

# Polymorphous One-Dimensional Tetrapyrrolylporphyrin Coordination Polymers Which Structurally Mimic Aryl Stacking Interactions

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Two polymorphic structures of rigid one-dimensional (1D) coordination polymers, [(HgBr<sub>2</sub>)<sub>2</sub>TPyP] · 2(1,1,2,2-tetrachloroethane, TCE) (1A, 1B), have been isolated in which the 1D polymers adopt either stacking or herringbone (or T-shaped) geometries as observed for simple aromatic hydrocarbons. Polymorph 1A has a 1D polymeric structure with each HgBr<sub>2</sub> tetrahedrally coordinated to a pyridyl moiety of two TPyP molecules. The 1D polymers in 1A are weakly cross-linked through long metal–halide bridges forming a 2D steplike sheet with each sheet stacked to form a continuous open porous structure. The 1D polymers in 1B adopt a T-shaped geometry such that the C–H groups of the pyrrole rings point toward the porphyrin cavity to maximize C–H···N or C–H···C interactions and the crest of the polymer (pyridyl–HgBr<sub>2</sub>–pyridyl moiety) interdigitates into the supramolecular cavities to form long, but significant Hg···Br interactions. Indeed, the cause of the stacked versus herringbone structures in 1A and 1B can be traced to the different possible secondary interactions between Br and Hg: edge-on in 1A and side-on in 1B. (This is in contrast to the electrostatic interactions leading to face-to-face versus hydrogen bonding in edge-to-face aromatic packing.) Polymorph 1A crystallizes in the triclinic space group *P*-1 with *a* = 7.3653(9), *b* = 12.920(2), and *c* = 14.320(2) Å, *α* = 72.218(2), *β* = 81.858(3), and *γ* = 79.505(3)°, *V* = 1270.5(3) Å<sup>3</sup>, *D*<sub>calc</sub> = 2.189 g cm<sup>-3</sup>, *Z* = 1, and *R* = 0.0672. Polymorph 1B is monoclinic, *P*2<sub>1</sub>/*c* with *a* = 15.2397(2), *b* = 30.4642(5), and *c* = 11.2657(1) Å, *β* = 93.212(1)°, *V* = 5222.06(12) Å<sup>3</sup>, *D*<sub>calc</sub> = 2.131 g cm<sup>-3</sup>, *Z* = 4, and *R* = 0.0929.

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**Key Words:** polymorph; tetrapyrrolylporphyrin; coordination polymer; stacking; herringbone; supramolecular isomerism; crystal engineering.

## INTRODUCTION

Supramolecular isomerism (the existence of two or more network structures for a given molecular building block)

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and polymorphism (the existence of two or more different crystal structures for a given molecular structure) are two important and intriguing aspects of crystal engineering (1–4). Supramolecular isomerism is a broader definition of polymorphism and is essentially invoked to explain different types of coordination polymers obtained for identical building blocks that are not polymorphs in a strict sense (3). In recent years, polymorphism has become one of the challenging aspects of crystal engineering and a cause of concern to the chemical industry because it highlights our limitations in predicting crystal structures and it introduces structural impurities that may affect the production, performance, and stability of solids (1). In this report, we discuss the polymorphic one-dimensional (1D) coordination polymers of tetrapyrrolylporphyrin (TPyP) that exhibit stacking features common to simple planar aromatic compounds resulting in distinct packing arrangements (4, 5).

## EXPERIMENTAL

**Syntheses.** All starting materials were purchased from Aldrich (Milwaukee, WI) and were used without further purification. The coordination polymers of tetrapyrrolylporphyrin with HgBr<sub>2</sub> were grown using a layering technique at ambient temperatures in which TPyP was dissolved in 3:1 solution mixtures of TCE and MeOH. TPyP (0.031 g, 0.5 mmol) dissolved in TCE–MeOH (20 mL) was layered with a methanolic solution of HgBr<sub>2</sub> (0.036 g, 1 mmol, 10 mL) to form [(HgBr<sub>2</sub>)<sub>2</sub>TPyP] · 2TCE, **1A**. A polymorph of **1A**, **1B** was obtained from the same reaction when Ni(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.014 g, 0.5 mmol) and phthalocyanine (0.025 g, 0.5 mmol) were added to HgBr<sub>2</sub> and TPyP solutions, respectively, while layering. A third isomer (not a polymorph) of polymorphs **1A** and **1B** can be obtained with different levels of solvent inclusion when Ni(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O or phthalocyanine is added, [(HgBr<sub>2</sub>)<sub>2</sub>TPyP]<sub>2</sub> · 6(TCE), **2** (6). We have also found that polymorph **1A** is preferentially formed when the metal-to-ligand ratio is changed to 1:1 or 3:1.

## X-Ray Crystallography

The X-ray data for both complexes were collected on a Siemens CCD area detector-equipped diffractometer with MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation and using the SMART and SAINT suite of software (7). Diffraction data ( $4 < \theta < 56^\circ$ ) were collected at  $-100^\circ\text{C}$  by using a stream of nitrogen gas. The crystal structures of **1A** and **1B** were solved by direct methods using the SHELXTL software package (8). Polymorph **1A** crystallizes in the triclinic, triclinic space group  $P\bar{1}$ , while **1B** is monoclinic  $P2_1/c$ . A summary of the crystallographic parameters is reported in Table 1.

