.75^\circ$ ).

**Structure of  $L^2$ .** The ligand  $L^2$  crystallizes in the monoclinic form with space group  $P2(1)/c$ . The structure of  $L^2$ , including two triazole rings and a carbazole unit, with a disordered hexyl group, also possesses good planarity. The dihedral angles between the two triazole rings and the central carbazole unit range from  $12.42^\circ$  to  $25.83^\circ$ . The adjacent molecules are also stacked through strong  $C-H\cdots N$  interactions between hexyl  $C-H$  and triazole  $N$  ( $C-H\cdots N$  is  $3.512\text{ \AA}$  and the angle is  $168.31^\circ$ ). Figure 1 shows the structures of ligands  $L^1$ ,  $L^2$  and their packing diagrams.

**Structure of  $[HgL^1(SCN)_2]_\infty$  (**1**).** The metal coordination polymer  $[HgL^1(SCN)_2]_\infty$  crystallizes in the monoclinic form with space group  $P2(1)/c$  as shown in Figure 2, which possesses perfect planarity with the dihedral angles between two triazole rings and the central carbazole unit to be  $2.45^\circ$  and  $9.26^\circ$ , respectively. Compared to ligand  $L^1$ , the metal complex exhibits better planarity in order to meet the geometrical preference of the metal centers. The single-crystal analysis of **1** reveals that the metal ion is four-coordinated completed via two triazoles from  $L^1$  and two sulfur atoms from  $SCN^-$  anions. Each bond angle around the mercury atom is in the range  $92.53(17)$ – $132.86(8)^\circ$ , indicating a quite distorted tetrahedral geometry. Selected bond lengths and angles are listed in Table 2. The triazole rings are almost perpendicularly twisted relative to each other, presumably to minimize the steric hindrance between them.

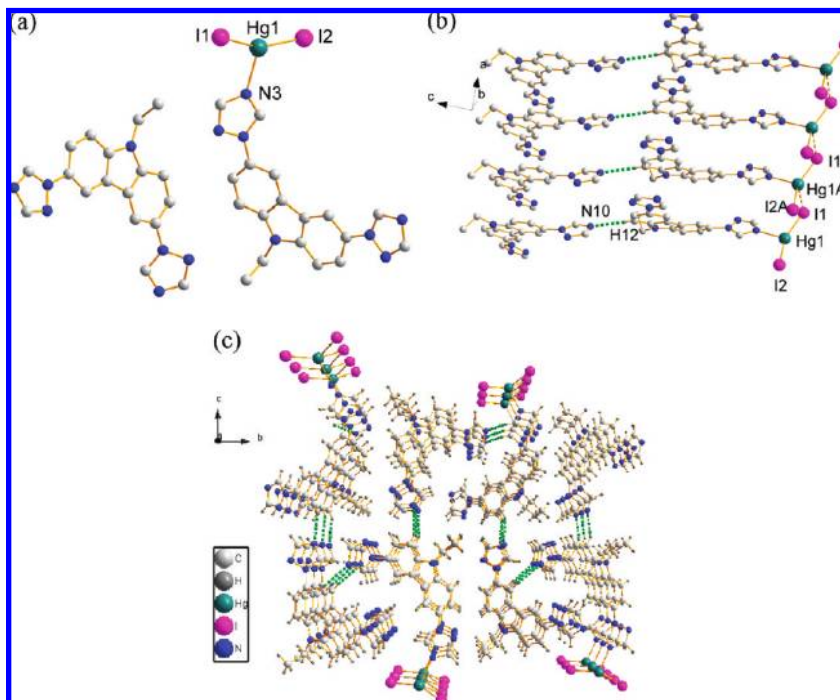
It is shown in Figure 2b (left) that the ligand links two crystallographically different  $Hg(II)$  ions. Two triazole rings are connected by  $Hg1$  to adopt the same orientation, while those connected by  $Hg1A$  taken on the opposite orientation. This connectivity extends the span of the two ligands and 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 consisting of the  $Hg(SCN)_2$  unit and the ligand. The width of the helix is calculated to be  $12.21\text{ \AA}$ , and the pitch is  $10.05\text{ \AA}$  (neighboring  $Hg\cdots Hg$  distances at the same phase). Right-handed helicates connect through three kinds of hydrogen bonds as seen from Figure 2(b). Two are between nitrogen atoms of  $SCN^-$  anion and carbazole unit  $C-H$  with the distances of  $3.287\text{ \AA}$ ,  $3.326\text{ \AA}$  and angles of  $154.2^\circ$ ,  $160.3^\circ$ , respectively. One is between  $SCN^-$  anion and triazole ring in an adjacent chain ( $C-H\cdots N = 3.780\text{ \AA}$  and the angle to be  $172.6^\circ$ ). Therefore a 2-D network is generated along the  $a$ -axis. The left-handed helix also is connected through weak interactions in this way. Unlike most double-helical complexes,<sup>22</sup> the adjacent right-handed and neighboring left-handed helical chains are not entangled together but interact through  $\pi-\pi$  stacking interactions with the shortest distance of  $3.425\text{ \AA}$ , and there is some evidence of a weak interaction  $C-H\cdots N$  between ethyl and  $SCN^-$  anion to be  $3.662\text{ \AA}$ . Both contribute to the stabilizing 3-D architecture along the  $b$ -axis. What is interesting here is the stacking manner of double-helicates. They are arranged as “footsteps” extended upward, different from common planar double-helicates. Due to the coexistence of right-handed and left-handed helical chains, the whole crystal is mesomeric and does not exhibit chirality. Double helical compounds always contain the same coordina-



