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Formation of A Novel 1D Supramolecule $[HgCl_2(ptz)]_2{\cdot}HgCl_2$ (ptz = Phenothiazine): A New Precursor to Submicrometer Hg_2Cl_2 Rods

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A novel supramolecule $[HgCl_2(ptz)]_2{\cdot}HgCl_2$ (ptz = phenothiazine) with uncoordinated inorganic salt $HgCl_2$ presented in a 1D chain was first prepared and then successfully applied as a new precursor in the preparation of submicrometer Hg_2Cl_2 rods. Single crystal X-ray analysis showed that the 1D chain structure is stabilized by hydrogen bonds between adjacent chains and the coordination mode of the ligand phenothiazine is unusual with large steric inhibition other than the chain directions. The results revealed that the particular chain structure plays a significant role in the formation of the Hg_2Cl_2 rods.

Introduction

Self-assembly through coordination and noncovalent interactions such as hydrogen bonds, aromatic $\pi-\pi$ stacking, steric repulsion, and van der Waals forces leads to well-organized organic and inorganic supramolecular structures, which can be applied in areas such as selective clathration,[1] molecular recognition,[2] and catalysis.[3] Recent progress demonstrates that some supramolecules can also be applied as precursors or templates in the preparation of nanomaterials.[4]

Among the numerous supramolecules reported, it is very common to find counterions, small organic molecules, and solvated species in the void spaces of coordination polymers.[5] However, to the best our knowledge, there is no report of a supramolecule with an uncoordinated inorganic salt incorporated into a 1D chain. What follows is our initial finding in the preparation of a new coordination complex, demonstrating its novel structure and application both as precursor and growth director in the preparation of submicrometer Hg_2Cl_2 rods.

Experimental Section

Synthesis of $[HgCl_2(ptz)]_2{\cdot}HgCl_2$ (1). Reaction of $HgCl_2$ (0.27 g, 1 mmol) and phenothiazine (0.39 g, 2 mmol) in benzene (80 mL) at 40 °C yielded a clear solution. After standing in air for 2 days, well-developed red single crystals formed in the filtrate. Anal. Calcd (Found) for $C_{24}H_{18}N_2S_2Hg_3Cl_6$: C, 23.76 (23.78); H, 1.50 (1.57); N, 2.31 (2.28).

Crystal Structure Determination of 1. The crystal structure was determined by single crystal X-ray analysis. Data were collected at 293 K on a Bruker P4 four-circle diffractometer by the $\theta/2\theta$ scan method. The structure solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXL 97 programs.[6] All non-hydrogen atoms were refined anisotropically. Crystal data and experimental details for **1** are listed in Tables 1 and 2.

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Table 1. Crystallographic Data for **1**

empirical formula	$C_{24}H_{18}Cl_6Hg_3N_2S_2$
fw	1213.01
cryst syst	triclinic
space group	$P\bar{1}$
T (K)	293
a (Å)	7.675(9)
b (Å)	8.919(13)
c (Å)	11.644(12)
α (deg)	83.81(10)
β (deg)	71.63(7)
γ (deg)	81.76(11)
V (Å^3)	747.05(16)
Z	1
D_c (g cm^{-3})	2.696
F(000)	550
μ (mm^{-1})	16.071
λ (Å)	0.71073
cryst size (mm^3)	0.16 × 0.18 × 0.19
$2\theta_{\max}$ (deg)	55
N	4184
N_o ($I > 2.0\sigma(I)$)	2852
$R1^a$	0.049
$wR2^b$	0.1284
largest difference peak and hole (e Å^{-3})	2.04, −1.77

^{a} $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F_o) = (\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2)^{1/2}$, $w = [\sigma^2(F_o) + (0.002F_o)^2]^{-1}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

Hg1	Cl1	3.067(2)	
Hg1	Cl3	2.287(3)	
Hg2	Cl1	2.340(2)	
Hg2	Cl2	2.329(2)	
Hg2	S1	2.771(2)	
Hg2	Cl2a	2.995(2)	
Cl1	Hg1	Cl1b	180.00(0)
Cl1	Hg1	Cl3b	92.29(8)
Cl1b	Hg1	Cl3b	87.71(8)
Cl1	Hg2	Cl2	162.49(9)
Cl1	Hg2	S1	103.65(7)

