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Metal–Organic Hybrids of 1,3,5-Tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene with Mercuric Halides

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Synthesis and solid-state structure elucidation of metal–organic hybrids of 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene with Hg^{II} halides ($HgCl_2$, $HgBr_2$, and HgI_2) are reported. In the metal-hybrids of $\mathbf{L^1}$, a reaction with $HgCl_2$ in dmso as well as in dmf gave host–guest complexes, **1a** and **1b**, respectively, with the corresponding solvent of crystallization as the guests, while a reaction with HgI_2 gave open-frame network structures without any solvent of crystallization from both dmso and dmf (**1c**). However, reaction with $HgBr_2$ gave crystals of two different morphologies from each solvent dmso and dmf (**1d**–**1f**), which corresponds to the structures with and without solvent of crystallization that resemble the related structures formed by $HgCl_2$ and HgI_2, respectively. Three-dimensional structures of all the compounds were characterized by single-crystal X-ray diffraction methods. While **1a** and **1b** crystallize in triclinic $P\bar{1}$ space groups **1a**: $a = 9.049(2)$, $b = 13.646(4)$, $c = 16.298(4)$ Å, $\alpha = 111.99(1)$, $\beta = 90.43(1)$, $\gamma = 101.57(1)°$, $Z = 2$, $V = 1820.6(8)$ Å^3; **1b**: $a = 8.979(3)$, $b = 13.611(5)$, $c = 16.355(5)$ Å, $\alpha = 111.57(1)$, $\beta = 92.37(1)$, $\gamma = 101.07(1)°$, $Z = 2$, $V = 1810.05(11)$ Å^3, complexes **1c**–**1f** crystallize into monoclinic space groups [**1c**: $C2/c$, $a = 27.661(7)$, $b = 18.821(4)$, $c = 15.786(4)$ Å, $\beta = 113.13(1)$, $Z = 4$, $V = 7558(3)$ Å^3, **1d**: $P2_1/c$, $a = 17.950(5)$, $b = 9.031(2)$, $c = 22.200(6)$ Å, $\beta = 113.62(1)$, $Z = 4$, $V = 3297.3(15)$ Å^3, **1e**: $C2/c$, $a = 26.753(15)$, $b = 18.415(10)$, $c = 14.940(7)$ Å, $\beta = 109.50(1)$, $Z = 4$, $V = 6938(6)$ Å^3, **1f**: $P2_1/n$, $a = 17.697(10)$, $b = 9.224(5)$, $c = 21.933(12)$ Å, $\beta = 112.50(1)$, $Z = 4$, $V = 3308(3)$ Å^3].
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Introduction

Design and synthesis of coordination polymers with exotic supramolecular architectures in the solid state are of current research interest because of the potential applications of the assemblies in the areas of separation technology, catalysis, gas storage devices, etc.[1–5] Thus, there are numerous reports of a myriad of supramolecular assemblies of coordination polymers utilizing different types of organic ligands possessing varied functionalities like carboxylates, aza-donor groups, etc., in recent literature.[6,7] In general, most of the assemblies known in the literature, however, were synthesized by utilizing organic moieties as rigid, spacer entities.[8] Thus, the crucial role of organic ligands with respect to the geometry and position of the functional groups was demonstrated in the formation of the desired topology. Also, another important feature of organic ligands is their conformational flexibility, which has been utilized in metal–organic framework structures in recent studies.[9] In this process, taking into account the well-established synthetic routes for the preparation of the required fluxional organic molecules, novel thio-based ligands with multi-armed, tripodal geometry, such as pyridylsulfanylmethyl derivatives, were synthesized, and these ligands demonstrated their significance in the supramolecular studies.[10]

Because of our continued interest in both molecular and supramolecular synthesis,[11] we were motivated to study the influence of such thio-based, flexible-armed molecules in the creation of assemblies with tailor-made geometries that possess cavities, channels, etc., and subsequently to evaluate possible applications. Thus, we have synthesized a pyridylsulfanyl compound 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene ($\mathbf{L^1}$) and prepared its host–guest complexes in the form of metal–organic hybrid assemblies in which solvents are incorporated in the channels. Thus, in this manuscript, we report on coordination polymers of $\mathbf{L^1}$ with different halides of Hg^{II} obtained by carrying out supramolecular synthesis from different solvents as illustrated in Scheme 1.

Results and Discussion

Solid-State Structure of Complex $[Hg(L^1)Cl_2]\cdot(dmso)_2$ (1a)

Crystallization of a precipitate of $\mathbf{L^1}$ and $HgCl_2$ from dmso gave single crystals that were suitable for analysis by