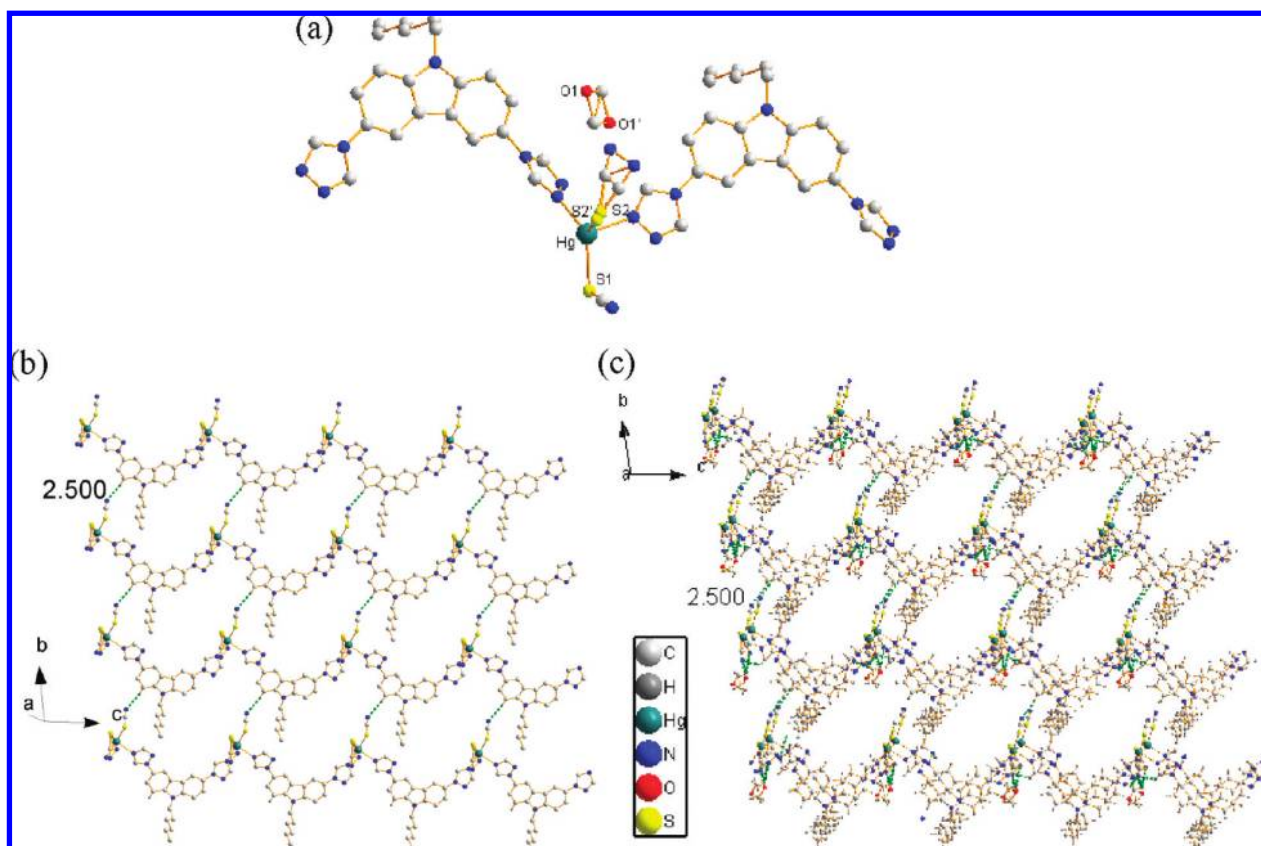
**Figure 2.** (a) Coordination environments of Hg with the atom numbering scheme; H atoms were omitted for clarity. (b) Single right-handed helical chain of **1** alongside (left), double helical structure stacked like upward footsteps (middle) and 2-D framework through  $C-H\cdots N$  interactions (right; green dashed line) along the  $a$ -axis direction. (c) The 3-D architecture is connected by the weak  $C-H\cdots N$  interactions and  $\pi-\pi$  interactions.

tion, supramolecular or covalent chains,<sup>23</sup> and we found the unique double helical chains constructed via both coordination and supramolecular chains. It is noted that it may not be possible for the nonchiral ligand and metal ion to produce a helical structure that is exclusively right-handed or left-handed, which always results in a racemic mixture of right- and left-handed helical products.

**Structure of  $[Hg(L^1)_2]L^1$  (**2**).** Compared to **1**,  $Hg(II)$  locates in a three coordination environment chelating with two iodine atoms and only one N atom from ligand  $L^1$ , accompanied by a free  $L^1$  as seen from Figure 3(a). The dihedral angles between two triazole rings and the central carbazole unit of metal complex are  $9.01^\circ$  and  $43.41^\circ$ , respectively, while those in the free ligand to be  $9.67^\circ$  and  $44.19^\circ$  show a severe distortion due to some weak interactions with adjacent molecules. N atom contributes the formation of a  $C-H\cdots N$  hydrogen bond between the free ligand and metal complex with the distance of  $H\cdots N$  to be  $2.610\text{ \AA}$  (the distance of  $C-H\cdots N$  is  $3.478\text{ \AA}$