Result and Discussion

An ORTEP view of [HgCl$_2$(ptz)]$_2$·HgCl$_2$ (**1**) is shown in Figure 1. The crystal structure consists of a continuous one-dimensional chain based on [HgCl$_2$(ptz)]$_2$ pairs and uncoordinated HgCl$_2$ molecules via weak Hg···Cl interactions with Hg(1D)···Cl(1F) and Hg(2A)···Cl(3A) distances of 3.067 and 3.183 Å, respectively. Although the Hg···Cl distances are long, they do lie within the sum of van der Waals' radii (3.45 Å[7]). As illustrated in Figure 1, the mercury atom in the [HgCl$_2$(ptz)]$_2$ pair has a T shaped HgCl$_2$S local coordination geometry. Surprisingly, uncoordinated linear "dumbbell" HgCl$_2$ molecules (Cl(3H)−Hg(1D)−Cl(3G) 180.00(15)°) are incorporated into the 1-D chain. It's a novel phenomenon, since it is very common to find counterions, small organic molecules, and solvated species in some supramolecules; up to now, there has been no report of a supramolecule with an uncoordinated inorganic salt incorporated into a 1D chain, especially in a system containing excess ligand. Interestingly, the equal Hg−Cl distance of 2.287(3) Å in uncoordinated HgCl$_2$ molecules is the same as the Hg−Cl bond length in HgCl$_2$ vapor (2.28 Å) which is slightly shorter than the coordinated Hg−Cl bonds in [HgCl$_2$(ptz)]$_2$ pairs. It is notable that the S−Hg bond length (2.771 Å) is apparently longer than common S−Hg bond, indicating weak coordination of phenothiazine (ptz) with HgCl$_2$.

In the crystal structure of **1**, the two benzene rings of phenothiazine form a butterfly geometry with a dihedral angle of 25.2° due to the deviation of S and N atoms (0.5375 and 0.5033Å, respectively) from the ptz plane. It is also very interesting to note that the coordination mode of ptz is unusual in that the large aromatic plane is almost parallel to the chain with large steric inhibition perpendicular to the S−Hg bond direction (the S(1E), Hg(2E), Cl(1E), and Cl(2E) plane form a dihedral angle of 87.4° with the ptz plane). This is different from most of the numerous known complexes with an aromatic ring containing ligand such as pyridine and bipyridine,[8] in which the metal atoms are almost coplanar with the aromatic rings to decrease the steric inhibition. To stabilize the uncoordinated HgCl$_2$ molecules and the whole chain structure, all the chloride atoms are fully utilized to form multiple Hg···Cl interactions.

The packing diagram of **1** is shown in Figure 2, which shows the $\pi-\pi$ stacking of the large aromatic rings between adjacent chains. The close contacts of 3.6153 Å between the two intermolecular ptz planes are slightly longer than 3.4 Å for the modeled porphrin−porphrin interactions in solution.[9] It is clearly seen that the Hg atoms are almost collinear and the 1D structure is stabilized by hydrogen bonds (N−H···Cl with H···Cl distance of 2.821 Å) between adjacent chains to form a 2D network.

This kind of coordinatively unsaturated complex with this particular structure may have some usefulness in catalysis or as a precursor for the preparation of inorganic nano- or micrometer inorganic materials because the complex [HgCl$_2$(ptz)]$_2$·HgCl$_2$ is a director-containing precursor itself, as revealed from the space-filling representation (Figure 3) which apparently demonstrates the large steric inhibition of the bulk ptz plane other than the chain directions. Detailed analysis of the collinear Hg atoms in one chain revealed that the Cl−Hg···Hg−Cl moiety in each [HgCl$_2$(ptz)]$_2$ pair is similar to the Cl−Hg−Hg−Cl unit in the Hg$_2$Cl$_2$ crystal, which also has a chainlike structure along the [001] axis.[10] Moreover, the weak coordination ligand ptz is also a strong electron donor with efficient electron transfer ability itself and can be easily oxidized to a radical ion,[11] which give us a inspiration that the complex [HgCl$_2$(ptz)]$_2$·HgCl$_2$ may be an excellent candidate for a new precursor to Hg$_2$Cl$_2$ rods. It is thought that if Hg(II) is reduced to Hg(I) by ptz, Hg$_2$Cl$_2$, which is a unique acousto-optic material[10b] and a good

