Novel Coordinated-Solvent Induced Assembly of Cd(II) Coordination Polymers Containing 4,4'-Dipyridylsulfide

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ABSTRACT: Novel coordinated-solvent induced assembly has been demonstrated upon reaction of Cd(II) ions and 4,4'-dipyridylsulfide, where different coordinating solvents used as the reaction media led to the formation of various dimensional coordination networks from one-dimension, two-dimension, to three-dimension.

Recently, there is a growing interest in crystal engineering for the construction of a wide range of infinite solid-state coordination architectures, which have been designed, isolated, and structurally characterized.1 In addition, their functionalities in chemical sieving, sensing, catalysis, and gas sorption have been also examined.2 To date, a challenge encountered in this research field is the predictability of the polymeric networks and dimensionality,1,2 since they have been found to be dependent on the coordination geometry of the metal ions, metal/ligand ratios, flexibility of the ligands' backbone, and the presence of counterions and solvents.3 Among these factors, the counterion and solvent effects on the self-assembly process are particularly of interest to give rise to a variety of self-assembled products. A benchmark example demonstrating the delicate anion and/or solvent effect on a series of Ag(I) complexes has recently been reported by Hannon et al.,4 where competing supramolecular interactions led to the formation of various supramolecular architectures in response to changes in anions and/or solvents. The architectures obtained display a remarkable dependence both on the choice of noncoordinating anions and the type of coordinating and/or noncoordinating solvents used. Indeed, the coordinating solvents can affect the coordination geometry of metal ions and the noncoordinating solvents can induce the different structural aggregates, and both effects most likely play an important role in crystal engineering.

Very recently, Chen et al. have reported a series of solvent molecules participating in coordination networks of Mn(II) ions, where four remarkable Mn(II)-based coordination polymers of the rigid ligand 2,3,5,6-tetrachloro-1,4-benzenedicarboxylic acid (H2BDC-Cl) have been obtained from different solvent media.5 Significantly, the solvents play an essential role in the bridging modes of BDC-Cl4 (µ2 or µ4) in the crystallization and construction of these coordination frameworks with distinct dimensionalities. To continue our previous efforts in constructing functional coordination polymers,6 we choose Py2S as flexible bridging ligands and Cd(II) ions as connectors to study the assembly process in this study. Unlike the work reported by Chen et al.,5 we report herein studies on the coordinated-solvent induced assembly of Cd(II) coordination networks with Py2S only acting as a bridging form, where the coordinated solvents play an important role leading to various dimensionalities from one-dimension (1D), two-dimension (2D), to three-dimension (3D).

The reaction scheme of 1–4 ([Cd2(Py2S)3(NO3)4]n, 1 (2-D coordination polymer); [Cd2(Py2S)3(DMF)2][ClO4]n, 2 (1-D coordination polymer); [Cd2(Py2S)3(CH3CN)2][ClO4]n, 3 (2-D coordination polymer); [Cd2(Py2S)3(CH3OH)2][ClO4]n, 4 (3-D coordination polymer)) is shown in Scheme 1, and they have been synthesized and isolated as air-stable solids by a layer method with medium yields of 58–80%. The structures were determined by X-ray single-crystal diffraction, confirming the coordination networks from 1-D, 2-D, to 3-D dependent on the coordinating solvents used in the synthesis. While the anion and/or solvent effects on self-assembly are not uncommon,3 there are some interesting examples reported so far for the influence of metal and counterions on the coordination networks based on Py2S and other ligand systems.3h,i,8 However, the related work regarding the coordinated-solvent induced assembly is rare.

1 crystallized in the space group of P1 comprising two independent Cd(II) ions with a seven-coordinate geometry and one CH2Cl2 solvate in an asymmetric unit.9 As shown in Figure 1, each Cd(II) ion coordinates to three bridging Py2S through N-coordination (Cd–N = 2.304(4)–2.375(4) Å) in an almost T-shape configuration and two chelating NO3− ions (one almost symmetric NO3− (Cd–O = 2.396(5), 2.417(4) Å) and the other unsymmetric one (Cd–O = 2.382(5), 2.586(5) Å) for Cd(1); two almost symmetric NO3− (Cd–O = 2.415(5), 2.423(5) Å; 2.421(5), 2.429(4) Å) for Cd(2)]. Such a connection mode makes I normally a 2-D coordination network with a 60-membered macrocycle constructed from six Cd(II) ions and six Py2S ligands, which are packed in an A−B−A−B manner in the crystal lattice with the CH2Cl2 solvates sitting within the sheet structures.