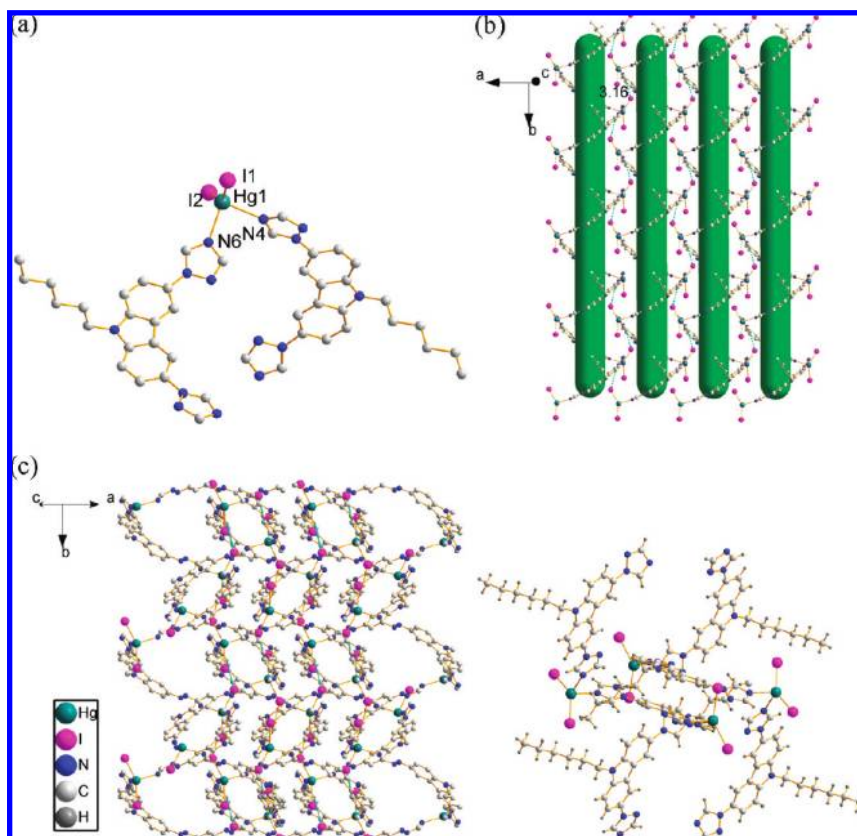
**Figure 3.** (a) Coordination environments of Hg with the atom numbering scheme; H atoms were omitted for clarity. (b) The 1-D framework of complex **2** showing Hg $\cdots$ I (yellow) and the weak C–H $\cdots$ N (green) interactions along the *a*-axis. Only H atoms that were from hydrogen-bonds were saved. (c) The 2-D architecture is connected by two kinds of C–H $\cdots$ N (distances between H and N: green) interactions.



**Figure 4.** (a) Coordination environments of Hg with the atom numbering scheme; H atoms were omitted for clarity. (b) The 2-D framework of complex **3** showing the weak C–H $\cdots$ N (green) interactions along the *b*-axis. Only H atoms that were from hydrogen bonds were saved. (c) The 3-D architecture is connected by the weak C–H $\cdots$ N and O–H $\cdots$ N interactions.

and the angle is 155.54°). Besides, along the *a*-axis in Figure 3(b), there is an additional weak interaction between mercury

and iodine of distance to be 3.314 Å, which indicates the formation of 1-D chains. Taking the van der Waals radii of Hg



**Figure 5.** (a) Coordination environments of Hg with the atom numbering scheme. (b) The 2-D framework of complex **3** showing the weak C–H···I (green) interactions along the *a*-axis. Only H atoms that were from hydrogen bonds were saved. (c) The 3-D architecture is stacked through  $\pi$ – $\pi$  interactions.

and I to be 1.70 and 2.15 Å,<sup>24</sup> respectively, any Hg···I contact less than 3.85 Å may therefore potentially be considered significant. Therefore we presume the 1-D chain built through Hg···I weak interaction. To our best knowledge, the mercury(II) ion is made softer by iodine and shows strong preference for softer donor with large atom size such as the iodine atoms and weak preference for nitrogen atoms.<sup>17</sup> That is probably why a free ligand existed. Of particular interest here is the generation of 2-D architecture stacked along the *b*-axis in pairs. If we treat the moiety in Figure 3(a) as a unit, then every unit arranged one by one in a reverse way to build a 2-D framework as shown in Figure 3(c). Two sets of hydrogen bonds cannot be neglected in forming and stabilizing the packing units. One is between triazole N and carbazole C, with distance of 3.477 Å and angle of 164.4°; the other is between two adjacent triazole rings with distance of 3.279 Å and angle to be 160.4°.

Making a comparison between **1** and **2**, only the anion is different, but the coordination modes vary, which results in various supramolecular structures. Complex **2** can only shape into 2-D topology structure due to the Hg···I and C–H···N weak interactions, while **1** forms into a 3-D architecture through different weak interactions and exhibits double helical structure. From above, we can safely propose that the selection of the anion can definitely adjust the topologies of coordination frameworks, even for structures containing the same metal cation and spacer ligand.

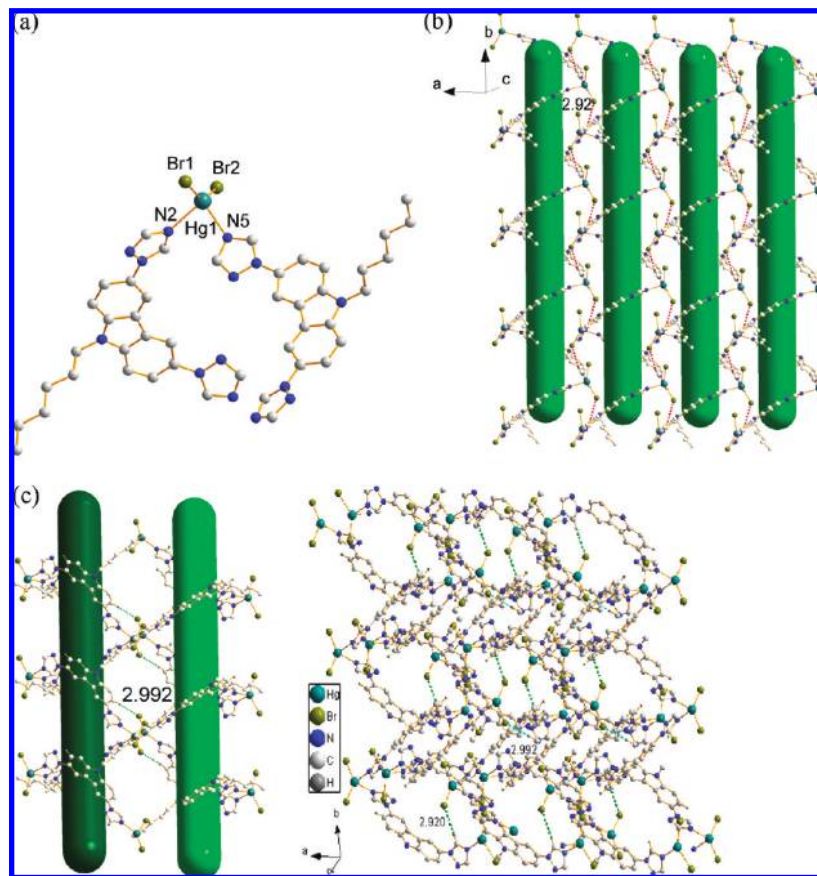
**Structure of [2{HgL<sub>2</sub>(SCN)<sub>2</sub>}·CH<sub>3</sub>OH]<sub>∞</sub> (**3**).** Complex **3** crystallizes in the triclinic form with space group *P*1̄, and the local coordination geometry around the Hg(II) atom in **3** is also similar to that in **1**. As shown in Figure 4 (a), Hg ion is four-coordinated with two SCN<sup>−</sup> anions, with one of them disordered,