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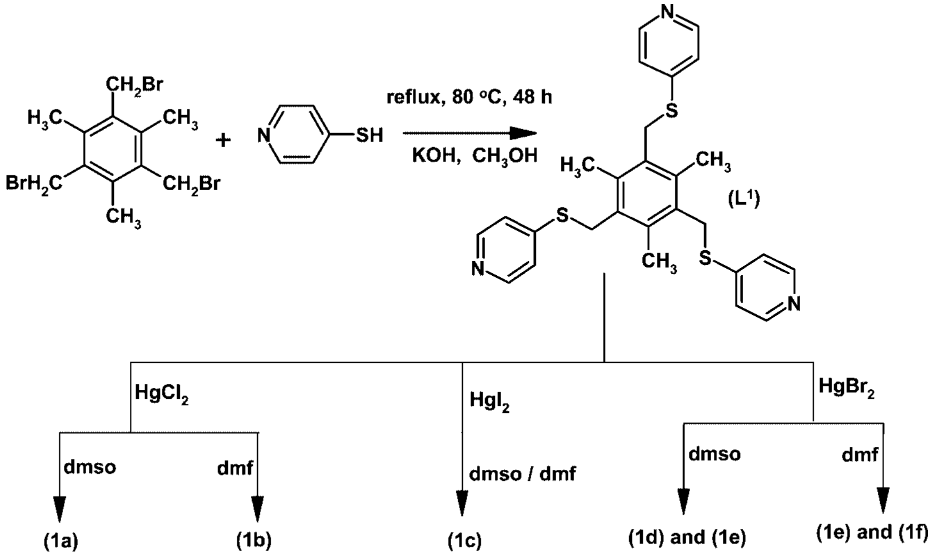
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 1.

X-ray diffraction methods. The crystal structure determination reveals that, as expected, the pyridyl N atoms of **L^1** form coordination bonds with Hg^{II} (Figure 1). The observed Hg–N bond distances (2.457–2.479 Å) are in agreement with distances presented in the literature.[12] Further, each Hg^{II} is connected to two halide ions to form Hg–Cl bonds with distances of 2.458 and 2.491 Å. The pertinent coordination bonds and angles are given in Table 1. Thus, each Hg^{II} with pentacoordination has a square-pyramidal geometry. This interaction results in the formation of a cavity of dimension 9 × 12 Å^2 and each cavity is created by two molecules of **L^1** and Hg^{II} as shown in Figure 2a. The cavities are further aligned in a three-dimensional arrangement to yield channels (see Figure 2b), which are occupied by dmso molecules (solvent of crystallization) that exist in both ordered and disordered forms. Furthermore, both types of dmso molecules exist as dimers independently through the formation of C–H···O hydrogen bonds (see insets in Figure 2a).

Solid-State Structure of Complex [Hg(L^1)Cl$_2$]·(dmf)$_2$ (1b)

A precipitate of ligand **L^1** with HgCl$_2$ from dmf gave solvent-incorporated crystals as confirmed by X-ray diffraction methods, and each Hg^{II} is connected to ligand **L^1** in exactly the same mode as that observed in **1a** (Figure 3a). The Hg–N distances are in the range 2.464–2.515 Å, and the Hg–Cl distances are 2.430 and 2.451 Å.

Thus, in the crystals of **1b**, dmf molecules are present in the cavities like the dmso molecules in **1a**, but both the dmf molecules are disordered in **1b**. Further, the symmetry-independent dmf molecules interact with each other through C–H···O hydrogen bonds with C···O distances of 3.07 and 3.13 Å. A typical hydrogen-bonding network between the dmf molecules is shown in the inset of Figure 3b. However, unlike in **1a**, no interaction exists between symmetry-dependent molecules.

Supramolecular Structure of [Hg(L^1)I$_2$] (1c)

A precipitate of ligand **L^1** and HgI$_2$ (used in a ratio of 2:3) from dmso gave **1c**. Crystallographic details of **1c** are given in Table 2. In this structure, ligand **L^1** forms coordination bonds with Hg^{II} with Hg–N distances of 2.353–2.440 Å. Furthermore, Hg^{II} forms Hg–I coordination bonds with distances in the range 2.623–2.661 Å (Figure 4).

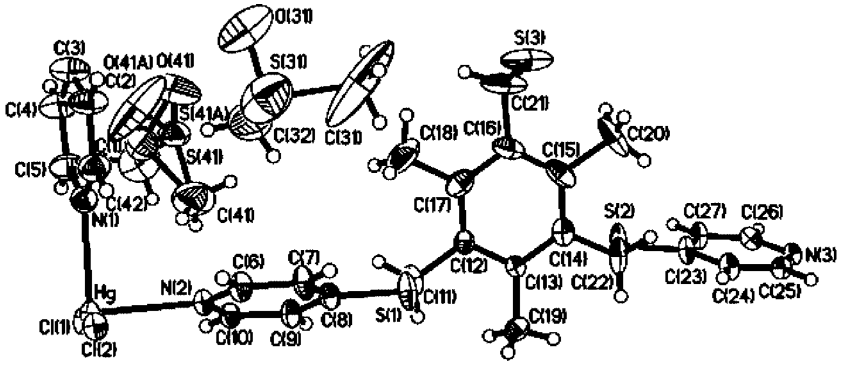


Figure 1. ORTEP drawing of the asymmetric unit in the coordination complex **1a**, along with dmso molecules.

Table 1. Selected bond lengths [Å] and bond angles [°] around the coordination sphere in complexes **1a**–**1f**.

