

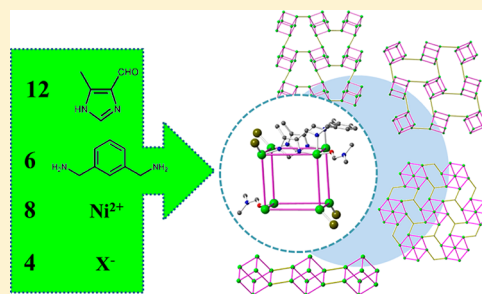
## Solvothermal Subcomponent Self-Assembly of Cubic Metal–Imidazolate Cages and Their Coordination Polymers

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## Supporting Information

**ABSTRACT:** A series of Ni–imidazolate cubic cages, one-dimensional and two-dimensional coordination polymers based on the cubic cages, have been prepared by solvothermal *subcomponent self-assembly* of 5-methyl-4-formylimidazole, *m*-xylylenediamine, and Ni<sup>II</sup> salts with varied anions. These compounds have been characterized by single-crystal X-ray diffractions, elemental analysis, IR spectra, and powder X-ray diffractions. The formation of an oligomerized coordination cage or an infinite coordination polymer depends on the anions chosen. An oligomerized 8-nuclear Ni–imidazolate cubic cage is formed when the anion Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, SCN<sup>−</sup>, NO<sub>2</sub><sup>−</sup>, or NO<sub>3</sub><sup>−</sup> is utilized in the reactions, and a two-dimensional coordination polymer based on the Ni–imidazolate cubic cage will be obtained when N<sub>3</sub><sup>−</sup>, (CN)<sub>2</sub>N<sup>−</sup>, or (CN)<sub>3</sub>C<sup>−</sup> act as the anions. When only ClO<sub>4</sub><sup>−</sup> or both ClO<sub>4</sub><sup>−</sup> and [Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]<sup>2−</sup> (C<sub>4</sub>N<sub>2</sub>S<sub>2</sub> = dimercaptomaleonitrile) as anions exist in the reaction mixture, a ladder-like one-dimensional coordination polymer based on the Ni–imidazolate cubic cage and formate is formed unpredictably.



## INTRODUCTION

Metal–organic cages (MOCs) have been widely studied in recent years due to their exquisite structures with unique confined spaces<sup>1,2</sup> and advanced functions (e.g., recognition,<sup>3,4</sup> stabilization of reactive species,<sup>5–8</sup> catalysis,<sup>9–12</sup> etc.). With fascinating host–guest chemistry, MOCs can also be employed as building blocks to construct extended metal–organic frameworks (MOFs) or coordination polymers (CPs).<sup>13–22</sup> MOFs based on MOCs usually use organic molecules as linkers. Few reported examples use anions as linkers to connect discrete MOCs to form infinite structures. Recently, Hong and co-workers successfully assembled a 1D coordination polymer from discrete octahedral nanocages via anion exchange,<sup>17</sup> and Zhang and co-workers reported an MOF based on metal boron imidazolate cages and I<sup>−</sup>.<sup>20</sup>

A classical method for the syntheses of MOFs and CPs is the self-assembly of elaborately prepared ligands and metal ions under hydro(solvo)thermal conditions, when coordination bonds are employed as linking interactions. In recent years, *in situ* ligand formation reactions were developed as an unconventional approach to construct CPs under hydro(solvo)thermal conditions, in which some unprecedented CPs can be obtained.<sup>23–26</sup> Yielding dynamic covalent C=N bonds between amino and aldehyde groups to form a Schiff base compound is one of the well-known and most fundamental reactions in chemistry. This simple and facilitated reaction involving the imine bond formation and loss of H<sub>2</sub>O has been employed widely in the construction of complicated compounds including complex organic molecules, supramolecular coordination complexes (SCCs), and covalent organic frame-