and two triazole rings to form a distorted tetrahedral geometry, and a free disordered solvent methanol molecule. The dihedral angles between two triazole rings and the central carbazole unit are 9.15° and 50.09°, which shows a great distortion after coordination. As shown in Figure 4(b), the infinite 1-D chains along the crystallographic *c*-axis connected through coordination bonds are shaped as “W” unlike the double-helix in **1**. The “W” chains stacked along the *b*-axis through C–H···N hydrogen bonds to generate a netlike 2-D framework in a good order with all hexyl groups adopting the same direction (C–H···N = 3.415 Å, H···N = 2.500 Å and the angle is 167.8°). The extended 2-D layers linked through hydrogen bonds seem to show pseudo cavities with the distances of adjacent Hg ions to be 12.72 Å. Functionally, it is noted that the free methanol molecules get stabilized by forming interchain hydrogen bonds, between disordered methanol and SCN<sup>−</sup> anion. These weak interactions (C–H···N = 3.355 Å, O–H···N = 2.664 Å)<sup>25</sup> play a vital role in determining the crystal packing and in the construction of the extended 3-D supramolecular network.

Taking complexes **1** and **3** into account, we use the same Hg(SCN)<sub>2</sub> inorganic salts, and make the length of the terminal group of the ligands different. Although the coordination modes are the same, the supramolecular structures vary. Complex **1** takes on a 3-D supramolecular structure based on double-helicates while **3** possesses 1-D “W” chains. Only a little change in the structure of connecting ligands leads to different topologies of the coordination polymers.

**Structure of [HgL<sup>2</sup>I<sub>2</sub>]<sub>∞</sub> (**4**).** The coordination environment of complex **4** is also a traditional distorted tetrahedral geometry similar to those of complexes **1** and **3**. The mercury ion connected two ligands L<sup>2</sup> and two iodine atoms. The X-ray





**Figure 6.** (a) Coordination environments of Hg with the atom numbering scheme. (b) The 2-D framework of complex **5** showing the weak C–H···Br (red) interactions ( $\text{H}\cdots\text{Br} = 2.920 \text{ \AA}$ ) along the  $a$ -axis. Only H atoms that were from hydrogen bonds were saved. (c) The 3-D architecture is connected by the weak C–H···Br (blue) ( $\text{H}\cdots\text{Br} = 2.992 \text{ \AA}$ ) and  $\pi$ – $\pi$  interactions.

single crystal reveals that the metal complex crystallizes in the monoclinic form with space group  $P(21)/c$ . A single-stranded right-handed helix is formed through coordination bonds along the  $b$ -axis just like that in complex **1**, as shown in Figure 5(b). Adjacent right-handed helical chains linked through C–H···I hydrogen bonds ( $\text{C–H}\cdots\text{I} = 4.02 \text{ \AA}$ ,  $\text{H}\cdots\text{I} = 3.16 \text{ \AA}$  and the angle to be  $154.35^\circ$ )<sup>17,26</sup> generates a 2-D framework along the  $a$ -axis. Left-handed helical chains were constructed in the same way. Therefore, the double-helical structure was given by evidence of  $\pi$ – $\pi$  stacking interaction ( $3.509 \text{ \AA}$ ) among carbazole units to lead to the 3-D architecture, as shown in Figure 5(c) (right). The width of the helix is calculated to be  $12.24 \text{ \AA}$ , and the pitch is  $7.008 \text{ \AA}$  (neighboring Hg···Hg distances at the same phase).