1a				**1b**			
Hg–N(1)	2.457(7)	N(1)–Hg–N(2)	88.1(2)	Hg–N(1)	2.464(4)	N(1)–Hg–N(2)	90.2(1)
Hg–N(2)	2.462(6)	N(1)–Hg–N(3)	86.5(2)	Hg–N(2)	2.493(4)	N(1)–Hg–N(3)	178.3(1)
Hg–N(3)	2.479(6)	N(2)–Hg–N(3)	174.5(2)	Hg–N(3)	2.515(4)	N(2)–Hg–N(3)	88.7(1)
Hg–Cl(1)	2.491(2)	N(1)–Hg–Cl(1)	92.0(2)	Hg–Cl(1)	2.430(1)	Cl(1)–Hg–N(2)	99.4(1)
Hg–Cl(2)	2.458(2)	N(1)–Hg–Cl(2)	97.2(2)	Hg–Cl(2)	2.451(1)	Cl(1)–Hg–N(1)	91.3(9)
		N(2)–Hg–Cl(1)	89.8(2)			Cl(1)–Hg–N(3)	87.5(9)
		N(3)–Hg–Cl(1)	90.9(2)			Cl(1)–Hg–Cl(2)	167.9(4)
		Cl(2)–Hg–Cl(1)	170.7(7)			Cl(2)–Hg–N(3)	91.3(9)
		Cl(2)–Hg–N(2)	91.3(2)			Cl(2)–Hg–N(1)	90.1(9)
		Cl(2)–Hg–N(3)	88.8(2)			Cl(2)–Hg–N(2)	92.7(1)
1c				**1d**			
Hg(1)–N(1)	2.353(1)	N(1)–Hg(1)–N(1)	83.0(7)	Hg–N(2)	2.342(1)	N(2)–Hg–N(3)	119.6(4)
Hg(1)–I(1)	2.634(2)	N(1)–Hg(1)–I(1)	104.7(4)	Hg–N(3)	2.348(1)	N(2)–Hg–Br(1)	103.0(3)
Hg(2)–N(2)	2.440(2)	N(1)–Hg(1)–I(1)	105.0(4)	Hg–Br(1)	2.520(2)	N(2)–Hg–Br(2)	101.2(3)
Hg(2)–N(3)	2.406(2)	I(1)–Hg(1)–I(1)	140.0(9)	Hg–Br(2)	2.515(2)	N(3)–Hg–Br(1)	98.8(3)
Hg(2)–I(2)	2.623(2)	N(3)–Hg(2)–N(2)	85.6(6)			N(3)–Hg–Br(2)	101.0(3)
Hg(2)–I(3)	2.653(2)	N(2)–Hg(2)–I(2)	102.2(4)			Br(2)–Hg–Br(1)	135.3(7)
		N(3)–Hg(2)–I(3)	101.1(4)				
		N(3)–Hg(2)–I(2)	107.8(4)				
		N(2)–Hg(2)–I(3)	101.3(4)				
		I(2)–Hg(2)–I(3)	143.8(7)				
1e				**1f**			
Hg(1)–N(1)	2.421(2)	N(1)–Hg(1)–N(1)	81.9(9)	Hg–N(1)	2.310(2)	N(1)–Hg–N(2)	116.7(9)
Hg(1)–Br(1)	2.455(3)	N(1)–Hg(1)–Br(1)	102.0(4)	Hg–N(2)	2.380(2)	N(1)–Hg–Br(1)	100.8(6)
Hg(2)–N(2)	2.346(2)	N(2)–Hg(2)–N(3)	88.1(7)	Hg–Br(1)	2.486(4)	N(1)–Hg–Br(2)	103.5(6)
Hg(2)–N(3)	2.370(2)	N(2)–Hg(2)–Br(2)	99.9(4)	Hg–Br(2)	2.509(3)	N(2)–Hg–Br(2)	98.6(7)
Hg(2)–Br(2)	2.485(3)	N(2)–Hg(2)–Br(3)	105.4(4)			N(2)–Hg–Br(1)	98.6(8)
Hg(2)–Br(3)	2.448(3)	N(3)–Hg(2)–Br(2)	100.5(4)			Br(1)–Hg–Br(2)	139.7(1)
		N(3)–Hg(2)–Br(3)	99.6(3)				
		Br(1)–Hg(1)–Br(1)	148.1(1)				
		Br(3)–Hg(2)–Br(2)	148.0(1)				