The geometrically constrained hydrogen atoms were placed in calculated positions ( $d_{\text{C-H}} = 0.95 \text{ \AA}$ ) and allowed to ride on the bonded atom with  $B = 1.2U_{\text{eqv}}(\text{C})$ . The unique porphyrin-cavity hydrogen atoms were clearly visible in difference Fourier maps and included with a riding model on the bonded nitrogen atom and  $B = 1.2U_{\text{eqv}}(\text{N})$ .

The TCE solvate molecules are disordered and exhibit high temperature factors. The two unique TCE molecules in **1B** could not be resolved into stable disordered fragments and were thus refined anisotropically with large thermal parameters. In **1A**, however, the Cl atoms of the one unique

solvent molecule were resolved into two orientations each. These atoms were refined anisotropically with site occupancy factors of 0.5. The carbon atoms (C21 and C22) exhibited high thermal motion, but could not be resolved into disordered positions. Hydrogen atoms were not included in the model for the solvent in **1A**, but they were for both solvent molecules in **1B**.

Crystals of coordination polymers of tetrapyrrolylporphyrin tend to be small and weakly diffracting (6) and these problems were also found with the current samples. This was exacerbated by the presence of the loosely held, disordered TCE solvent. As a result, a few atoms could not be refined anisotropically, including N2 in **1A** and C2, C4, C8, C16, C21, and C26 in **1B**. Refinement of all other nonhydrogen atoms was carried out with anisotropic temperature factors. The final fractional atomic coordinates and equivalent isotropic thermal parameters for polymorph **1A** and **1B** are given in Tables 2 (**1A**) and 3 (**1B**), and selected interatomic distances and bond angles are presented in Table 4.

## RESULTS AND DISCUSSION

Polymorphism is widely studied in the context of molecular organic crystals because the subtle interplay between

TABLE 1  
Crystallographic Parameters

Compound	$[(\text{HgBr}_2)_2\text{TPyP}] \cdot 2\text{TCE}$ ( <b>1A</b> )	$[(\text{HgBr}_2)_2\text{TPyP}] \cdot 2\text{TCE}$ ( <b>1B</b> )	$[(\text{HgI}_2)_2\text{TPyP}] \cdot 2\text{TCE}$ ( <b>6</b> )	$[(\text{HgBr}_2)_2\text{TPyP}] \cdot 2\text{CHCl}_3$ ( <b>10</b> )
Empirical formula	$\text{C}_{44}\text{H}_{30}\text{Br}_4\text{Cl}_8\text{Hg}_2\text{N}_8$	$\text{C}_{44}\text{H}_{30}\text{Br}_4\text{Cl}_8\text{Hg}_2\text{N}_8$	$\text{C}_{44}\text{H}_{30}\text{Cl}_8\text{Hg}_2\text{I}_4\text{N}_8$	$\text{C}_{42}\text{H}_{28}\text{Br}_4\text{Cl}_6\text{Hg}_2\text{N}_8$
Formula weight	1675.18	1675.18	1863.14	1578.24
Color/shape	Purple/fragment	Purple/fragment		
Crystal dimensions	$0.12 \times 0.20 \times 0.24 \text{ mm}^3$	$0.12 \times 0.28 \times 0.32 \text{ mm}^3$		
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
$T, ^\circ\text{C}$	$-100$	$-100$	$-100$	$-102$
$a, \text{ \AA}$	7.3653(9)	15.2397(2)	10.0350(7)	9.507(3)
$b, \text{ \AA}$	12.920(2)	30.4642(5)	11.9656(8)	11.641(2)
$c, \text{ \AA}$	14.320(2)	11.2657(1)	12.9198(8)	12.732(4)
$\alpha, \text{ deg}$	72.218(2)	90	98.935(1)	73.418(9)
$\beta, \text{ deg}$	81.858(3)	93.212(1)	101.752(1)	80.316(16)
$\gamma, \text{ deg}$	79.505(3)	90	113.669(1)	66.294(7)
$V, \text{ \AA}^3$	1270.5(3)	5222.06(12)	1342	1234.2
$Z$	1	4	1	1
$\rho_{\text{calc}}, \text{ g cm}^{-3}$	2.189	2.131	2.306	2.213
$\mu, \text{ mm}^{-1}$	9.642	9.384		
$\theta$ Range	1.50 to $28.04^\circ$	1.34 to $23.29^\circ$		
Reflections collected	8252	3144		
Independent/observed reflections	5743 ( $R_{\text{int}} = 0.0745$ )/2614 [ $I > 2\sigma(I)$ ]	7448 ( $R_{\text{int}} = 0.1099$ )/5660 [ $I > 2\sigma(I)$ ]		
Data/restraints/parameters	5738/0/330	7442/0/566		
Extinction Coefficient	0.0024(3)	0.0004(1)		
Goodness-of-fit	0.925	1.116		
Final $R$ indices $R, wR$ , [ $I > 2\sigma(I)$ data]	0.0672, 0.1002	0.0929, 0.2158		

