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Temperature-Dependent Supramolecular Motif in Coordination Compounds

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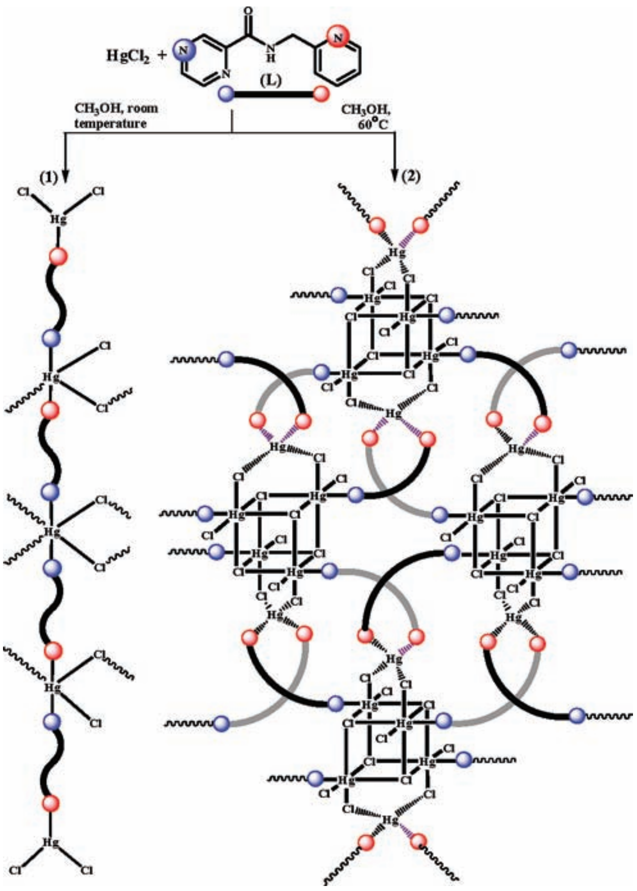
The temperature-dependent structures of 1D and 2D $HgCl_2$ coordination polymers containing a *N*-(2-pyridylmethyl)-2-pyrazinecarboxamide flexible ligand with different motifs have been investigated. Results show that when the reaction was carried out at 60 °C, a 2D framework containing cubane-like units was generated, whereas in room temperature, L-bridged pentanuclear units, which are extended to a 1D band through a Hg−Cl−Hg-bridged compound, will be obtained.

Scheme 1. Synthesis of **1** and **2**



Crystal engineering of coordination frameworks is attracting great industrial and academic attention in recent years. The planning in crystal engineering, construction of the structures of crystalline materials,[1] depends on the chemical structure of the organic ligand,[2] preferred coordination geometry of the metal,[3] guest molecules and counterions,[4] and a number of experimental variables such as the solvent,[5] time of reaction,[6] reagent ratio,[7] and pH.[8] On the other hand,

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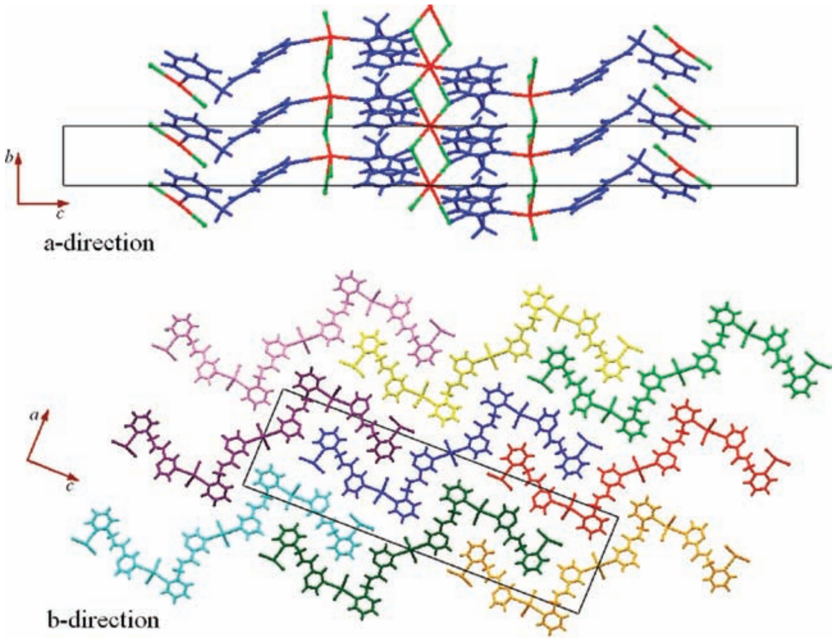