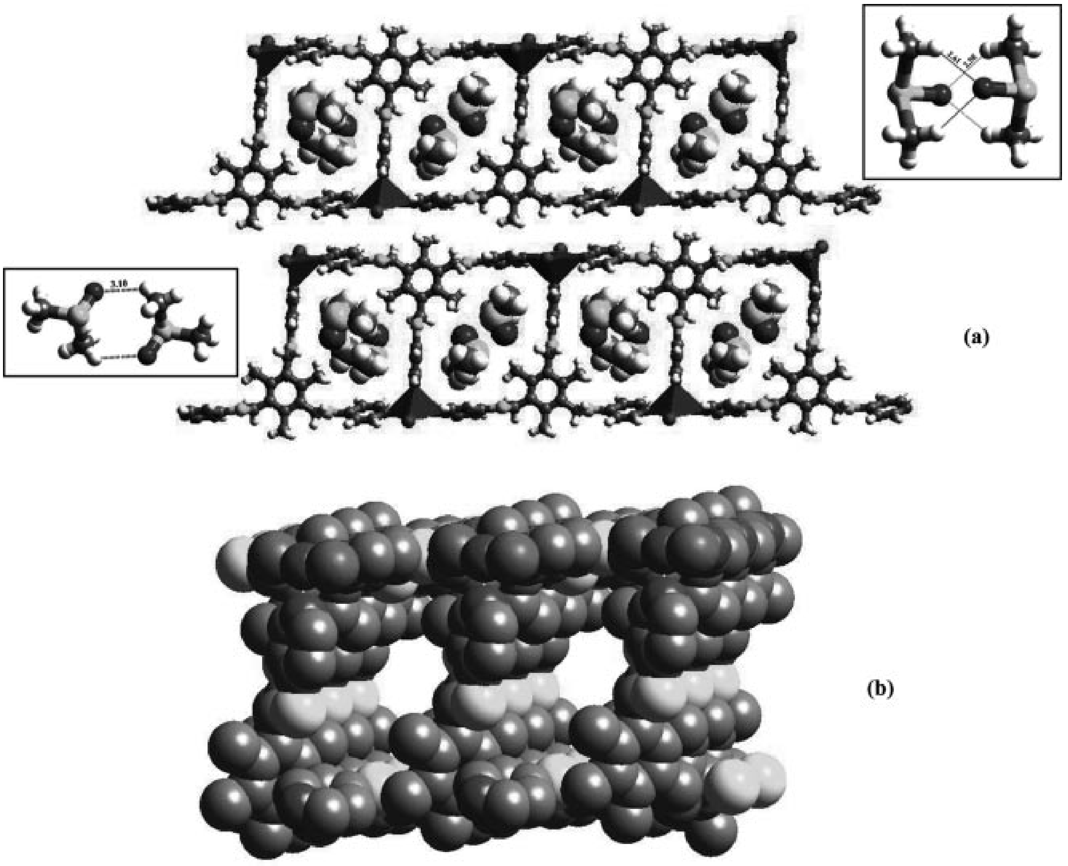


Figure 2. (a) Presentation of the cavities occupied by dmso molecules in the crystal structure of **1a**. The different types of interaction between the dmso molecules are shown in the insets. Disorder in dmso is omitted for purposes of clarity. (b) Three –dimensional formation of the channels; the alignment of the cavities is shown in (a).

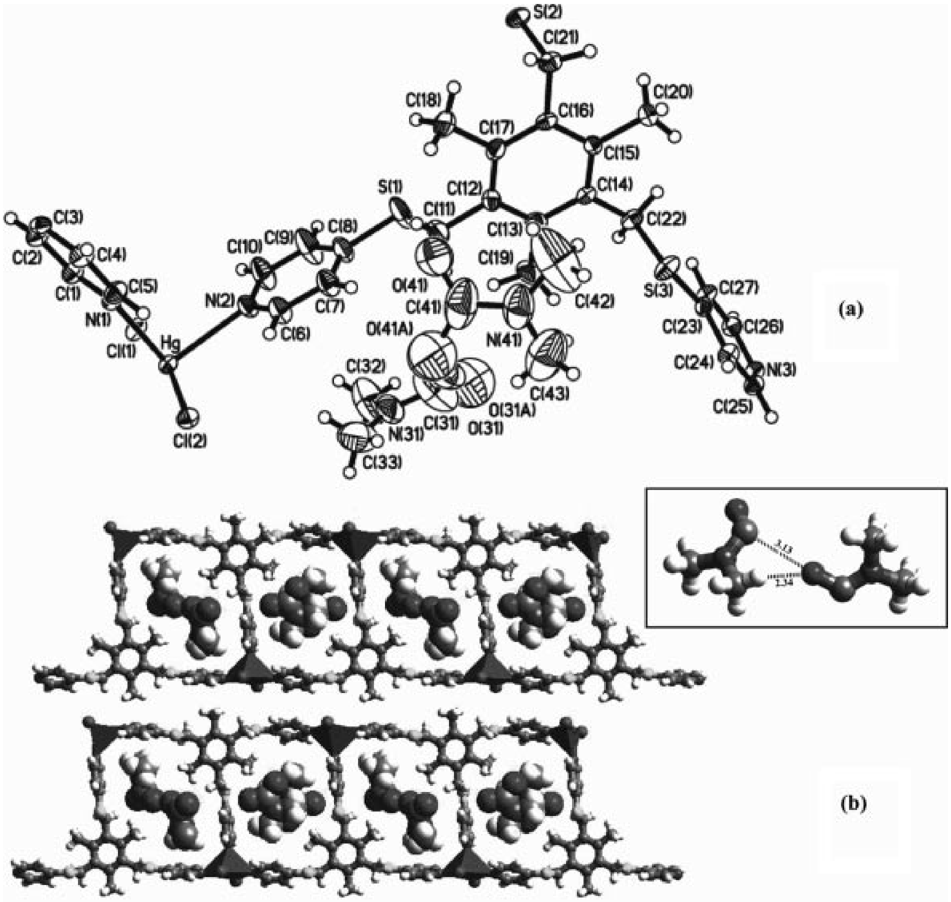


Figure 3. (a) ORTEP drawing of the asymmetric unit in the crystal structure of **1b** along with the solvent of crystallization, dmf. (b) Arrangement of dmf molecules in the cavities, and the intermolecular interactions between the adjacent molecules are shown in the inset.

Table 2. Crystallographic data of metal complexes of **L**^{1}, **1a**–**1f**.