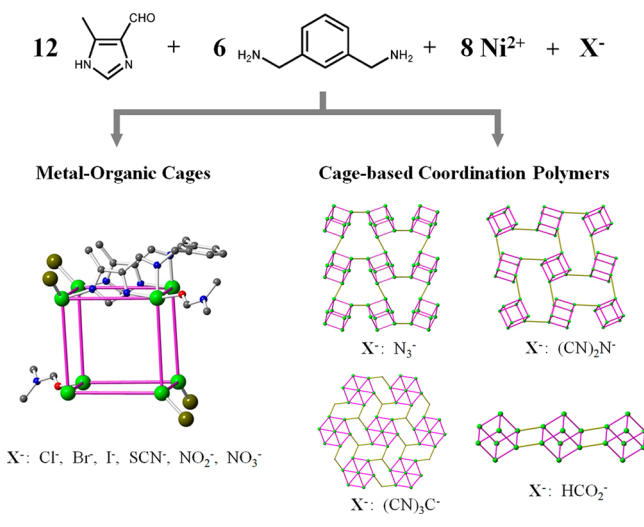
works (COFs)<sup>27</sup> in state-of-the-art chemistry from relatively simple precursors. Developed by Nitschke and co-workers,<sup>28,29</sup> the *subcomponent self-assembly* technology involving formation of coordination and dynamic covalent bonds (C=N bonds) spontaneously during the self-assembly process has been used for preparing sophisticated and beautiful artificial discrete molecules (e.g., macrocycles,<sup>30,31</sup> pentafoil knot,<sup>32</sup> Borromen rings,<sup>33</sup> helicates,<sup>34</sup> catenanes,<sup>30</sup> and MOCs<sup>29</sup>). The technology was recently extended to prepare polymeric metal–organic complexes by a conventional solution method<sup>35</sup> or under solvothermal conditions.<sup>36</sup>

As a continuing study of metal–imidazolate cages and gyroidal MOFs by using the *subcomponent self-assembly* technology under solvothermal reaction conditions,<sup>36–38</sup> we attempt to assemble the metal–imidazolate cages to extended coordination networks. Recently, we have successfully obtained a series of mesoporous supramolecular frameworks by the self-assembly of Co–imidazolate cages and inorganic anions (BF<sub>4</sub><sup>−</sup>, ClO<sub>4</sub><sup>−</sup>, and PF<sub>6</sub><sup>−</sup>) through unconventional C–H⋯X (X = O, F and  $\pi$ ) hydrogen bonds.<sup>39</sup> In this work, the combination of nickel(II) salts, 5-methyl-4-formylimidazole, *m*-xylylenediamine, and judiciously chosen inorganic anions resulted in a series of cages or cage-based products featuring diverse structures ranging from discrete cages to 2D sheets (Scheme 1). For each case, we obtained (1) a discrete cubic 8-nuclear Ni–imidazolate cage formulated as Ni<sub>8</sub>L<sub>6</sub>X<sub>4</sub>(DMF)<sub>2</sub>·H<sub>2</sub>O (X = Cl<sup>−</sup>, 1; Br<sup>−</sup>, 2; I<sup>−</sup>, 3; SCN<sup>−</sup>, 4; NO<sub>2</sub><sup>−</sup>, 5; or NO<sub>3</sub><sup>−</sup>, 6; H<sub>2</sub>L = 1,3-

Received: August 17, 2015

Published: October 29, 2015

**Scheme 1. Illustration of Solvothermal Subcomponent Self-Assembly of Ni–Imidazolate Cubic Cages and Coordination Polymers Based on the Cubic Cages**



bis[(5-methyl-1H-imidazol-4-yl) methyleneaminomethyl]-benzene, DMF = *N,N'*-dimethylformamide); (2) a one-dimensional ladder-like coordination polymer ( $\{[\text{Ni}_8\text{L}_6(\text{HCO}_2)_2(\text{DEF})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}\}_n$  **7**, DEF = *N,N'*-diethylformamide) constructed by Ni–imidazolate cages and formic anions *in situ* yielded by the decomposition of DEF molecules;<sup>41–44</sup> (3) a two-dimensional layer coordination polymer  $[(\text{Ni}_8\text{L}_6\text{X}_4) \cdot \text{H}_2\text{O}]_n$  ( $\text{X} = \text{N}_3^-$ , **8**;  $(\text{CN})_2\text{N}^-$ , **9**) or  $\{[\text{Ni}_8\text{L}_6((\text{CN})_3\text{C})_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}\}_n$  (**10**); and (4) a one-dimensional ladder-like coordination polymer ( $\{[\text{Ni}_8\text{L}_6(\text{HCO}_2)_2(\text{DMF})_2][\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot \text{H}_2\text{O}\}_n$  (**11**) using a tetratopic anionic metal complex  $[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]^{2-}$  ( $\text{C}_4\text{N}_2\text{S}_2 = \text{dimercaptomaleonitrile}$ ) as anions. This simple method of changing the anions should allow facile tuning of assembly structures.