TABLE 2

Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\times 10^3$ ) for  $[(\text{HgBr}_2)_2\text{TPyP}] \cdot 2\text{TCE}$  (1A)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq) <sup>a</sup>
Hg	1162(1)	8396(1)	9761(1)	30(1)
Br(1)	− 2100(2)	10275(1)	9037(1)	39(1)
Br(2)	− 937(2)	7125(2)	9725(1)	51(1)
Cl(1) <sup>b</sup>	10485(13)	11993(9)	15918(8)	53(3)
Cl(2) <sup>b</sup>	13224(15)	10000(10)	15691(8)	76(4)
Cl(3) <sup>b</sup>	7991(45)	10302(23)	17314(21)	42(5)
Cl(4) <sup>b</sup>	10735(11)	8493(7)	17072(6)	45(2)
Cl(1') <sup>b</sup>	10245(13)	11705(9)	15275(8)	75(3)
Cl(2') <sup>b</sup>	13545(15)	10555(14)	16167(9)	106(5)
Cl(3') <sup>b</sup>	7701(47)	10578(26)	17069(23)	52(6)
Cl(4') <sup>b</sup>	10549(14)	8973(10)	16292(9)	77(3)
N(1)	10447(12)	5057(8)	16376(7)	20(3)
N(2)	7401(12)	5913(8)	15076(7)	16(2) <sup>c</sup>
N(3)	2751(14)	7693(9)	11196(7)	24(3)
N(4)	4041(15)	7506(11)	18858(7)	32(3)
C(1)	11921(17)	4566(11)	16876(9)	22(3)
C(2)	11700(17)	4845(11)	17792(9)	26(3)
C(3)	10030(17)	5504(11)	17806(9)	28(4)
C(4)	9212(16)	5610(11)	16945(9)	22(3)
C(5)	7471(17)	6170(11)	16705(8)	22(3)
C(6)	6616(15)	6302(11)	15862(8)	21(3)
C(7)	4778(16)	6885(12)	15625(9)	29(4)
C(8)	4558(17)	6915(11)	14710(9)	26(4)
C(9)	6162(15)	6284(11)	14355(9)	21(3)
C(10)	6516(15)	6094(11)	13432(9)	20(3)
C(11)	6264(16)	6634(12)	17493(9)	24(3)
C(12)	6085(17)	7753(12)	17385(10)	33(4)
C(13)	4898(19)	8129(13)	18111(10)	36(4)
C(14)	4253(21)	6422(16)	18987(12)	52(5)
C(15)	5418(18)	5964(13)	18308(10)	38(4)
C(16)	5107(16)	6649(11)	12697(9)	19(3)
C(17)	5686(16)	7383(11)	11829(9)	26(4)
C(18)	4523(17)	7884(11)	11092(9)	28(4)
C(19)	2209(17)	6997(12)	12067(9)	29(4)
C(20)	3302(15)	6502(10)	12818(8)	15(3)
C(21)	11158(34)	10674(43)	16414(18)	205(24)
C(22)	10059(30)	10109(29)	16779(23)	143(13)

<sup>a</sup>*U*(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>b</sup>These Cl atoms were refined as disordered with 50% occupancy each.

<sup>c</sup>Isotropic refinement.

various weak intermolecular interactions plays a key role in determining molecular geometry and resultant crystal packing. The huge commercial interest associated with drug polymorphs has also fueled the pace of research in this area (4). In coordination polymers, the robust and directional coordination bonds between metals and organic ligands form well-defined network structures and limit the number of possible local minima (unless the organic ligands have the flexibility and/or rotational degrees of freedom to coordinate with metals) (3,9). However, we have encountered two polymorphic structures of rigid 1D coordination polymers,