	1a	**1b**	**1c**	**1d**	**1e**	**1f**
Empirical formula	$(HgCl_2)(C_{27}H_{27}N_3S_3)\cdot 2C_2H_6SO$	$(HgCl_2)(C_{27}H_{27}N_3S_3)\cdot 2C_3H_7NO$	$(HgI_2)_3(C_{27}H_{27}N_3S_3)_2$	$(HgBr_2)(C_{27}H_{27}N_3S_3)\cdot C_2H_6SO$	$(HgBr_2)_3(C_{27}H_{27}N_3S_3)_2$	$(HgBr_2)(C_{27}H_{27}N_3S_3)\cdot C_3H_7NO$
Formula mass	917.44	905.36	2342.56	928.23	2060.62	922.19
Crystal shape	blocks	blocks	blocks	thin plates	blocks	thin plates
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/n$
a [Å]	9.049(2)	8.979(3)	27.661(7)	17.950(5)	26.753(15)	17.697(10)
b [Å]	13.646(4)	13.611(5)	18.821(4)	9.031(2)	18.415(10)	9.224(5)
c [Å]	16.298(4)	16.355(5)	15.786(4)	22.200(6)	14.940(7)	21.933(12)
α [°]	111.99(1)	111.57(1)	90	90	90	90
β [°]	90.43(1)	92.37(1)	113.13(1)	113.62(1)	109.50(1)	112.50(1)
γ [°]	101.57(1)	101.07(1)	90	90	90	90
V [Å^3]	1820.6(8)	1810.5(11)	7558(3)	3297.3(15)	6938(6)	3308(3)
Z	2	2	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.674	1.661	2.059	1.870	1.973	1.852
T [K]	133	133	133	133	133	133
Mo-K_α	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	4.693	4.609	8.730	7.373	10.295	7.289
2θ range [°]	46.54	52.12	46.66	46.62	46.82	46.62
$F(000)$	912	900	4296	1800	3864	1788
Total reflections	15091	18822	15672	13942	4747	13554
Unique reflns.	5225	7103	5451	4755	4002	4758
[R (int)]	[0.0469]	[0.0468]	[0.1232]	[0.0543]	[0.0255]	[0.1469]
No. reflns. used	4931	6481	2929	4411	2542	3305
No. parameters	403	425	339	356	339	320
GOF on F^2	1.512	0.747	0.927	1.380	1.265	1.142
R_1 [$I > 2\sigma(I)$]	0.0532	0.0354	0.0570	0.0729	0.0517	0.1079
wR_2	0.1486	0.0928	0.1374	0.1558	0.1493	0.3029

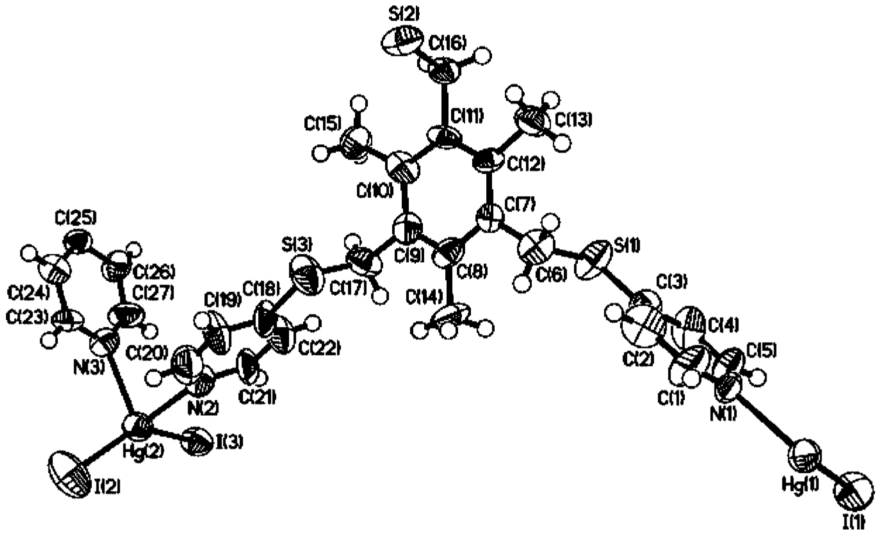


Figure 4. ORTEP drawing of the coordination geometry in the crystal structure of **1c**.

Further, the coordination geometry around Hg^{II} in **1c** is distorted tetrahedral and differs from the square pyrimidal geometry observed in **1a** and **1b**. Thus, the coordination moieties in **1c** yield a polymer network comprising interconnected square grids with cavities (Figure 5a, b). However, the cavities could not be translated into channels in a three-dimensional arrangement as the void space is filled by moieties from adjacent chains as shown in Figure 5c.