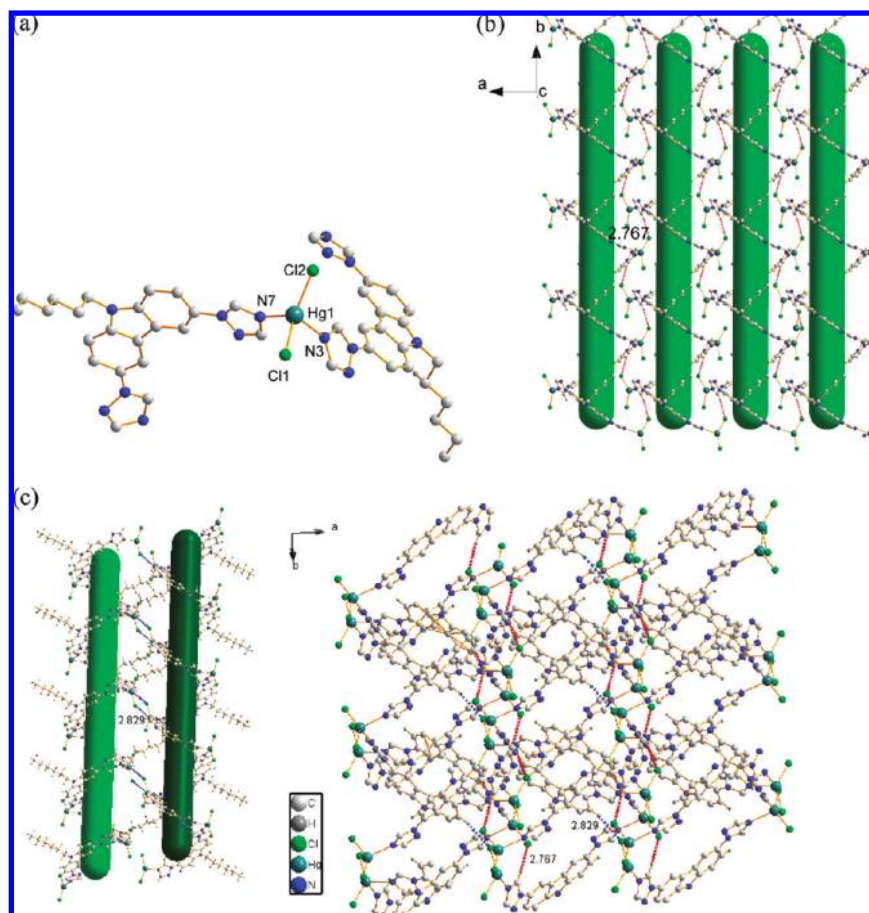
**Structure of  $[\text{HgL}^2\text{Br}_2]_\infty$  (**5**).** Complex **5** adopts the same coordination mode as complexes **1**, **3** and **4**. The mercury coordinated with two ligands  $\text{L}^2$  and two bromine atoms. The bond angles around mercury are in the range  $98.07$ – $110.04^\circ$ , indicating a distorted tetrahedral geometry. Seen along the  $b$ -axis in Figure 6(b), right-handed helicates stranded each other through C–H···Br weak interactions with distance of  $3.798 \text{ \AA}$  (the distance of  $\text{H}\cdots\text{Br}$  to be  $2.92 \text{ \AA}$ , angle to be  $157.866^\circ$ ). Due to an additional further C–H···Br hydrogen bonds and  $\pi$ – $\pi$  stacking interactions, right-handed and neighboring left-handed chains are stacked into 3-D architecture. The distance of C–H···Br is  $3.879 \text{ \AA}$  with  $\text{H}\cdots\text{Br}$  to be  $2.992 \text{ \AA}$ , and the angle is  $157.866^\circ$ , in addition to  $\pi$ – $\pi$  to be  $3.526 \text{ \AA}$ ; both contribute greatly to the supramolecular topologies. The width of the helix is calculated to be  $12.46 \text{ \AA}$ , and the pitch is  $6.62 \text{ \AA}$ .

**Structure of  $[\text{HgL}^2\text{Cl}_2]_\infty$  (**6**).** The same with complexes **4** and **5**, complex **6** is also in a distorted tetrahedral geometry as shown in Figure 7(a). Here although we use  $\text{HgCl}_2$  instead of  $\text{HgBr}_2$ , the packing of the molecules is very similar to that in complex **5**. Through C–H···Cl hydrogen bonding ( $\text{C–H}\cdots\text{Cl} = 3.648 \text{ \AA}$ ,  $\text{H}\cdots\text{Cl} = 2.767 \text{ \AA}$ , angle to be  $158.55^\circ$ ), right- or left-handed helicates formed into a 2-D network structure along the  $b$ -axis as seen from Figure 7(b). Also contributed by another C–H···Cl hydrogen bonding ( $\text{C–H}\cdots\text{Cl} = 3.737 \text{ \AA}$ ,  $\text{H}\cdots\text{Cl} = 2.829 \text{ \AA}$ , angle to be  $165.46^\circ$ ), along with  $\pi$ – $\pi$  interactions ( $3.576 \text{ \AA}$ ), a 3-D double helical supramolecular architecture is produced, the same as complex **5**. The width of the helix is calculated to be  $12.62 \text{ \AA}$ , and the pitch is  $6.435 \text{ \AA}$ .

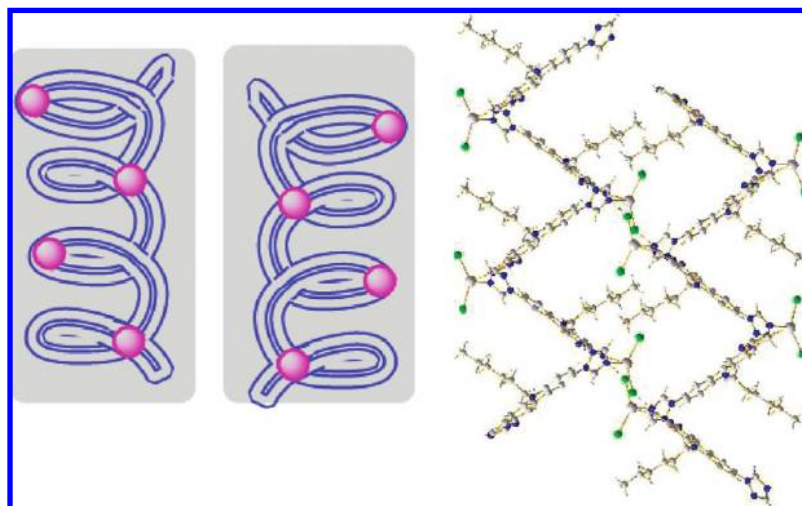
Making comparison with complexes **4**, **5** and **6**, we use the same ligand  $\text{L}^2$ , but different halogen metal inorganic salts. All of them formed into a 3-D supramolecular topology structure based on double-helicates through C–H···X hydrogen bonding and  $\pi$ – $\pi$  stacking, which predicates that weak supramolecular interactions, especially C–H···X hydrogen bonding, have an effect on the ultimate species. Crystal engineering and supramolecular chemistry are based on the prior knowledge of the characteristic of noncovalent bonds. It is surprising to note that attention toward the determination of the 3-D structure of mercury halogen has been so alike, especially complexes **5** and **6** are almost the same.

Taking all the six complexes discussed above into account, the four supramolecular polymers **1**, **4**, **5** and **6** contained double-helicates based on supramolecular weak interactions. But **1** features an unusual double-helicate just like upward “foot-steps” while the double-helicates formed by  $\text{HgX}_2$ , complexes





**Figure 7.** (a) Coordination environments of Hg with the atom numbering scheme. (b) The 2-D framework of complex 6 showing the weak C–H···Cl (red) interactions ( $\text{H}\cdots\text{Cl} = 2.767 \text{ \AA}$ ) along the  $a$ -axis. Only H atoms that were from hydrogen bonds were saved. (c) The 3-D architecture is connected by the weak C–H···Cl (blue) interactions ( $\text{H}\cdots\text{Cl} = 2.829 \text{ \AA}$ ) and  $\pi$ – $\pi$  interactions.