TABLE 3

Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\times 10^3$ ) for  $[(\text{HgBr}_2)_2\text{TPyP}] \cdot 2\text{TCE}$  (1B)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Hg(1)	− 1869(1)	13172(1)	5947(1)	27(1)
Hg(2)	− 1547(1)	9752(1)	13335(1)	33(1)
Br(1)	− 1806(2)	13930(1)	6774(2)	44(1)
Br(2)	− 1837(1)	12748(1)	4026(2)	32(1)
Br(3)	− 1642(2)	10056(1)	15375(2)	47(1)
Br(4)	− 1573(2)	9067(1)	12152(3)	73(1)
Cl(1)	− 5680(16)	10650(10)	15026(17)	284(15)
Cl(2)	− 5667(10)	10971(5)	17359(11)	146(6)
Cl(3)	− 7490(12)	11240(6)	14529(17)	182(8)
Cl(4)	− 5995(17)	11737(7)	15476(14)	262(15)
Cl(5)	− 692(8)	11193(3)	17121(14)	135(5)
Cl(6)	− 2243(11)	10805(4)	18215(13)	156(7)
Cl(7)	− 3422(7)	11119(5)	16050(20)	187(9)
Cl(8)	− 1906(8)	11611(4)	15125(9)	108(3)
N(1)	− 8062(9)	11609(5)	10126(12)	16(3)
N(2)	− 6767(12)	12141(6)	8897(14)	28(4)
N(3)	− 5389(10)	11530(6)	9783(13)	23(4)
N(4)	− 6688(11)	11001(6)	10980(13)	27(4)
N(5)	− 10650(11)	12834(6)	6982(15)	27(4)
N(6)	− 3127(11)	12867(6)	6764(16)	29(4)
N(7)	− 2908(12)	10098(6)	12475(16)	34(5)
N(8)	− 10324(11)	10152(6)	12676(15)	29(4)
C(1)	− 8568(12)	11304(7)	10685(17)	25(5)
C(2)	− 9467(14)	11406(7)	10465(17)	24(5) <sup>a</sup>
C(3)	− 9498(13)	11773(7)	9739(18)	29(5)
C(4)	− 8620(12)	11881(6)	9521(16)	17(4) <sup>a</sup>
C(5)	− 8352(14)	12230(7)	8747(15)	24(5)
C(6)	− 7533(14)	12345(8)	8482(19)	33(5)
C(7)	− 7302(15)	12683(8)	7672(22)	42(6)
C(8)	− 6397(15)	12682(7)	7611(19)	33(5) <sup>a</sup>
C(9)	− 6090(15)	12331(7)	8386(17)	29(5)
C(10)	− 5204(14)	12189(8)	8497(18)	33(6)
C(11)	− 4906(12)	11818(7)	9150(17)	23(5)
C(12)	− 3990(14)	11668(8)	9258(18)	30(5)
C(13)	− 3962(14)	11300(7)	9939(18)	28(5)
C(14)	− 4833(12)	11216(7)	10279(17)	22(5)
C(15)	− 5075(13)	10868(8)	10994(17)	29(5)
C(16)	− 5937(12)	10762(6)	11305(16)	18(4) <sup>a</sup>
C(17)	− 6196(13)	10390(8)	12006(18)	30(5)
C(18)	− 7052(14)	10407(7)	12035(18)	29(5)
C(19)	− 7379(12)	10776(7)	11422(18)	22(5)
C(20)	− 8245(15)	10925(7)	11329(18)	30(5)
C(21)	− 9111(13)	12464(7)	8133(17)	22(4) <sup>a</sup>
C(22)	− 9442(14)	12846(7)	8508(17)	27(5)
C(23)	− 10211(14)	13034(8)	7930(19)	34(6)
C(24)	− 10271(15)	12465(7)	6584(18)	32(5)
C(25)	− 9540(14)	12260(8)	7138(19)	36(6)
C(26)	− 4513(12)	12427(6)	7873(16)	17(4) <sup>a</sup>
C(27)	− 4103(14)	12249(9)	6924(18)	38(6)
C(28)	− 3394(14)	12481(9)	6431(18)	35(6)
C(29)	− 3533(16)	13063(7)	7650(19)	34(6)
C(30)	− 4242(14)	12850(7)	8211(18)	26(5)
C(31)	− 4349(12)	10570(7)	11497(17)	21(4)
C(32)	− 3903(15)	10299(7)	10807(18)	31(5)
C(33)	− 3165(15)	10044(8)	11323(20)	37(6)
C(34)	− 3354(13)	10370(8)	13164(18)	29(5)
C(35)	− 4055(15)	10607(8)	12670(18)	37(6)
C(36)	− 8958(14)	10640(7)	11831(19)	28(5)
C(37)	− 9410(14)	10786(8)	12781(18)	30(5)
C(38)	− 10073(13)	10534(6)	13162(16)	21(5)
C(39)	− 9859(14)	10008(9)	11784(22)	40(6)

TABLE 3—Continued.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
C(40)	− 9180(15)	10250(10)	11322(20)	45(7)
C(41)	− 6798(56)	11336(22)	15699(44)	203(39)
C(42)	− 6256(22)	10889(13)	16118(37)	86(12)
C(43)	− 1892(37)	11226(15)	17065(47)	135(20)
C(44)	− 2204(36)	11206(14)	15788(79)	208(40)

<sup>a</sup>Isotropic refinement.

