



Solvent-controlled assembly of crystal structures: From centrosymmetric structure to noncentrosymmetric structure



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ABSTRACT

Reported here are two isomeric organic crystals and two HgI₂-based coordination compounds by solvo(hydro)thermal method: [(TPTA)·H₂O]_n (**1**, Cc), [(TPTA)·H₂O]_n (**2**, Pbc_a), [Hg_{1.5}I₃(TPTA)_{0.5}(CH₃CN)·(H₂O)_{0.5}]_n (**3**, P2₁) and [HgI₂(TPTA)·H₂O]_n (**4**, P2₁/c) (TPTA = N,N,N'-tris(3-pyridyl)trimesic amide). Single crystal X-ray diffraction show that they afford noncentrosymmetric and centrosymmetric structures, respectively. Note that this kind of formations can be precisely controlled by changing the reaction solvent, thus indicating a facile method towards generating noncentrosymmetric structure.

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1. Introduction

Synthesis and design of coordination compounds (CCs) have attracted ever increasing interest due to not only their structural novelty but also promising applications in the fields of adsorptions, catalysis, luminescence, magnetism, conductivity, nonlinear optics (NLO), etc [1–4]. However, the formation of the CCs is highly influenced by various reaction conditions, such as solvent system, reaction temperature, pH value of the solution, ratio of ligand to metal ion, and coordination geometry of central metals and organic ligands [5–8].

In particular, the coordination compounds (CCs) crystals with noncentrosymmetric structures (NCS) have received significant attention, owing to the extensive potential applications in ferroelectric, pyroelectric, piezoelectric, and second harmonic generation (SHG) properties [9–11]. Furthermore, to date, it remains a considerable challenge to control the structures to NCS [12,13]. Generally, noncentrosymmetric materials can be well-designed by using preferred coordination geometries of metal centers and/or carefully chosen bridging ligands [14]. Several methods have been developed to synthesize coordination compounds with noncentrosymmetric structures. First of all, it is to use optically pure chiral multidentate ligands, which has been proved to be the most

effective and straightforward approach [15,16]. Then, we can use of asymmetric ligand or flexible ligand to prepare noncentrosymmetric materials [17]. Moreover, noncentrosymmetric compounds can be also obtained through unpredictable spontaneous resolution and topology-building [18,19]. The investigation of spontaneous resolution has been carried out by many researchers during the past decades. It has been found that spontaneous resolution occurs in the course of crystallization is closely related to many external factors which are similar as to the formation of CCs [20–22]. Therefore, it is such a challenging work to accurately control the crystals from centrosymmetric structure to noncentrosymmetric structure by changing the reaction conditions. Herein, based on a tripodal ligand of N,N,N'-tris(3-pyridyl)trimesic amide (TPTA), we found that the presence of a small quantity of water molecules as co-solvents would control the final structures from centrosymmetry to noncentrosymmetry.

2. Experimental

2.1. Materials and methods

Commercially available reagents were used throughout without further purification and TPTA was synthesized according to the literature method [23–26]. Elemental analyses for C, H, and N were performed with a Perkin–Elmer 2400 Series II element analyzer. Thermogravimetric analysis (TGA) experiments were carried out with a DuPont Thermal Analyzer from room temperature to 800 °C

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Table 1
Selected bond lengths/Å and bond angles° for **3** and **4**.

Compound 3			
Hg(1)–N(2)	2.376(7)	N(2)–Hg(1)–I(3)	104.09(17)
Hg(1)–I(3)	2.6321(7)	N(2)–Hg(1)–I(4)	102.08(17)
Hg(1)–I(4)	2.6650(7)	I(3)–Hg(1)–I(4)	149.87(3)
Hg(1)–I(4B)	3.1741(7)	N(2)–Hg(1)–I(4B)	90.47(18)
Hg(2)–N(1)	2.413(6)	I(3)–Hg(1)–I(4B)	102.66(2)
Hg(2)–I(1)	2.6347(7)	I(4)–Hg(1)–I(4B)	91.74(2)
Hg(2)–I(2)	2.6341(7)	N(1)–Hg(2)–I(1)	99.23(19)
Hg(2)–I(1A)	3.3248(7)	N(1)–Hg(2)–I(1A)	97.9(2)
Hg(3)–N(3)	2.392(7)	I(2)–Hg(2)–I(1)	158.80(2)
Hg(3)–I(5)	2.6731(7)	I(2)–Hg(2)–I(1A)	93.79(2)
Hg(3)–I(5B)	3.5271(7)	I(1)–Hg(2)–I(1A)	89.01(2)
Hg(3)–I(6)	2.6305(7)	N(3)–Hg(3)–I(6)	102.64(16)
Hg(3)–I(6A)	3.3960(7)	N(3)–Hg(3)–I(5)	100.99(17)
		I(6)–Hg(3)–I(5)	156.36(3)
		Hg(1)–I(4)–Hg(1A)	91.74(2)
		Hg(2)–I(1)–Hg(2B)	89.01(2)
Compound 4			
Hg(1)–N(1)	2.396(6)	N(1)–Hg(1)–N(6A)	88.5(2)
Hg(1)–N(6A)	2.441(6)	N(1)–Hg(1)–I(1)	104.17(16)
Hg(1)–I(1)	2.6290(9)	N(6)–Hg(1)–I(1A)	103.01(15)
Hg(1)–I(2)	2.6581(9)	N(1)–Hg(1)–N(2)	106.43(16)
Hg(1)–N(6B)	2.441(6)	N(6)–Hg(1)–I(2A)	100.97(16)
		I(1)–Hg(1)–I(2)	141.26(3)

Symmetry code: (A): 1 + x, y, z; (B): -1 + x, y, z.

in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. In the measurements of emission and excitation spectra, the pass width is 5.0 nm.