Figure 1. Overall structure of **1** along the *a* (up) and *b* (down) directions. In the *a* direction, Cl and Hg atoms are shown in green and red colors, respectively, and only one of the bands is shown for clarity. In the *b* direction, different colors show different pentanuclear moieties.

it is well-known that different structural motifs arise from variable conformation of flexible ligands under different reaction conditions, especially temperature. Because the thermal energy is dependent on the temperature proportionally, the thermodynamically favored conformer associated with a large activation barrier can be obtained at high temperature, while low temperature favors the kinetic conformer. Hence, by controlling the reaction temperature, we were able to synthesize thermodynamically and/or kinetically favored conformers.[9] So, the reaction temperature is an additional factor in controlling the framework topology and the dimensionality of the structures.[10] Notably, the temperature-dependent motifs in coordination polymers have received little attention.[11]

In this regard, here we present the structures of two conformational supramolecular compounds, L-bridged pentanuclear units that are extended to a 1D band through Hg−Cl−Hg bridges, **1**, and a 2D framework containing cubane-like units, **2**,[12] obtained from the self-assembly of a flexible ligand, *N*-(2-pyridylmethyl)-2-pyrazinecarboxamide, L,[13] and $HgCl_2$ in different reaction conditions (Scheme 1), in which the freedom of C−C and C−N single-bond rotation in the ligand gives rise to variable conformations (for details of the experimental procedures, see the Supporting Information).

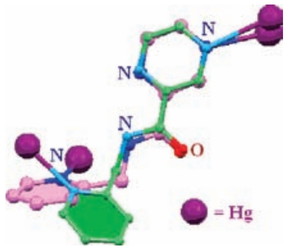

Figure 2. Individual Hg−L−Hg fragments of compounds **1** (green) and **2** (purple) superimposed to illustrate the conformational freedom of the flexible carboxamide ligand.

Compound **1** displays 2/*m* point symmetry in the solid state, making half of the pentanuclear compound crystallographically unique. So, the asymmetric unit of **1** consists of three crystallographically independent Hg^{2+} ions, two *N*-(2-pyridylmethyl)-2-pyrazinecarboxamide [Hg−N = 2.527(7)−2.633(8) Å], two bridges, and three terminal chloride [$Hg-Cl_{bridge}$ = 2.357(2) and 2.359(2) Å; $Hg-Cl_{terminal}$ = 2.315(3)−2.361(2) Å] ions (Supporting Information, Figure S1).

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[12] Crystal data for **1**: $C_{44}H_{40}Cl_{10}Hg_5N_{16}O_4$ (M_r=2214.37), monoclinic, space group $P2_1/n$, a = 14.482(3) Å, b = 4.0378(8) Å, c = 49.631(10) Å, β=91.58(3)°, V=2901.1(10) $Å^3$, Z=2, D_{calc}=2.535 g cm^{-3}, μ=13.702 mm^{-1}, T = 298(2) K, crystal size 0.50 × 0.05 × 0.03 mm^3, R1 = 0.0650, wR2 = 0.1641, GOF = 1.099 with $I > 2\sigma(I)$, CCDC 767822. Crystal data for **2**: $C_{22}H_{20}Cl_6Hg_3N_8O_2$ (M_r = 1242.93), orthorhombic, space group *Ccca*, a = 25.2948(12) Å, b = 14.6275(11) Å, c = 17.2954(11) Å, V = 6399.3(7) $Å^3$, Z = 8, D_{calc} = 2.580 g cm^{-3}, μ = 14.896 mm^{-1}, T = 298(2) K, crystal size 0.50 × 0.40 × 0.15 mm^3, R1 = 0.0485, wR2 = 0.1198, GOF = 1.187 with $I > 2\sigma(I)$, CCDC 767823.

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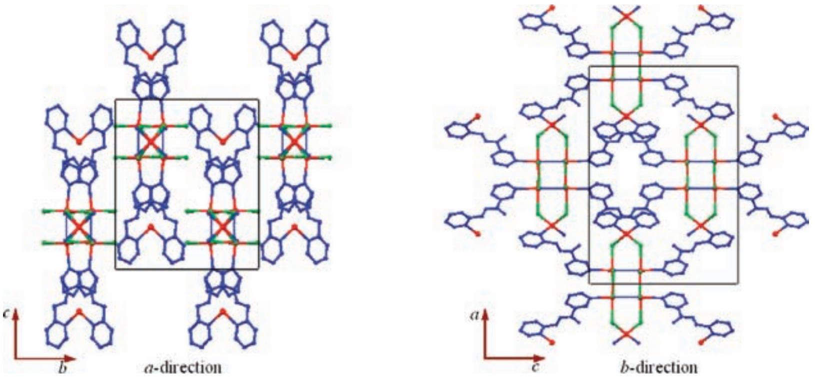

Figure 3. Overall structure of **2** along the *a* (left) and *b* (right) directions. Cl and Hg atoms are shown in green and red colors, respectively, and in both directions, only one of the 2D nets is shown for clarity.