**Figure 8.** The model selected to calculate the interaction between the helical chains. Example:  $[\text{HgL}^2\text{Cl}_2]_\infty$ .

**4**, **5** and **6**, are very similar, which is different from the previous report.<sup>27</sup> In the work from Sun et al., based on the same ligand and metal, similar structures are obtained from different halides of Cl and Br, but a different structure for I. Here, different halides of Cl, Br, I have very little effect on the structures, which may be attributed to the weak interactions between the two helicates. So we were very interested in the weak interactions and performed DFT calculations on it further. Herein, a minor change in connected ligands can lead to various topologies,

based on the same anion, taking **1** and **3** as an example: **1** presents an unusual double-helicate while **3** possesses “W” chains. On the other hand, varying the metal inorganic salts based on the same ligand can also give interesting outcomes, see example **1** and **2**; **4**, **5** and **6**. Through weak interactions, **2** can only form into a 2-D topology structure through  $\text{Hg}\cdots\text{X}$  bonding while **1** exhibits a 3-D network containing double-helical structure. C–H···X hydrogen bonding and  $\pi$ – $\pi$  stacking both play significant roles in building the ultimate topology

Table 3. Weak Interactions between the Finite Units Selected

complex	weak interaction		BPW91	BP86	BLYP
6	C–H...Cl	3.737 Å	–128.44 kJ/mol	–78.79 kJ/mol	–86.01 kJ/mol
	$\pi$ – $\pi$	3.576 Å			
5	C–H...Br	3.879 Å	–123.61 kJ/mol	–63.72 kJ/mol	–69.72 kJ/mol
	$\pi$ – $\pi$	3.526 Å			
4	C–H...I	4.02 Å	–103.56 kJ/mol	–41.40 kJ/mol	–44.66 kJ/mol
	$\pi$ – $\pi$	3.509 Å			
1	C–H...N	3.78 Å	–84.91 kJ/mol	13.45 kJ/mol	46.39 kJ/mol
	$\pi$ – $\pi$	3.425 Å			

structures in complexes **4–6**. We are of the opinion that this study further leads to the systematic investigation of mercury coordination complexes based on the weak interactions adjusted by the selection of different ligands and various anions.

**DFT Calculations.** Crystal structure analysis shows that complexes **1**, **4**, **5** and **6** possess similar double-helical topology structure through C–H...X hydrogen bonding and  $\pi$ – $\pi$  stacking. The energy obtained from DFT calculation on the fragments from four different helicates (complexes **1**, **4**, **5** and **6**) provides us a method to evaluate the weak interactions. The model we chose is shown in Figure 8. The outcomes obtained from three different DFT methods are listed in Table 3. It indicates the interaction is going down from complexes **1** to **4–6**, however, the  $\pi$ – $\pi$  interaction is contracted with the trend. Compound **1** with the strongest  $\pi$ – $\pi$  interaction shows the smallest total interaction between interchain. All the data show the same trend in the interactions vs the halogen. The chloride possesses the largest interaction, then the bromide, and the iodide is the lowest. Although the interaction between the helicate is different from one to another, it was thought that the interaction between the two helicates is dominated by the C–H...X. The most interesting fact is that only a little change of alkyl substitution from the ligand in compound **1**, but the alkyl chain does not take part in the weak interaction between the helicates. SCN is widely known as a pseudo-halogen which can be safely compared with the interactions of the other three complexes **4–6**. The trend is the smaller the anion, the stronger the interaction indicated by DFT calculations.

### Conclusion

Complexes **1–6** are synthesized by self-assembly of the flexible ligand 3,6-di-(1,2,4-triazol-1-yl)-*N*-alkylcarbazole with HgX<sub>2</sub> (X = I, Br, Cl, SCN) to yield a short series of new coordination polymer complexes (**1**, **3–6**) with double-helical, “W”, and single molecular structure of complex **2**. C–H...X hydrogen bonds, metal halogen bonds and  $\pi$ – $\pi$  stacking play significant roles in the final crystal structures. The study further leads to the systematic investigation of mercury coordination polymers and complexes adjusted by the selection of different ligands and various anions. Three different DFT calculations are performed to evaluate the infinite chains from the similar double-helical topology structure (complexes **1**, **4–6**). The result shows that the interactions strongly depend on the C–H...X on the basis of the same metal and the similar ligand, and suggests a regular trend that the smaller the anion, the stronger the interaction. This article provides useful information on the synthesis of the inorganic–organic hybrid materials with high stable properties.

**Acknowledgment.** The work was supported by a grant for the National Natural Science Foundation of China (50532030, 50703001, 20771001), the Natural Science Foundation of Anhui Province (070414188), Doctoral Program Foundation of the Ministry of Education of China, Education Committee of Anhui

Province (2006KJ032A, KJ2009A52), Team for scientific Innovation Foundation of Anhui Province (2006KJ007TD), Young Teacher Foundation of Institution of High Education of Anhui Province (2007jq1019), Ministry of Education and Person with Ability Foundation of Anhui University.