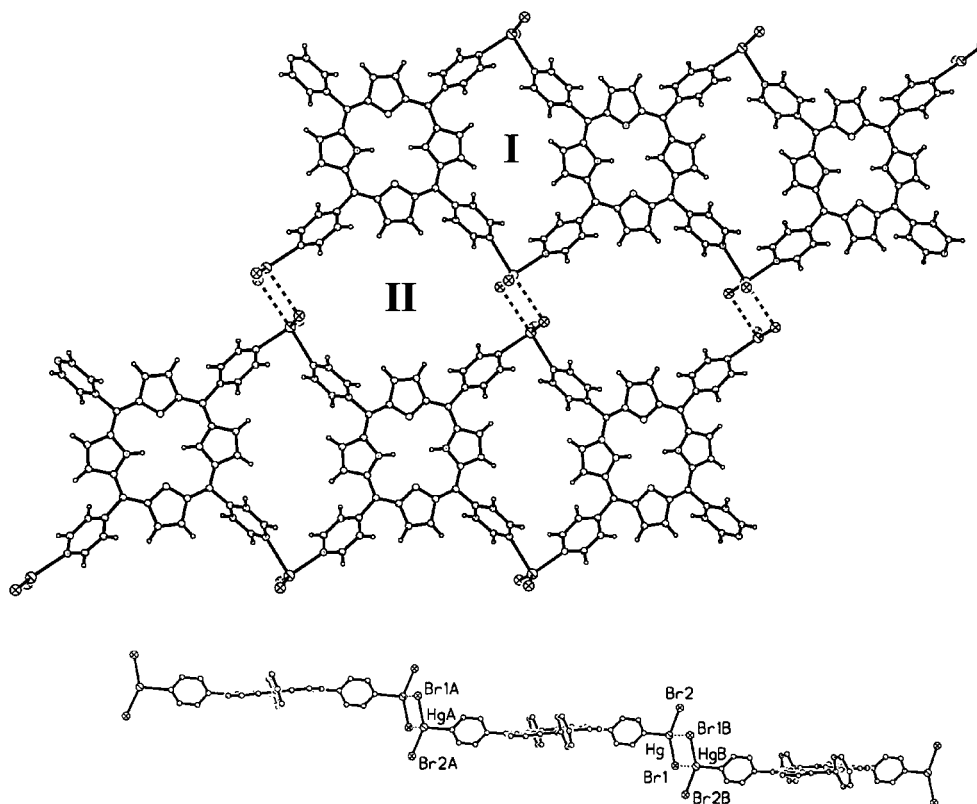
[(HgBr<sub>2</sub>)<sub>2</sub>TPyP] · 2(1,1,2,2-tetrachloroethane, TCE) (**1A**, **1B**), in which the 1D polymers adopt either stacking or herringbone (or T-shaped) geometries as observed for simple aromatic hydrocarbons (e.g., benzene, naphthalene,

pyrene (4b)). Interestingly, we have also found an indication for the existence of a third polymorph and for isomeric structures for these polymorphs! (Complexes of [(HgBr<sub>2</sub>)<sub>2</sub>TPyP] · 6TCE, **2**, and [(HgI<sub>2</sub>)<sub>2</sub>TPyP] · 2TCE, **3**, similar to **1A** and **1B**, but with different cell parameters, packing arrangement, and solvent inclusion properties have been isolated (6).)

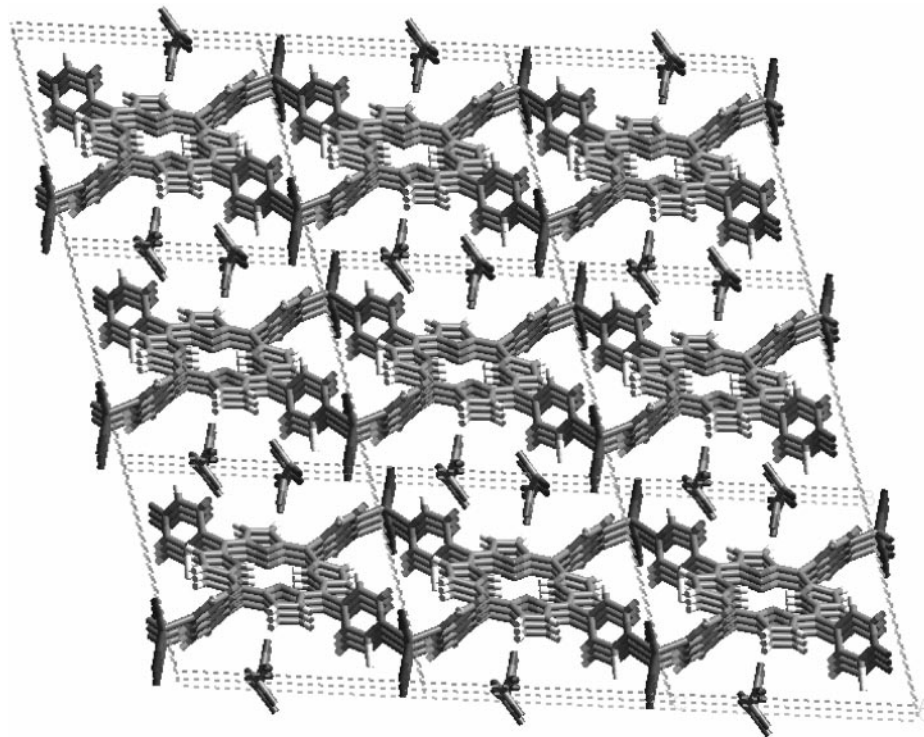
Polymorph **1A** resides on a crystallographic center of inversion with one-half of the formula unit crystallographically unique. It has a 1D polymeric structure with each HgBr<sub>2</sub> tetrahedrally coordinated to a pyridyl moiety (Hg–N, 2.360(9) Å, 2.594(11) Å) of two TPyP molecules. Two HgBr<sub>2</sub> units bridge TPyP molecules forming a supramolecular cavity with an effective cavity size of 2.5 × 7.7 Å<sup>2</sup>

TABLE 4  
Comparison of Geometrical Parameters (Å, °)