## EXPERIMENTAL SECTION

**Materials and Measurements.** The reagents and solvents employed were commercially available and were used without further purification. Infrared spectra were obtained as KBr disks on a Nicolet Avatar 360 FT-IR spectrometer in the range of 4000–400  $\text{cm}^{-1}$  (abbreviations for the IR bands: w = weak, m = medium, b = broad, and vs = very strong). Elemental analyses were carried out with an Elementar vario EL Cube equipment. Powder X-ray diffraction patterns (PXRD) of the bulk samples were measured on a Bruker D8 Advance diffractometer ( $\text{Cu K}\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) under room temperature. Thermogravimetric measurements were performed on a TA Instruments Q50 Thermogravimetric Analyzer (TGA) under a nitrogen flow of 40  $\text{mL min}^{-1}$  at a typical heating rate of 10  $^\circ\text{C min}^{-1}$ .

**Synthesis of Complexes.**  $\text{Ni}_8\text{L}_6\text{Cl}_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 0.8\text{DMF}$  (**1**). A mixture of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (9.5 mg, 0.04 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and mixed solvent *N,N'*-dimethylformamide (DMF)/methanol (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120  $^\circ\text{C}$  for 72 h and cooled to room temperature at a rate of 5  $^\circ\text{C/h}$ . Dark green rodlike crystals were obtained (9.7 mg, 70.7%, based on  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ). IR spectrum (KBr pellets,  $\text{cm}^{-1}$ ): 3435.66(m), 3020.18(w), 2915.60(w), 2825.66(w), 1655.73(s), 1615.38(vs), 1490.26(m), 1478.42(m), 1438.27(m), 1400.19(m), 1339.56(m), 1285.49(s), 1220.09(w), 1195.59(w), 1139.29(m), 1093.31(w), 1055.22(m), 975.68(m), 882.72(w), 851.43(m), 796.05(w), 739.50(w), 694.14(w), 664.76(w), 602.06(w), 552.40(w), 515.28(w). Elemental analysis (CHN),  $\text{C}_{116.4}\text{H}_{129.6}\text{Cl}_4\text{N}_{38.8}\text{Ni}_8\text{O}_{3.8}$

(corresponding to  $\text{Ni}_8\text{L}_6\text{Cl}_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 0.8\text{DMF}$ ), calculated (%): C 50.94, H 4.76, N 19.80; found (%): C 51.57, H 5.04, N 19.75.

$\text{Ni}_8\text{L}_6\text{Br}_4(\text{DMF})_2 \cdot \text{H}_2\text{O}$  (**2**). A mixture of  $\text{NiBr}_2$  (8.7 mg, 0.04 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/methanol mixed solvent (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120  $^\circ\text{C}$  for 72 h and cooled to room temperature at a rate of 5  $^\circ\text{C/h}$ . Dark green rodlike crystals were obtained (10.2 mg, 71.2%, based on  $\text{NiBr}_2$ ). IR spectrum (KBr pellets,  $\text{cm}^{-1}$ ): 3435.36(m), 3019.38(w), 2914.30(w), 2823.54(w), 1646.25(s), 1616.27(vs), 1477.59(m), 1437.49(m), 1399.20(m), 1338.47(m), 1285.54(s), 1218.91(w), 1194.16(w), 1138.97(m), 1091.09(w), 1054.67(m), 974.91(m), 882.80(w), 850.98(m), 792.53(w), 738.31(w), 693.38(w), 663.64(w), 602.69(w), 552.14(m), 476.69(w). Elemental analysis (CHN),  $\text{C}_{114}\text{H}_{124}\text{Br}_4\text{N}_{38}\text{Ni}_8\text{O}_3$  (corresponding to  $\text{Ni}_8\text{L}_6\text{Br}_4(\text{DMF})_2 \cdot \text{H}_2\text{O}$ ), calculated (%): C 47.81, H 4.36, N 18.59; found (%): C 48.75, H 4.73, N 18.60.

$\text{Ni}_8\text{L}_6(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 1.6\text{DMF}$  (**3**). A mixture of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (14.2 mg, 0.04 mmol), NaI (15.0 mg, 0.1 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/ethanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120  $^\circ\text{C}$  for 72 h and cooled to room temperature at a rate of 5  $^\circ\text{C/h}$ . Dark green rodlike crystals were obtained (4.7 mg, 29.7%, based on  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ). IR spectrum (KBr pellets,  $\text{cm}^{-1}$ ): 3463.91(m), 3022.56(w), 2920.16(w), 1655.13(m), 1613.95(vs), 1560.98(w), 1475.70(m), 1439.17(m), 1401.05(m), 1384.70(m), 1340.29(m), 1284.77(s), 1220.01(w), 1193.90(w), 1138.92(m), 1121.94(w), 1056.27(m), 975.77(m), 873.42(m), 849.89(s), 794.89(w), 739.22(w), 662.99(w), 604.56(w), 552.25(m), 456.63(w). Elemental analysis (CHN),  $\text{C}_{118.8}\text{H}_{135.2}\text{I}_4\text{N}_{39.6}\text{Ni}_8\text{O}_{4.6}$  (corresponding to  $\text{Ni}_8\text{L}_6\text{I}_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 1.6\text{DMF}$ ), calculated (%): C 45.03, H 4.30, N 17.51; found (%): C 44.91, H 4.57, N 17.70.