### References

- (1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Swieggers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (c) Ma, B.-Q.; Gao, S.; Su, G.; Xu, G.-X. *Angew. Chem., Int. Ed.* **2001**, *40*, 434. (d) Li, Q. D.; Li, J. R.; Gao, S.; Ma, B. Q.; Kou, H. Z.; Ouyang, L.; Huang, R.-L.; Zhang, X.-X.; Yu, K.-B. *Eur. J. Inorg. Chem.* **2003**, *4*, 731. (e) Jing, W.; Zheng, L. L.; Li, C. J.; Zheng, Y. Z.; Tong, M. L. *Cryst. Growth Des.* **2006**, *6*, 357. (f) Liu, C. M.; Gao, S.; Zhang, D. Q.; Zhu, D. B. *Cryst. Growth Des.* **2007**, *7*, 1312. (g) Fromm, K. M. *Coord. Chem. Rev.* **2008**, *252*, 856.
- (2) (a) Seo, J.-S.; Whang, D.; Lee, H.; Jun, I.; Oh, J.; Jeon, Y.-J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Pang, J.; Marcotte, E. J. P.; Seward, C.; Brown, R.-S.; Wang, S.-N. *Angew. Chem., Int. Ed.* **2001**, *40*, 4042. (c) Ch.; Luebke, R.; Eddaoudi, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3278. (d) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176. (e) Horike, S.; Bureekaew, S.; Kitagawa, S. *Chem. Commun.* **2008**, 471. (f) Li, Y. W.; Yang, R. T. *Langmuir* **2007**, *23*, 12937. (g) Hu, S.; Zhang, J. P.; Li, H. X.; Tong, M. L.; Chen, X. M.; Kitagawa, S. *Cryst. Growth Des.* **2007**, *7*, 2286. (h) Kondo, A.; Noguchi, H.; Carlucci, L.; Proserpio, D. M.; Ciani, G.; Kajiro, H.; Ohba, T.; Kanoh, H.; Kaneko, K. *J. Am. Chem. Soc.* **2007**, *129*, 12362.
- (3) (a) Inoue, K.; Imai, H.; Ghalsasi, P. S.; Kikuchi, K.; Ohba, M.; Okawa, H.; Yakhmi, J. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 4242. (b) Cave, D.; Gascon, J. M.; Bond, A. D.; Teat, S. J.; Wood, P. T. *Chem. Commun.* **2002**, 1050. (c) Wu, C. D.; Hu, A. G.; Zhang, L.; Lin, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (d) Han, J. W.; Hill, C. L. *J. Am. Chem. Soc.* **2007**, *129*, 15094. (e) Shimomura, S.; Matsuda, R.; Tsujino, T.; Kawamura, T.; Kitagawa, S. *J. Am. Chem. Soc.* **2006**, *128*, 16416. (f) Liu, Y.; Xu, X.; Zheng, F. K.; Cui, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 4538. (g) Zhang, J. P.; Chen, X. M. *J. Am. Chem. Soc.* **2008**, *130*, 6010. (h) Wang, Z.-W.; Ji, Ch.-Ch.; Li, J.; Guo, Z.-J.; Li, Y.-Zh.; Zheng, H.-G. *Cryst. Growth Des.* **2009**, *9*, 475–482.
- (4) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466. (c) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217. (d) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273. (e) Hill, R. J.; Long, D.-L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 335. (f) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Solid State Chem.* **2005**, *178*, 2452. (g) Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313. (h) Ockwig, N. W.; Delgado-Friedrichs, O.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176. (i) Hargman, P. J.; Hargman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (j) Qu, Z.-R.; Zhao, H.; Wang, Y.-P.; Wang, X.-S.; Ye, Q.; Li, Y.-H.; Xiong, R.-G.; Abrahams, B. F.; Liu, Z.-G.; Xue, Z.-L.; You, X.-Z. *Chem.–Eur. J.* **2004**, *10*, 53. (k) Bu, X.-H.; Tong, M.-L.; Chang, H. C.; Kitagawa, S.; Batten, S. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 192. (l) Yang, J.; Ma, J.-F.; Liu, Y.-Y.; Ma, J.-Ch.; Batten, S. R. *Cryst. Growth Des.* **2008**, *8*, 4383.
- (5) (a) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem.–Eur. J.* **1997**, *3*, 765. (b) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M.; Rizzato, S. *Chem.–Eur. J.* **1999**, *5*, 237. (c) Bu, X.-H.; Chen, W.; Hou, W.-F.; Du, M.; Zhang, R.-H.; Brisse, F. *Inorg. Chem.* **2002**, *41*, 3477. (d) Zheng, Y.; Du, M.; Li, J.-R.; Zhang, R.-H.; Bu, X.-H. *J. Chem. Soc., Dalton Trans.* **2003**, 1509. (e) Zheng, G.-L.; Ma, J.-F.; Yang, J.; Li,