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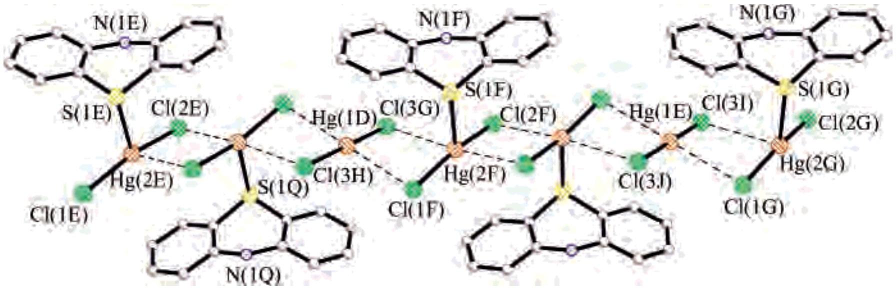

Figure 1. ORTEP drawing of one chain of the title supramolecule **1** with atomic numbering at 50% probability ellipsoids.

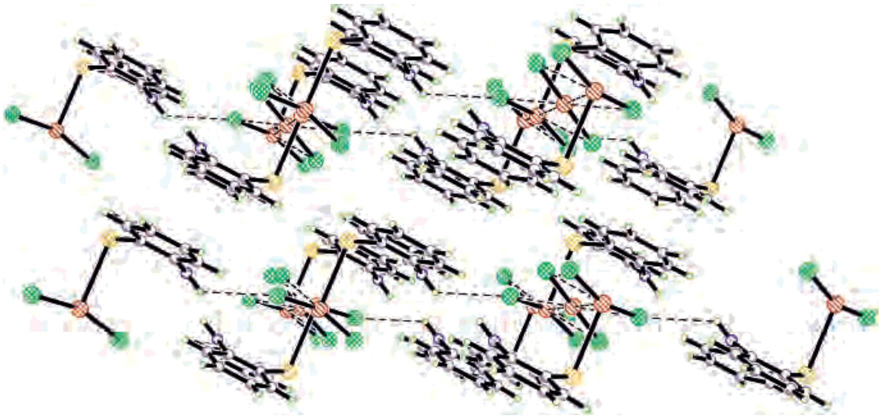

Figure 2. Packing diagram of **1** showing the hydrogen bond interaction between adjacent chains and the $\pi-\pi$ stacking of the aromatic rings.

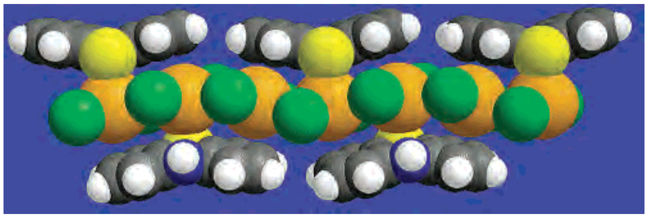

Figure 3. Space-filling model of **1** showing the 1D chain structure and unusual coordination mode of the ligand ptz with large steric inhibition (Hg orange, Cl green, S yellow, N blue, C black, H white).