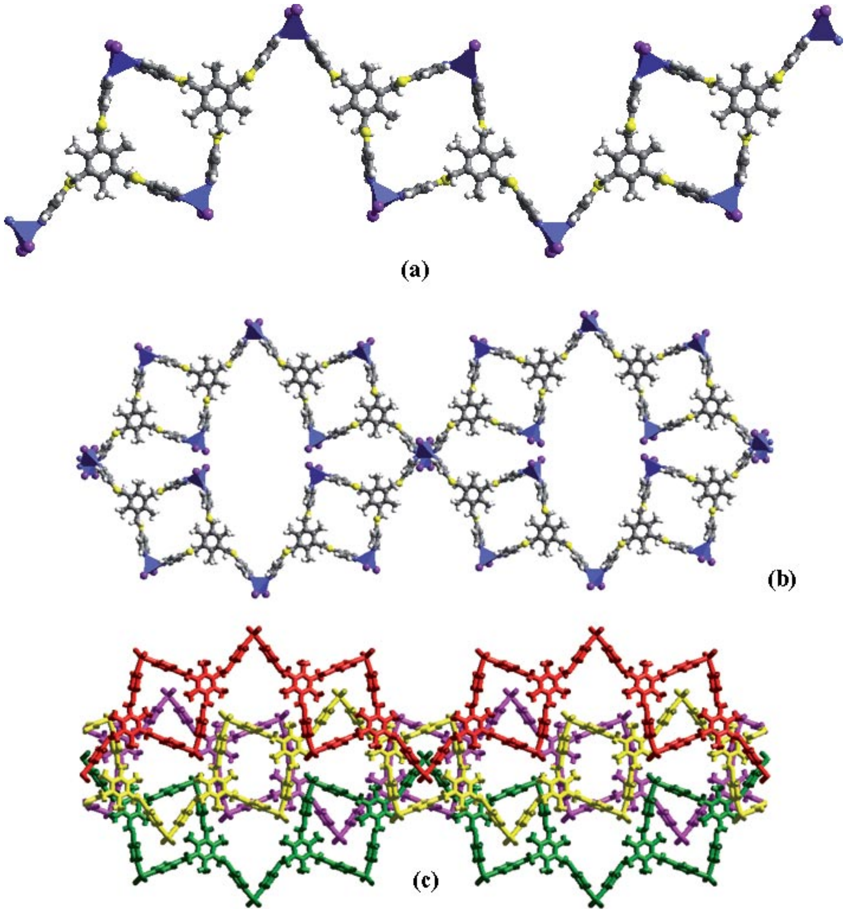


Figure 5. (a) Square-grid network mediated coordination polymers in the crystal structure of **1c**. (b) Arrangement of two adjacent polymer networks. (c) The three-dimensional arrangement of the coordination polymers. Each polymer network is shown in different colors.

Solid-State Structures of Complexes of L^1 with $HgBr_2$ (1d–1f)

The complexes formed by $HgBr_2$ are quite intriguing and in fact further reinforce the systematic changes generally observed in the halogen series. Crystallization of a solid mixture of L^1 and $HgBr_2$ from dmso and dmf gave concomitant crystals of two different morphologies from each solvent. Structure analysis reveals that, while one of the morphologies from each solvent [**1d** (dmso) and **1f** (dmf)] corresponds to a solvated structure such as for $HgCl_2$ (**1a** and **1b**, respectively), the other morphologies gave structures without a solvent of crystallization (**1e**) like **1c** formed by HgI_2.

Although **1d** and **1f** have similar unit cell parameters, they are not isomorphous, as they crystallize in different space groups, $P2_1/c$ and $P2_1/n$, respectively. The full crystallographic details are given in Table 2. However, structure analysis reveals that both **1d** and **1f** are isostructural with the formation of identical three-dimensional arrangements. In a typical interaction, as shown in Figure 6, the ligand L^1 interacts with Hg^{II} by forming Hg–N bonds (Table 1) to yield an infinite coordination polymer chain.

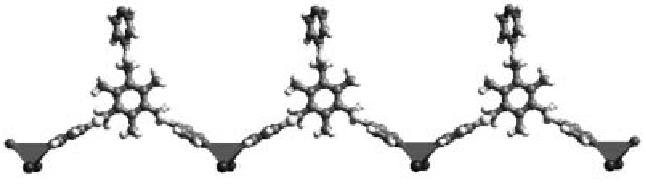


Figure 6. Coordination polymer formed between L^1 and $HgBr_2$ yielding a chain.

Thus, out of the available three pyridyl moieties only two interact with Hg^{II}. Also, each Hg^{II} is bonded to two Br atoms (Table 1). Thus, in **1d** and **1f**, the coordination geometry around each Hg^{II} atom is also distorted tetrahedral as shown in Figure 6. Such adjacent chains are held together by C–H···N hydrogen bonds with H···N distances of 2.66–2.89 Å, as observed in the structure of the free ligand (Supporting Information) and form cavities of dimension 11 × 16 Å^2 (Figure 7), which are aligned in a three-dimensional arrangement to yield channels. The channels are occupied by the solvent molecules dmso and dmf in **1d** and **1f**, respectively. Thus, **1d** and **1f** show some similarities with **1a** and **1b** in the formation of an open-frame network. However, the metal coordination and geometry around each Hg^{II} in **1d** and **1f** has a close resemblance to that of **1c**. Further, the solvent molecules present in the channels of the structures **1d** and **1f** do not interact with each other but are bound to the host lattice through numerous intermolecular interactions.

However, complex **1e**, obtained as concomitant crystals along with **1d** and **1f**, crystallizes in the monoclinic space group $C2/c$. Further, packing analysis reveals that the structure of **1e** is identical to that formed by HgI_2 (**1c**) in all respects except for the difference of the halogen atoms. A typical structural arrangement in complex **1e** is shown in Figure 8 for purposes of comparison with the structure of **1c**.