- Y.-Y.; Hao, X.-R. *Chem.—Eur. J.* **2004**, *10*, 3761. (f) Ma, J.-F.; Yang, J.; Zheng, G.-L.; Li, L.; Liu, J.-F. *Inorg. Chem.* **2003**, *42*, 7531. (g) Yang, J.; Ma, J.-F.; Liu, Y.-Y.; Li, S.-L.; Zheng, G.-L. *Eur. J. Inorg. Chem.* **2005**, 2174. (h) Yang, J.; Ma, J.-F.; Liu, Y.-Y.; Ma, J.-C.; Jia, H.-Q.; Hu, N.-H. *Eur. J. Inorg. Chem.* **2006**, 1208. (i) Li, F.-F.; Ma, J.-F.; Song, S.-Y.; Yang, J.; Liu, Y.-Y.; Su, Z.-M. *Inorg. Chem.* **2005**, *4*, 9374. (j) Xu, G.-H.; Ma, J.-F.; Yu, H.-X.; Li, S.-L.; Yang, J.; Su, M.; Shi, C.-F. *Organometallics* **2006**, *25*, 5996. (k) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103.
- (6) Ojala, W. H.; Lystad, K. M.; Deal, T. L.; Engebretson, J. E.; Spude, J. M.; Balidemaj, B.; Ojala, C. R. *Cryst. Growth Des.* **2009**, *9*, 964.
- (7) (a) Aakeröy, C. B.; Salmon, D. J. *CrystEngComm* **2005**, *7*, 439. (b) MacGillivray, L. *CrystEngComm* **2004**, *6*, 77. (c) Lehn, J.-M. *Science* **2002**, *295*, 2400. (d) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565. (e) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (f) Desiraju, G. R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2311. (g) Wenger, M.; Bernstein, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7966. (h) Childs, S. L.; Hardcastle, K. I. *CrystEngComm* **2007**, *9*, 364. (i) Bosch, E. *CrystEngComm* **2007**, *9*, 191.
- (8) (a) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386. (b) Metrangolo, P.; Pilati, T.; Resnati, G.; Stevenazzi, A. *Chem. Commun.* **2004**, 1492. (c) De Santis, A.; Forni, A.; Liantonio, R.; Metrangolo, P.; Pilati, T.; Resnati, G. *Chem.—Eur. J.* **2003**, *9*, 3974. (d) Walsh, R. B.; Padgett, C. W.; Metrangolo, P.; Resnati, G.; Hanks, T. W.; Pennington, W. T. *Cryst. Growth Des.* **2001**, *1*, 165. (e) Cincic, D.; Friscic, T.; Jones, W. J. *Am. Chem. Soc.* **2008**, *130*, 7524. (f) Cincic, D.; Friscic, T.; Jones, W. J. *Chem.—Eur. J.* **2008**, *14*, 747. (g) Shirman, T.; Freeman, D.; Posner, Y. D.; Feldman, I.; Facchetti, A.; van der Boom, M. E. *J. Am. Chem. Soc.* **2008**, *130*, 8162–8163. (h) Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 1617. (i) Triguero, S.; Llusar, R.; Polo, V.; Fourmigue, M. *Cryst. Growth Des.* **2008**, *8*, 2241–2247. (j) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210.
- (9) (a) Barooah, N.; Sarma, R. J.; Baruah, J. B. *CrystEngComm* **2006**, *8*, 608. (b) Motohiro, N. *CrystEngComm* **2004**, *6*, 130.
- (10) Ding, B.; Liu, Y.-Y.; Huang, Y.-Q.; Shi, W.; Cheng, Peng.; Liao, D.-Zh.; Yan, Sh.-P. *Cryst. Growth Des.* **2009**, *9*, 593.
- (11) Zhou, H.-P.; Wang, P.; Hao, F.-Y.; Ye, H.-P.; Zhao, Q.; Zhang, R.-L.; Tian, Y.-P.; Wu, J.-Y.; Tao, X.-T.; Jiang, M.-H. *J. Mol. Struct.* **2008**, *892*, 316.
- (12) (a) Sabounchei, S. J.; Nemattalab, H.; Salehzadeh, S.; Bayat, M.; Khavasi, H. R.; Adams, H. J. *Organomet. Chem.* **2008**, *693*, 1975. (b) Li, L. K.; Song, Y. L.; Hou, H. W.; Liu, Z. S.; Fan, Y. T.; Zhu, Y. *Inorg. Chim. Acta* **2005**, *358*, 3259. (c) Ebrahim, M. M.; Stoeckli-
- Evans, H.; Panchanatheswaran, K. *Polyhedron* **2007**, *26*, 3491. (d) Louise, J. M.; William, H.; Brian, K. N. *Polyhedron* **1998**, *17*, 221. (e) Burchell, T. J.; Eisler, D. J.; Puddephatt, R. J. *Inorg. Chem.* **2004**, *43*, 5550.
- (13) Nam, H. J.; Lee, H. J.; Noh, D. Y. *Polyhedron* **2004**, *23*, 115.
- (14) (a) Sarker, K. K.; Chand, B. G.; Suwa, K.; Cheng, J.; Lu, T. H.; Otsuki, J.; Sinha, C. *Inorg. Chem.* **2007**, *46*, 670. (b) Dai, J.; Wang, X.; Bian, G. Q.; Zhang, J. S.; Guo, L.; Munakata, M. *J. Mol. Struct.* **2004**, *690*, 115. (c) Garoufis, A.; Perlepes, S.; Schreiber, A.; Bau, R.; Hadjiliadis, N. *Polyhedron* **1996**, *15*, 177.
- (15) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, 1997.
- (16) Parr, R. G.; Young, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (17) Zhou, H. P.; Wang, P.; Zheng, L. X.; Geng, W. Q.; Yin, J. H.; Gan, X. P.; Xu, G. Y.; Wu, J. Y.; Tian, Y. P.; Kan, Y. H.; Tao, X. T.; Jiang, M. H. *J. Phys. Chem. A* **2009**, *113*, 2584.
- (18) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (19) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (20) Baerends, E. J.; Branchadell, V.; Sodupe, M. *Chem. Phys. Lett.* **1997**, *265*, 481.
- (21) Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.
- (22) (a) Maggard, P. A.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 7742. (b) Wang, Y.; Yu, J. H.; Guo, M.; Xu, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 4089. (c) Barboiu, M.; Vaughan, G.; Graff, R.; Lehn, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 10256. (d) Vinje, J.; Parkinson, J. A.; Sadler, P. J.; Brown, T.; Sletten, E. *Chem.—Eur. J.* **2003**, *9*, 1620.
- (23) Wang, X.; Qin, C.; Wang, E.; Li, Y.; Hao, N.; Hu, C.; Xu, L. *Inorg. Chem.* **2004**, *43*, 1850.
- (24) (a) Grdenic, D. *Q. Rev.* **1965**, *19*, 303. (b) Grdenic, D. *Connections in the Crystal Structures of Mercury Compounds*. In *Structural Studies of Molecules of Biological Interest*; Dodson, G., Glusker, J. P., Sayre, D., Eds.; Clarendon Press: Oxford, U.K., 1981; p 207. (c) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
- (25) Sharif, S.; Huot, M. C.; Tolstoy, P. M.; Toney, M. D.; Jonsson, K. H. M.; Limbach, H. H. *J. Phys. Chem. B* **2007**, *111*, 3869.
- (26) Zhou, H. P.; Wang, P.; Hu, Z. J.; Li, L.; Chen, J. J.; Cui, Y.; Tian, Y. P.; Wu, J. Y.; Yang, J. X.; Tao, X. T.; Jiang, M. H. *Eur. J. Inorg. Chem.* **2007**, 1854.
- (27) Wu, G.; Wang, X. F.; Okamura, T.; Sun, W. Y.; Ueyama, N. *Inorg. Chem.* **2006**, *45*, 8523.

CG900520J