When Cd(ClO4)2 was used instead of Cd(NO3)2, the reaction with Py2S led to the formation of 2, 3, and 4 with various dimensionalities in the presence of DMF, CH3CN, and CH3OH, respectively.2 crystallized in the space group of P21/c containing a six-coordinate Cd(II) ion.3 As shown in Figure 2a, each Cd(II) ion coordinates to four bridging Py2S through N-Coordination (Cd–N = 2.318(3)–2.347(3) Å) and two trans coordinated-DMF (Cd–O = 2.314(3), 2.338(3) Å), and every two neighboring Py2S further connect to the same Cd(II) ion to form a 1-D double-zigzag chain with a 20-membered ring, constructed from two Cd(II) ions and two Py2S ligands. Moreover, two noncoordinated ClO4− anions sit over and below the ring, and therefore this structure is similar to that of [Co(Py2S)2(SCN)2]n,9 whereas the latter has two trans NCS−. It is noted that when DMF was replaced by CH3CN, a 2-D square-grid structure of 3 was delicately formed instead of the previous double-zigzag chain of 2. As shown in Figure 2b, 3 crystallized in the

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space group of $P2_1/n$ consisting of a six-coordinate Cd(II) ion and two CH$_3$CN solvates in an asymmetric unit. Each Cd(II) ion in 3 coordinates to four bridging Py$_2$S through N-coordination (Cd–N = 2.311(3)–2.340(3) Å) and two trans-configuration coordinated-CH$_3$CN (Cd–N = 2.373(4), 2.434(4) Å). The noncoordinated ClO$_4^-$ and CH$_3$CN were stacked into the square cavities (with a 40-membered ring), constructed from four Cd(II) ions and four Py$_2$S ligands, where its sheet structure is also packed in an A–B–A–B manner in the crystal lattice. The square-grid structure of 3 are similar to those of [Co(Py$_2$S)$_2$Cl$_2$]$_n$ and [Cu(L)(SCN)$_2$]$_n$. The noncoordinating anions and solvents are omitted for clarity.

Figure 2. (a) A perspective view of cation 2, (b) a perspective view of cation 3, (c) a perspective view of cation 4, and (d) an interesting polyknotted structure of cation 4 with only Cd (gray balls), S (yellow balls), and stick symbols. Noncoordinating anions and solvents are omitted for clarity. As shown in Figure 2(c), each
Figure 3. The TGA trace of 4.

Cd(II) ion coordinates to five bridging Py2S through N-coordination (Cd−N = 2.287(3)−2.412(3) Å) and one coordinated-CH3OH (Cd−O = 2.405(3) Å) to lead to a 3-D coordination framework. 4 is topologically related to a uniform 5-connected net that has a long vertex symbol of $6_2^1 \cdot 6_3^1 \cdot 6_3^1 \cdot 6_3^1 \cdot 6_3^1 \cdot 6_3^1$. In the 3-D structure, Py2S ligands containing S2 and S3 atoms connected to Cd(II) ions result in a 2-D interpenetrated 4-connected network, and the third Py2S ligand (containing S1 atom) acting as bridges cross-links two networks leading to a special 3-D polyknotted network. A simplified graph with only Cd and S symbols is shown in Figure 2d, which highlights an interesting polyknotted structure \[4\] for 4.