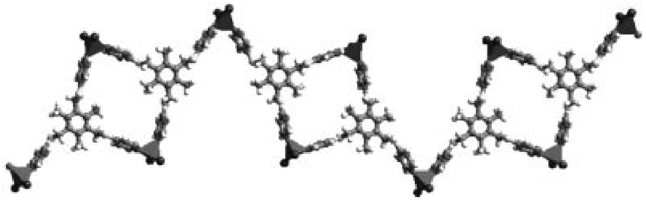


Figure 8. Square-grid network found in the solid-state structure of complex **1e**.

By comparing the crystal structures of the metal complexes described herein, it is clearly evident that the structures obtained are in agreement with the proposition of

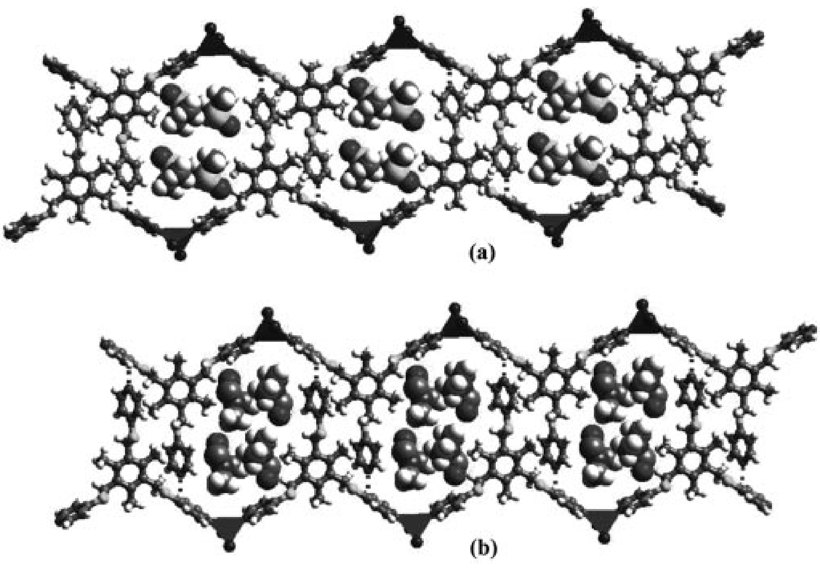


Figure 7. Representation of cavities formed by the interaction of the adjacent polymeric chains through C–H···N hydrogen bonds in the crystal structures (a) **1d** and (b) **1f**, along with the solvent molecules dmso and dmf, respectively.

utilization of pyridylsulfanyl ligands in the supramolecular synthesis through either dative bonds (**1a**–**1c**, **1e**) or a combination of dative bonds and hydrogen bonds (**1d** and **1f**). Another intriguing feature of these metal complexes is the systematic variation with the change in halogen. While $HgCl_2$ forms solvated structures, HgI_2 forms structures exclusively without solvents of crystallization.

One more interesting feature is the conformational changes in ligand $\mathbf{L^1}$ that occur when the ligand is uncoordinated and when it is in the different complexes (Figure 9). It is apparent that all the metal complexes, except **1d** and **1f**, adopt the same conformation (*cis*, *trans*, *trans*), which is different from that of the conformation observed in the pure structure of $\mathbf{L^1}$ (*cis*, *cis*, *cis*). It is well known from the literature that tripodal ligands like $\mathbf{L^1}$ show both types of conformation observed in this study, but often the conformation was attributed to the nature of the anion present in the structures. However, it is apparent from this study that the coordination environment of the metal species as well as denticity of the ligands also may play a significant role in determining the conformation. In particular, the complexes formed by $HgBr_2$ are quite significant in this respect. Since, the same halogen (Br) gave structures of both conformations, which can be differentiated by the number of metal coordination centers, it may be understood that interaction with three metal ions like Hg^{II} leads to strained crowding in a *cis*, *cis*, *cis* geometry, which might have forced the transformation of the conformation to *cis*, *trans*, *trans* in **1e**, whereas in **1d** and **1f**, with only two Hg^{II} involved in complex formation, the conformation is retained as such, as in $\mathbf{L^1}$.

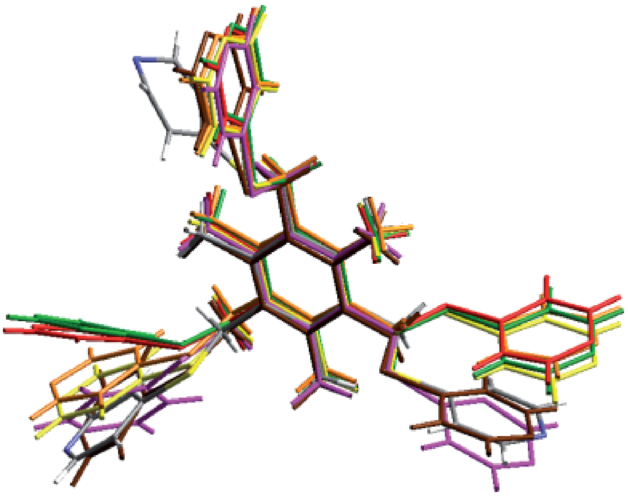


Figure 9. An overlay diagram of the molecular conformation of ligand $\mathbf{L^1}$ in its crystal structure (gray) and also in the complexes **1a**–**1f**. Brown and pink correspond to **1d** and **1f**.