2.2. Synthesis of [(TPTA)·H₂O]_n (**1**)

N,N',N''-tris(3-pyridyl) trimesic amide(TPTA) (0.2 mmol) with 5 mL DMF and 1 mL H₂O was mixed in a Teflon container and sealed in an autoclave. The autoclave was heated to 115 °C in a programmable oven, and this temperature was maintained for three days before it was cooled to room temperature. Light yellow block-shaped crystals were obtained. EA analysis (%): calc. C/63.15, N/18.41, H/4.42; exp. C/63.17, N/18.48, H/4.40.

2.3. Synthesis of [(TPTA)·H₂O]_n (**2**)

N,N',N''-tris(3-pyridyl) trimesic amide(TPTA) (0.2 mmol) with

5 mL DMF was mixed in a Teflon container and sealed in an autoclave. The autoclave was heated to 115 °C in a programmable oven, and this temperature was maintained for three days before it was cooled to room temperature. Light yellow bar-type crystals were obtained. EA analysis (%): calc. C/63.15, N/18.41, H/4.42; exp. C/63.14, N/18.42, H/4.45.

2.4. Synthesis of [Hg_{1.5}I₃(TPTA)_{0.5}(CH₃CN)·(H₂O)_{0.5}]_n (**3**)

The mixture of HgI₂ (0.2 mmol) and TPTA(0.2 mmol) in the 5 mL acetonitrile and 1 mL H₂O solution was stirred for 30 min, and then transferred to a Teflon container and sealed in an autoclave. The autoclave was heated to 160 °C in a programmable oven, and this temperature was maintained for three days before it was cooled to room temperature (cooling rate 3 °C/h). Light yellow crystals were obtained in the yield of 65% based on Hg. EA analysis (%): calc. C/17.70, N/5.90, H/1.27; exp. C/17.73, N/5.90, H/1.26.

2.5. Synthesis of [HgI₂(TPTA)·H₂O]_n (**4**)

The mixture of HgI₂ (0.2 mmol) and TPTA(0.2 mmol) in the 5 mL acetonitrile solution was stirred for 30 min, and then transferred to a Teflon container and sealed in an autoclave. The autoclave was heated to 160 °C in a programmable oven, and this temperature was maintained for three days before it was cooled to room temperature (cooling rate 3 °C/h). Light brown crystals were obtained in the yield of 68% based on Hg. EA analysis (%): calc. C/32.29, N/9.41, H/2.03; exp. C/32.27, N/9.45, H/2.01.

2.6. Crystallographic measurements

Single-crystal diffraction intensity data were collected on Bruker Smart Breeze CCD employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 296(2)K, the measurement method is phi and omega scans, and corrected with SADABS program. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full matrix least-squares on F^2 using SHELXTS 97 and SHELXTL 97 program [29,30]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. The important interatomic distances and angles are listed in Table 1, and The crystallographic data

Table 2
Crystal data, experimental conditions, and structure refinement parameters of **1**, **2**, **3** and **4**.

	1	2	3	4
Empirical formula	C ₂₄ H ₂₀ O ₅ N ₆	C ₂₄ H ₂₀ N ₆ O ₃	C ₁₄ H ₁₂ Hg _{1.5} I ₃ N ₄ O ₂	C ₂₄ H ₁₈ Hg I ₂ N ₆ O ₃
Formula weight/g mol	456.46	456.46	949.86	892.83
Temperature/K	296(2)	296(2)	296(2)	296(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal size/mm	0.30 × 0.28 × 0.25	0.20 × 0.20 × 0.18	0.20 × 0.20 × 0.19	0.20 × 0.20 × 0.18
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	Cc	Pbca	P2 ₁	P2 ₁ /c
D _{calc} /g cm ⁻³	1.423	1.404	2.934	2.369
a/Å	17.7919(14)	8.1083(15)	4.2062(3)	14.429(5)
b/Å	14.5737(9)	22.087(4)	29.6215(19)	19.984(7)
c/Å	8.3397(7)	24.109(4)	17.2646(10)	8.724(3)
β /°	99.900(5)	90.00	91.269(3)	95.681(9)
V/Å ³	2130.2(3)	4317.6(13)	2150.5(2)	2503.2(15)
Z	4	8	4	4
F(000)	952	1904	1676	1656
θ range for data collection/°	1.82–25.00°	1.69–25.00°	1.37–25.00°	1.75–25.00°
Reflections collected	8049	16981	15040	16463
R _{int}	0.0429	0.0627	0.0513	0.0457
Goof	1.079	1.071	1.111	1.100
Final R indices [I > 2 σ (I)] ^[a]	R ₁ = 0.0456, wR ₂ = 0.0845	R ₁ = 0.0595, wR ₂ = 0.1252	R ₁ = 0.0646, wR ₂ = 0.1573	R ₁ = 0.0395, wR ₂ = 0.1036
R indices (all data) ^[b]	R ₁ = 0.0587, wR ₂ = 0.0948	R ₁ = 0.0982, wR ₂ = 0.1442	R ₁ = 0.0668, wR ₂ = 0.1599	R ₁ = 0.0430, wR ₂ = 0.1070
Largest diff. peak and hole/e Å ⁻³	0.128, -0.158	0.203, -0.209	4.112, -2.160	1.431, -1.655

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