	[(HgBr <sub>2</sub> ) <sub>2</sub> TPyP] · 2TCE ( <b>1A</b> )	[(HgBr <sub>2</sub> ) <sub>2</sub> TPyP] · 2TCE ( <b>1B</b> )	[(HgI <sub>2</sub> ) <sub>2</sub> TPyP] · 2TCE ( <b>6</b> )	[(HgBr <sub>2</sub> ) <sub>2</sub> TPyP] · 2CHCl <sub>3</sub> ( <b>10</b> )
Hg–Br	2.467(2) 2.514(2)	2.474(3) 2.491(3) 2.492(3) 2.523(2)	2.6401(8) [I] 2.6429(8) [I]	2.467(1) 2.477(1)
Hg–N	2.360(9) 2.594(11)	2.36(2) 2.37(2) 2.38(2) 2.48(2)	2.416(7) 2.500(7)	2.410(6) 2.482(6)
Hg...Hg (cavity I)	14.290	13.327	14.131	14.2
Hg...Br	3.289(1)	4.457(4) 4.392(4)	4.886(1) [I]	
Br–Hg–Br	146.75(6)	142.52(9) 144.19(12)	147.27(3) [I]	
Br–Hg–N	92.0(3) 96.3(3) 102.5(3) 110.0(3)	96.4(4) 98.5(4) 99.2(4) 100.6(4) 100.8(5) 101.9(4) 103.5(5) 104.7(4)	99.8(2) [I] 100.2(2) [I] 100.8(2) [I] 103.5(2) [I]	
N–Hg–N	87.1(3)	105.5(6) 108.3(6)	93.7(2)	
Br–Hg...Br	82.1(1) 91.5(1)	91.2(1) 107.1(1) 110.2(1) 123.8(1)	72.0(1) [I] 106.2(1) [I]	
N – Hg...Br	89.2(3) 96.3(3)	51.0(4) 53.1(4) 54.8(4) 57.4(4)	51.7(2) [I] 139.9(2) [I]	
Interplanar angles of pyridyl groups	61.1 77.1	67.5 70.5 73.0 81.6	82.7 72.8	73.2 67.8



**FIG. 1.** In polymorph 1A,  $\text{HgBr}_2$  tetrahedrally coordinates with TPYP to form a 1D coordination polymer with supramolecular cavities (I). The 1D polymers are additionally linked together by weak  $\text{Hg} \cdots \text{Br}$  bridges (3.289(11) Å) to form a 2D steplike structure resulting in a second type of cavity (II) occupied by two TCE molecules (not shown).



**FIG. 2.** Open porous structure of polymorph 1A viewed along the crystallographic  $a$  axis. The weak metal  $\cdots$  halide bridges are not shown connected in this figure (compare with Fig. 1).

(cavity I, Fig. 1). (In this report, we have excluded van der Waals radii of appropriate atoms while calculating the cavity dimensions; thus the effective sizes of the cavities represent the true void space available.) This type of linear polymeric structure has been previously observed for  $\text{HgX}_2$  coordination polymers of TPyP (6,10) including the structures of the similar  $[(\text{HgBr}_2)_2\text{TPyP}] \cdot 6\text{TCE}$  (6) and  $[(\text{HgBr}_2)_2\text{TPyP}] \cdot 2\text{CHCl}_3$  (10). (The latter compound is not isostructural with either **1A** or **1B** but the supramolecular features of the crystal structure were not reported in the paper (10).)

Interestingly, the 1D polymers in **1A** appear to be weakly cross-linked through long metal-halide bridges ( $\text{Hg} \cdots \text{Br}$ , 3.289(11) Å) and  $\text{Br} \cdots \text{Br}$  interactions (3.857(10) Å) to form a two-dimensional polymeric steplike structure with additional cavities (cavity II, effective cavity size  $4.6 \times 9.0 \text{ \AA}^2$ ) (11). Each of the type II cavities are occupied by two TCE molecules as shown in Fig. 2. The 1D polymers are stacked at an interplanar distance of 3.725 Å and form a continuous open porous structure (Fig. 2).

Unlike polymorph **1A**, **1B** has no crystallographically imposed symmetry and the asymmetric unit contains a full formula unit. **1B** exhibits the same 1D coordination polymer as observed in **1A** ( $\text{Hg-N}$ , 2.36(2) Å, 2.37(2) Å, 2.38(2) Å, 2.48(2) Å), but these 1D polymers form a herringbone-type structure and not the open porous structure observed for **1A**. The 1D polymers adopt a T-shaped geometry such that the C-H groups of the pyrrole rings point toward the porphyrin cavity to maximize  $\text{C-H} \cdots \text{N}$  or  $\text{C-H} \cdots \text{C}$  interactions and the crest of the polymer (pyridyl-HgBr<sub>2</sub>-pyridyl moiety) interdigitates into the supramolecular cavities of type I (Fig. 3).

Note that the difference in  $\text{Hg} \cdots \text{Br}$  contacts may be the cause of the lower local symmetry found for **1B**. Br1 and Br2 interdigitate neighboring coordination polymers to make a closer approach to Hg1 and Hg2; however, Br3 and Br4 do not have any secondary interactions with either Hg (Fig. 3).