Is the structural conformation of Py2S responsible for the structural variations in 1−4? In fact, these magic angles (represented by the C−S−C angles) in 1−3 are 103.7(2)−104.8(2), 100.8(2)−101.5(2), 102.0(2)−103.9(2), and 103.4(2)−105.8(2)° in 1−4, respectively, which are within a similar range and also comparable to 103.1(1)° in free Py2S.\[11\] This indicates that the structural conformations of coordinated Py2S cannot significantly contribute to the structural variations in this study. For 1, two chelating NO3− anions occupy most of the coordination sites of Cd(II) and probably prevent the solvent coordination from occurring, although coordinating solvents (i.e., CH3CN) were used in the reaction process. When the ClO4− salts of Cd(II) were used, the reaction products 2−4 are highly dependent on the coordinating solvents used (i.e., DMF, CH3CN, or CH3OH). In addition, DMF with the more steric hindrance is expected to reduce the possibility for the formation of 2- or 3-D extended structures, and thus a 1-D chain formed for 2 is not unreasonable. The less steric hindrance for CH3CN and CH3OH (the angles of CH2=CH2−O−Cd and CH2=CH2−OH−Cd are 145.7(3)−172.6(3)° and 134.6(3)° for 3 and 4, respectively) are suggested to be responsible for the formation of 2- or 3-D networks for 3 and 4, respectively. Finally, the correlation between the structural feature and the number of bridging Py2S ligands that are connected to each Cd(II) ion in the 1−4 can be observed. Nevertheless, the same number of bridging Py2S (four) in 2 and 3 containing 1- and 2-D structural frameworks, respectively, does not permit any concrete comment on this correlation. Thus, this structural feature can readily account for the different dimensionalities seen in 1, 2, 3, and 4, but the subtle change between 2 and 3 is against this trend.

To examine the thermal stabilities of 1−4, their TGA analyses were recorded and that of 4 is shown in Figure 3 as a representative example. A total weight loss of 13.1% (two CH3CN + one coordinated CH3OH: 14.5%) can be reached when the temperature is raised to 292 °C. Above this temperature, 4 starts to decompose. Indeed, 2 and 3 can be also thermally stable up to 280 and 305 °C, respectively. Although 2−4 are composed of different coordination networks (from 1-D, 2-D to 3-D) and coordinated solvents, they do have similar thermal stabilities. Surprisingly, unlike those of 2−4 containing ClO4− anions, 1 containing NO3− anions can be only thermally stable up to 172 °C.

In summary, this work reports the structural variations of reaction products of CdX2 (X = NO3−, ClO4−) and Py2S, and their coordination networks are highly dependent on the anions and coordinating solvents used. I was synthesized from the reaction of Cd(NO3)2 with Py2S leading to a 2-D coordination network with a 60-membered macrocycle, whereas 2−4 were made from a similar reaction except using Cd(ClO4)2 instead of Cd(NO3)2 and different coordinating solvents used (i.e., 2, DMF; 3, CH3CN; 4, CH3OH). Surprisingly, unlike that of 1 the coordinating solvents used for 2−4 are all involved in coordination, exhibiting an interesting series of coordination networks dependent on DMF (2: a 1-D double-zigzag chain), CH3CN (3: a 2-D square-grid structure), and CH3OH (4: a 3-D network), respectively. Although 2−4 are composed of different coordination networks and coordinated solvents, they have similar coordination units (Cd-Py2S) and really similar thermal stabilities. This work highlights a delicate coordinated-solvent induced assembly in crystal engineering; however, the solvent polarity playing a role in the crystal-growing process cannot be excluded.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

References


(7) Synthesis of [Cd2(Py2S)3(NO3)4]2+: a 3-D network containing NO3−···OH−. The effect of DMF on the crystal structure. The crystal structure of Cd(NO3)2·4H2O was carefully layered onto a 2 mL CH3Cl solution of Py2S (23 mg, 0.12 mmol). Colorless crystals were obtained in two days in ca. 63% yield. FT-IR (KBr): v(NO3−) = 1581 and 1479 cm−1; v(H2O) = 1835 cm−1. Anal. Calcd.
(9) Crystal data: C$_3$H$_6$N$_2$CdCl$_2$O$_2$S$_2$: C, 34.73; H, 2.33; N, 13.50. Found (%): C, 34.86; H, 2.46; N, 13.25. Synthesis of ([Cd(PyS)$_2$]_2(DMF)$_2$)[ClO$_4$]$_2$.