Of the three Hg^{2+} ions, Hg(1) is three-coordinated by two Cl atoms and one N atom from the pyridine ring. Hg(2) has a square pyramid, being surrounded by two pyrazine N atoms, and four-coordination by three Cl atoms, one pyridine N atom, and one pyrazine N atom from two carboxamide ligands. The Hg(3) atom adopts a distorted octahedral geometry. The Hg atoms are bridged by the carboxamide ligands into petnanuclear zigzag coordination moieties (Scheme 1). Adjacent Hg_5(*N*-(2-pyridylmethyl)-2-pyrazinecarboxamide)$_4$$Cl_{10}$ moieties are further linked into 1D coordination bands along the *b* direction via two Cl atoms of six-coordinated Hg(3) and one Cl atom of five-coordinated Hg(2). It is notable that such mixed-ligand bridges involving halides are frequently observed for the soft late transition metals.[14] In **1**, The resulting 1D bands are further linked by the weak intermolecular C−H···Cl and C−H···O hydrogen bonds (Supporting Information, Table S1) to generate a 3D framework. Packing diagrams in the *a* and *b* directions are shown in Figure 1.

When the reaction was carried out at 60 °C, compound **2** was generated with a 2D sheet structure (Supporting Information, Figure S2). From **1** to **2**, the dramatic structural change observed clearly results from the different conformations adopted by flexible carboxamide ligands at various temperatures. Because the CH_2 group connecting the pyrazine amide unit and the pyridine ring in L is flexible, this allows subtle conformational adaptation of L to produce different compounds via bending or twisting of the rings (Figure 2). This conformational variation can be discussed by a dihedral angle of N(NH)−C(CH_2)−C(Py)−N(Py) that is 81.57(10)° and 69.90(11)° for **1** and **2**, respectively. The structure of **2** is remarkably different and contains an alternating array of Hg^{2+} and Cl^- ions at the vertices of a cubane, with a terminal Cl ion and a pyrazine N atom from bridging L. One μ_2-bridging chlorine between Hg_{Oh} and Hg_{Td} completes each octahedral Hg^{II} coordination sphere. Cubic bond angles of Hg_{Oh}−Cl−Hg_{Oh} differ by less than −6.59°, and μ_2-Cl−Hg_{Oh}−μ_2-Cl by less than +6.59°, from the ideal cubic geometry. This type of structure has already been observed for silylmercury chloride in *tetrahedral* geometry for Hg,[15] but this report is the first example of such an *octahedral* coordination sphere around a Hg ion. The Hg−Cl distances of 3.149(2), 3.130(3), and 2.362(2) Å for Hg−μ_3-Cl, 2.926(2) Å for Hg−μ_2-Cl, and 2.325(3) Å for Hg−$Cl_{terminal}$ compare well to those found in the related complex $[(^tBu)_3SiHgCl]_4$.[15] The $[Hg_4Cl_{12}L_4]$ cubes are bridged by tetrahedral Hg(μ_2-Cl)$_2$(μ_2-pyridine nitrogen)$_2$ moieties to form a 2D network along the crystallographic *bc* plane. There is an imposed C_2 axis of symmetry that runs perpendicularly to one of the faces of the cube and possesses tetrahedral Hg centers. The layers are further stacked to form a 3D framework through $\pi\cdots\pi$ interactions[16] parallel to the *ab* plane between adjacent pyridine rings [centroid-to-centroid distance of 3.528(5) Å; symmetry code $^1/_2 - x, 1 - y, z$] and weak C−H···O and C−H···Cl intermolecular hydrogen-bonding interactions (Supporting Information, Table S1). The packing diagrams are shown in Figure 3.

In summary, we have demonstrated the temperature-dependent structure of 1D and 2D $HgCl_2$ coordination polymers containing a *N*-(2-pyridylmethyl)-2-pyrazinecarboxamide flexible ligand with different motifs. This report shows that the temperature parameter can be used to control the topology of the metal−organic frameworks. Further studies are in progress to synthesize new complexes from other flexible carboxamide ligands based on this approach.

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Supporting Information Available: Detailed synthesis of L1, **1** (CCDC 767822), and **2** (CCDC 767823), full crystallographic data for **1** and **2**, and asymmetric units of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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