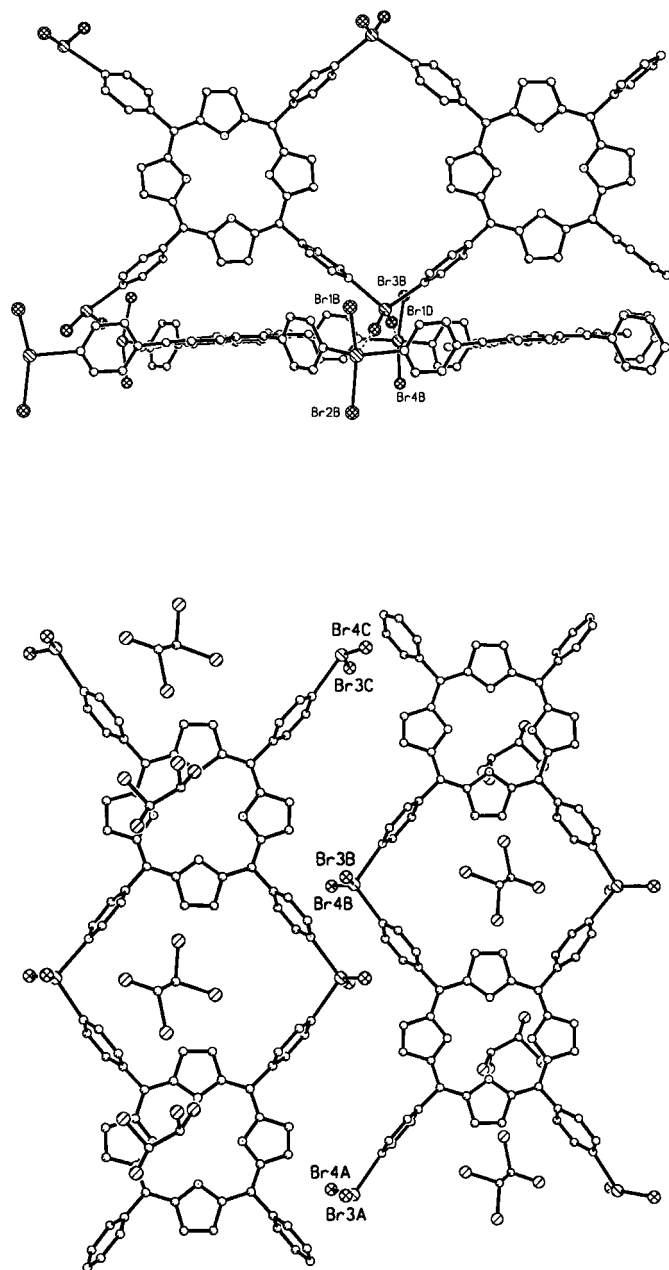
The  $\text{Hg} \cdots \text{Br}_{1,2}$  contacts are long (4.457(4), 4.392(4) Å) and well outside van der Waals contact distances, but are in geometrically significant positions which may indicate true secondary interactions (12). In polymorph **1A**, the long  $\text{Hg} \cdots \text{Br}$  contacts occur outside the 1D polymer and can thus make a closer approach. Indeed these interactions are within van der Waals contact separation and cause significant deviation of the tetrahedral Hg coordination sphere in **1A**, but not in **1B** where the distances are much longer and outside van der Waals contact:  $\text{N-Hg-Br} = 92.0(3)$ – $110.0(3)^\circ$  (**1A**),  $96.4(4)$ – $104.7(4)^\circ$  (**1B**);  $\text{N-Hg-N} = 87.1(3)^\circ$  (**1A**),  $105.5(6)$ ,  $108.3(6)^\circ$  (**1B**);  $\text{Br-Hg-Br} = 146.75(6)^\circ$  (**1A**),  $142.52(9)$ ,  $144.19(12)^\circ$  (**1B**).

The packing diagram for polymorph **1B** is presented in Fig. 4. The sandwiched herringbone structure of **1B** results in three-dimensional cavities that enclathrate two TCE mol-