2. Cd(CIO$_4$)$_2$·6H$_2$O (34 mg, 0.16 mmol) dissolved in a DMF solution (2 mL) was carefully layered onto a 2 mL CHCl$_3$ solution of Py$_2$S (30 mg, 0.16 mmol). Colorless crystals were obtained in three days in ca. 75% yield. FT-IR (KBr): ν$_{sym}$ (2 mL) was carefully layered onto a 2 mL CHCl$_3$ solution of Py$_2$S (2 mL) was carefully layered onto a 2 mL CHCl$_3$ solution of Py$_2$S (30 mg, 0.16 mmol). Colorless crystals were obtained in two days in ca. 60% yield. FT-IR (KBr): ν$_{sym}$ = 1581 and 1481 cm$^{-1}$; ν$_{asym}$ = 1144, 1114, and 1084 cm$^{-1}$. Anal. Calcd (%) for C$_{30}$H$_{24}$Cd$_2$N$_{10}$O$_{12}$S$_3$: C, 34.73; H, 2.33; N, 13.50. Found (%): C, 37.20; H, 2.67; N, 11.11. Synthesis of [Cd$_2$(Py$_2$S)$_5$(CH$_3$OH)$_2$](ClO$_4$)$_4$

3. Cd(CIO$_4$)$_2$·6H$_2$O (34 mg, 0.16 mmol) dissolved in a CH$_3$CN solution (2 mL) was carefully layered onto a 2 mL CHCl$_3$ solution of Py$_2$S (30 mg, 0.16 mmol). Colorless crystals were obtained in one week in ca. 60% yield. FT-IR (KBr): ν$_{sym}$ = 1579 and 1480 cm$^{-1}$; ν$_{asym}$ = 1145, 1115, and 1086 cm$^{-1}$. Anal. Calcd (%) for C$_3$H$_6$N$_2$CdCl$_2$O$_2$S$_2$: C, 38.36; H, 2.97; N, 8.60. Found (%): C, 38.12; H, 2.76; N, 8.79.


(9) Crystal data: 1·CH$_3$Cl$_2$, C$_3$H$_6$N$_2$CdCl$_2$O$_2$S$_2$: M = 1122.50, triclinic, space group P1, T = 295(2) K, a = 11.2141(1), b = 12.5092(1), c = 17.26(2) Å, α = 104.3433(4), β = 100.1570(5), γ = 109.3781(5)$^\circ$, V = 2121.32(4) Å$^3$. Z = 2, μ = 1.345 mm$^{-1}$. F(000) = 1112, 30 381 reflections collected, 9720 independent, R$_{int}$ = 0.0396, final residuals R1 = 0.0560, wR2 = 0.1529 (I $>$ 2σ(I)); R1 = 0.0886, wR2 = 0.1878 (all data).

Crystal data: 2·CH$_3$H$_2$CdCl$_3$N$_2$O$_2$S$_2$: M = 834.01, monoclinic, space group P2$_1/n$, T = 273(2) K, a = 10.4730(8), b = 19.2211(14), c = 19.0207(11) Å, β = 113.1143(3)$^\circ$, V = 3521.6(4) Å$^3$, Z = 4, μ = 0.950 mm$^{-1}$. F(000) = 1688, 30 864 reflections collected, 8439 independent, R$_{int}$ = 0.0275, final residuals R1 = 0.0576, wR2 = 0.1394 (I $>$ 2σ(I)); R1 = 0.0704, wR2 = 0.1475 (all data).

Crystal data: 3·2CH$_3$CN, C$_3$H$_6$H$_2$CdCl$_3$N$_2$O$_2$S$_2$: M = 852.00, monoclinic, space group P2$_1/n$, T = 150(2) K, a = 10.8272(1), b = 17.2375(2), c = 19.3098(2) Å, β = 92.1574(6)$^\circ$, V = 3601.31(7) Å$^3$, Z = 4, μ = 0.928 mm$^{-1}$. F(000) = 1720, 34350 reflections collected, 8235 independent, R$_{int}$ = 0.0689, final residuals R1 = 0.0464, wR2 = 0.1072 (I $>$ 2σ(I)); R1 = 0.0858, wR2 = 0.1291 (all data).

Crystal data: 4·CH$_3$OH·4CHCl$_3$, C$_3$H$_6$H$_2$CdCl$_3$N$_2$O$_2$S$_2$: M = 2135.40, tetragonal, space group P4$_1$/2, T = 150(1) K, a = 16.8687(5), b = 16.8687(5), c = 28.5613(9) Å, V = 8127.2(4) Å$^3$, Z = 4, μ = 1.249 mm$^{-1}$. F(000) = 4264, 53299 reflections collected, 9343 independent, R$_{int}$ = 0.0575, final residuals R1 = 0.0364, wR2 = 0.0853 (I $>$ 2σ(I)); R1 = 0.0407, wR2 = 0.0872 (all data).


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