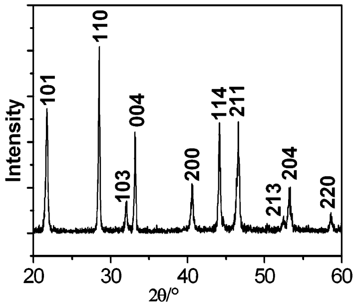

Figure 4. XRD pattern of the as-prepared Hg_2Cl_2.

nonlinear optical material with effective nonlinear susceptibilities $\chi^{(3)}_{\mathrm{eff}}$,[10c] will be produced and grow along the chain direction. On the basis of this strategy, we have synthesized Hg_2Cl_2 as follows: $HgCl_2$ (0.81 g, 3 mmol) and phenothiazine (1.14 g, 6 mmol) were mixed in benzene (80 mL) at 80 °C. Immediate precipitation of a red crystalline solid occurred, which then gradually turned into a dark-blue powder upon heating under stirring. The dark-blue powder was washed with ethanol thoroughly, and the final pale-white Hg_2Cl_2 was collected by filtration. In the synthesis, the dark-blue powder is $[ptz]^+Cl^-$ according to the elemental analysis, which can be easily dissolved in polar solvents such as methanol, ethanol, and water but cannot be dissolved in nonpolar solvent such as benzene.

The final products were characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). As shown in its XRD pattern in Figure 4, all peaks can be indexed to the tetragonal phase Hg_2Cl_2 with $a = 4.480$ Å, $c = 10.906$ Å, in good agreement with JCPDS no. 26-312. A representative Hg_2Cl_2 rod with a diameter of 300 nm and a length of several microns is presented in Figure 5, in which the electron diffraction exhibits sharp diffraction spots characteristic of crystalline Hg_2Cl_2. Moreover, the ED patterns taken from different positions along the rod are found to be identical within experimental accuracy, indicating that the entire rod is a single crystal and elongated along the crystallographic [001] axis that is also in agreement with our postulation.

On the basis of the design strategy and the experiment results, a mechanism was put forward to explain the formation of the Hg_2Cl_2 rods, which is most probably facilitated by the preorientation of the 1D chain structure of the precursor. The driving forces for the growth of Hg_2Cl_2 are probably Hg···Cl interactions and the template formed by the chain itself. The known weak interactions acting as a template in the preparation of 1D nanomaterial are hydrogen bond interactions, as evidenced by several recent reports such

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Figure 5. TEM image of a representative Hg_2Cl_2 rod and its ED pattern (inset).

as hydrogen bonding[4] for the formation of linear structures derived from cyclic polypeptides,[4a] for the synthesis of nanotubes originated from organic calix[4] hydroquinone,[4b] and for the formation of cobalt oxide nanotubes from 1D Co^{III} complexes.[4c] On the other hand, the effect of large steric inhibition of phenanthroline was also observed in the formation of silver nanorods,[12] whereas in our approach, both the weak Hg···Cl interactions and the templating effect of the chain structure play a significant role in the formation of the Hg_2Cl_2 rods.

As shown in the packing diagram of **1** (Figure 2), the crystal structure is stabilized by N−H···Cl hydrogen bonds. It is thought that the chain structure would not form if the hydrogen atom of the N−H group was substituted by an alkyl group. Thus, a comparison experiment was carried out for a similar process except 10-ethyl-phenothiazine was used instead of phenothiazine. The comparison experiment result showed that there was neither coordination complex nor Hg_2Cl_2 formed, as speculated. Although the ethylated phenothiazine can be considered as a stronger reductant compared with phenothiazine, there is not any Hg_2Cl_2 formed even upon heating the mixture of 10-ethyl-phenothiazine and $HgCl_2$ in a Teflon-lined autoclave at 180 °C for 2 days. From the result of the comparison experiments, we can conclude that the formation of the 1D chain structure is a prerequisite for the formation of Hg_2Cl_2 rods in this system.

In conclusion, a unique suparmolecule with uncoordinated inorganic salt $HgCl_2$ incorporated into a 1D chain and an unusual coordination mode was first synthesized and then successfully applied as a new precursor in the preparation of submicrometer Hg_2Cl_2 rods. The understanding of the structural relationship between the precursor and the final product at the molecular level may in turn help one obtain some other useful nano- or submicrometer inorganic materials by molecular design of appropriate precursor complexes. The complexes with this kind of structure may be applied as useful precursors for the preparation of nano- and micrometer rodlike materials.

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Supporting Information Available: X-ray crystallographic tables in a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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