Conclusions

In conclusion, we have reported the solid-state structures of metal–organic hybrids of conformationally flexible thio ligand $\mathbf{L^1}$ with different mercuric halides. Complexes **1a**–**1f** were prepared and the supramolecular assembly networks have been analyzed, and it is understood that all the complexes have open-frame networks with void space. In complexes **1a**, **1b**, **1d**, and **1f**, solvent of crystallization occupies the void space, while in other structures (**1c** and **1e**), the void space was filled by the self-protrusion of functional groups from adjacent molecules. In particular, the variations observed in the conformations of the ligand $\mathbf{L^1}$ are intriguing and may provide further insight in modeling experiments, especially for the evaluation of metal-hybrids as catalysts, which has increased demands under the current research themes.

Experimental Section

Synthesis of 1,3,5-Tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene ($\mathbf{L^1}$): 1,3,5-tris-(bromomethyl)-2,4,6-trimethylbenzene (399 mg, 1 mmol) was added to an ice-cooled solution of pyridine-4-thiol (333 mg, 3 mmol) and KOH (560 mg, 10 mmol, slight excess) in methanol whilst stirring. The mixture was heated at reflux for 48 h at 80 °C. The solution was poured into ice-cold water, the crude product was filtered and separated by column chromatography, and a colorless microcrystalline solid was obtained ($\mathbf{L^1}$) in 72% yield (m.p. 228–230 °C). Single crystals of $\mathbf{L^1}$ suitable for X-ray diffraction were obtained from methanol solution after 2–3 d.

Preparation of Complex $[Hg(L^1)Cl_2]\cdot(dmso)_2$ (1a): A white precipitate obtained by dissolving $HgCl_2$ (81 mg, 0.3 mmol) and $\mathbf{L^1}$ (49 mg, 0.1 mmol) in methanol was filtered and dissolved in dmso and allowed to slowly evaporate at room temperature. Within 48 h, well-grown colorless single crystals of **1a** were obtained in 36% yield (m.p. 204–206 °C).

Preparation of Complex $[Hg(L^1)Cl_2]\cdot(dmf)_2$ (1b): A white precipitate was obtained as described for **1a**; however dmf was used instead of dmso. After slow evaporation under ambient conditions, gave colorless single crystals of **1b** were obtained in 42% yield (m.p. 213–215 °C).

Preparation of Complex $[Hg(L^1)I_2]$ (1c): A solution of HgI_2 (135 mg, 0.3 mmol) in methanol was added to a solution of $\mathbf{L^1}$ (49 mg, 0.1 mmol) in methanol, and a white precipitate was obtained. The precipitate was filtered and dissolved in dmso to obtain colorless crystals of **1c** in 31% yield (m.p. 208–210 °C). The complex **1c** was also obtained by dissolving the precipitate in dmf and by evaporating the solution under ambient conditions.

Preparation of Complexes $[Hg(L^1)Br_2]\cdot(dmso)$ (1d) and $[Hg(L^1)Br_2]$ (1e): A solution of $HgBr_2$ (108 mg, 0.3 mmol) in methanol was added to a solution of $\mathbf{L^1}$ (49 mg, 0.1 mmol) in methanol. The resulting white precipitate was filtered and dissolved in dmso. Colorless crystals of two morphologies (plates **1d** and blocks **1e**) were obtained in 21 and 11% yields, respectively [m.p. 177–179 (**1d**) and 197–199 °C (**1e**)].

Preparation of Complex $[Hg(L^1)Br_2]\cdot(dmf)$ (1f): A solution of $HgBr_2$ (108 mg, 0.3 mmol) in methanol was added to a solution of $\mathbf{L^1}$ (49 mg, 0.1 mmol) in methanol. The white precipitate obtained was filtered and dissolved in dmf. Colorless crystals of two morphologies (blocks **1e**; plates **1f**) were obtained in 28 and 14% yields, respectively, (**1f**: m.p. 184–186 °C).

Crystal Structure Determination: Good quality, single crystals of **L**^{1} and **1a**–**1f**, grown as described above, were carefully chosen with the aid of a polarized optical microscope and glued to glass fiber to mount on a X-ray diffractometer goniometer equipped with a CCD area detector.[13] The data collection proceeded without any complication and was processed using the Bruker suite of software. The structures were determined and refined by using the SHELXTL suite of programs, and absorption corrections were made on all the crystals with SADABS.[14] All the non-hydrogen atoms were refined anisotropically except a few atoms in **1d** (one atom) and **1f** (nine atoms). All hydrogen atoms were placed in the calculated positions.

The structural parameters are given in Table 2. All the intra- and intermolecular distances were computed with PLATON software.[15] The packing drawings were generated either by an XP package of SHELXTL or Cerius^2 of Accelrys, Inc. CCDC-625087–625093 for **L**^{1} and **1a**–**1f**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Discussion of the structure of **L**^{1} and corresponding figures, its crystallographic information and powder X-ray diffraction patterns (both experimental and simulated from crystal data) are given.

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