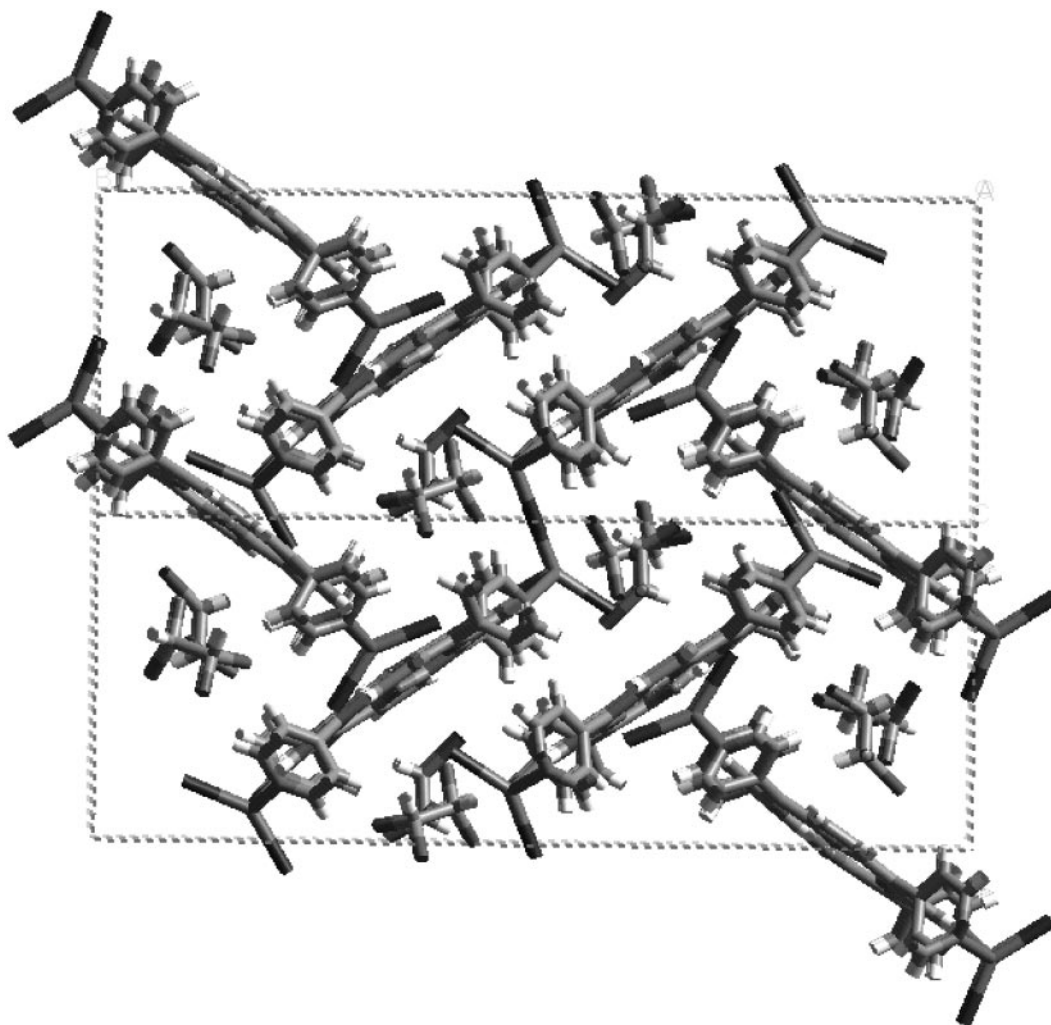
ecules. The dramatic differences in the two polymorphs are evident in comparing the overall packing in Fig. 4 with that for **1A** in Fig. 2.

## CONCLUSIONS

The striking differences in stacking features of polymorphs **1A** (stacked, open porous) and **1B** (herringbone,



**FIG. 3.** The T-shaped geometry adopted by the 1D coordination polymers in polymorph **1B** facilitates interdigitation of the crest of the polymer into cavities within the neighboring polymer using Br1 and Br2 to form secondary interactions with Hg1 and Hg2 and maximizing the interaction between pyrrole C-H groups and the porphyrin core.



**FIG. 4.** The packing diagram of polymorph **1B**. The sandwiched herringbone structure of **1B** results in three-dimensional cavities that enclathrate two TCE molecules. (Compare with the packing diagram of polymorph **1A**, Fig. 2).

three-dimensional) result from the infinite 1D polymers of TPyP in these complexes exhibiting stacking, herringbone, and sandwiched herringbone-type interactions as observed for simple aromatic organic compounds. Further, these results also suggest that rigid infinite coordination polymers can exhibit polymorphism (in addition to network isomerism) as do simpler aromatic organic molecules.

The cause of the stacked versus herringbone structures in **1A** and **1B** can be traced to the different possible secondary interactions between Br and Hg: edge-on in **1A** and side-on in **1B**. This is in contrast to the electrostatic interactions leading to face-to-face versus hydrogen bonding in edge-to-face aromatic packing.

The synthesis and structural characterization of polymorphs **1A**, **1B**, and analogous coordination complexes **2** and **3** suggest that polymorphism or supramolecular isomerism exhibited by these complexes can be traced back

to the additives (passive metal salts) used during crystallization (metal nitrates and phthalocyanine). At present, with the limited data available, we are not able to identify the nucleation mechanism of these complexes in the presence of additives.

Isolation of  $[(\text{HgI}_2)_2\text{TPyP}] \cdot 2\text{TCE}$ , analogous to polymorphs **1A** and **1B** (i.e., similar chemical composition and solvent inclusion) but with yet different unit cell parameters, indicates the existence additional polymorphs for  $\text{HgX}_2 \cdot \text{TPyP}$  complexes (6)! These possible polymorphs are under active investigation in our laboratories.

#### ACKNOWLEDGMENTS

C.V.K.S. is grateful for a postdoctoral fellowship from The University of Alabama, College of Arts and Sciences. The Siemens CCD area detector-equipped diffractometer was purchased with support from the U.S. National Science Foundation (Grant CHE-9626144).

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