$\text{Ni}_8\text{L}_6(\text{SCN})_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 2\text{DMF}$  (**4**). A mixture of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (14.2 mg, 0.04 mmol), NaSCN (8.1 mg, 0.1 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/methanol mixed solvent (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120  $^\circ\text{C}$  for 72 h and cooled to room temperature at a rate of 5  $^\circ\text{C/h}$ . Dark green blocklike crystals were obtained (9.4 mg, 64.34%, based on  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ). IR spectrum (KBr pellets,  $\text{cm}^{-1}$ ): 3441.59(m), 3052.69(w), 3020.11(w), 2917.92(w), 2833.71(w), 2078.64(vs), 1655.12(s), 1613.48(vs), 1491.92(m), 1476.97(m), 1438.78(m), 1398.60(m), 1332.29(m), 1285.89(s), 1220.12(w), 1196.89(w), 1166.92(w), 1137.86(m), 1095.99(w), 1053.21(m), 975.23(m), 882.71(w), 850.27(m), 794.81(w), 738.60(w), 693.21(w), 664.30(m), 602.78(w), 551.94(w), 475.36(w). Elemental analysis (CHN),  $\text{C}_{124}\text{H}_{138}\text{N}_{44}\text{Ni}_8\text{O}_5\text{S}_4$  (corresponding to  $\text{Ni}_8\text{L}_6(\text{SCN})_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 2\text{DMF}$ ), calculated (%): C 50.94, H 4.82, N 21.06, S 4.33; found (%): C 51.92, H 4.53, N 21.16, S 4.39.

$\text{Ni}_8\text{L}_6(\text{NO}_3)_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 0.5\text{DMF}$  (**5**). A mixture of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (14.2 mg, 0.04 mmol),  $\text{NaNO}_2$  (6.9 mg, 0.1 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120  $^\circ\text{C}$  for 72 h and cooled to room temperature at a rate of 5  $^\circ\text{C/h}$ . Dark green blocklike crystals were obtained (9.0 mg, 65.1%, based on  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ). IR spectrum (KBr pellets,  $\text{cm}^{-1}$ ): 3465.90(m), 3019.38(w), 2914.30(w), 2823.54(w), 1656.07(m), 1615.12(vs), 1481.39(m), 1439.44(m), 1400.40(m), 1385.10(m), 1339.90(m), 1284.75(s), 1121.27(m), 1193.84(w), 1138.62(m), 1055.32(m), 1015.34(w), 976.34(m), 882.27(w), 850.70(m), 793.19(w), 739.29(w), 692.28(w), 663.76(w), 605.00(w), 551.85(w), 471.22(w). Elemental analysis (CHN),  $\text{C}_{115.5}\text{H}_{127.5}\text{N}_{42.5}\text{Ni}_8\text{O}_{11.5}$  (corresponding to  $\text{Ni}_8\text{L}_6(\text{NO}_3)_4(\text{DMF})_2 \cdot \text{H}_2\text{O} \cdot 0.5\text{DMF}$ ), calculated (%): C 50.18, H 4.65, N 21.53; found (%): C 50.67, H 4.62, N 21.63.

$\text{Ni}_8\text{L}_6(\text{NO}_3)_4(\text{DMF})_2 \cdot \text{H}_2\text{O}$  (**6**). A mixture of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (11.6 mg, 0.04 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/methanol mixed solvent (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and

heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h. Dark green rodlike crystals were obtained (9.8 mg, 70.2%, based on Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O). IR spectrum (KBr pellets, cm<sup>-1</sup>): 3467.87(m), 3020.53(w), 2916.53(w), 2833.24(w), 1657.90(s), 1615.41(vs), 1475.01(m), 1438.69(m), 1384.24(vs), 1340.18(m), 1304.99(w), 1284.98(m), 1220.72(w), 1193.77(w), 1054.77(m), 975.12(m), 882.27(w), 850.66(m), 793.92(w), 739.02(w), 692.87(w), 664.20(w), 603.28(w), 552.02(m), 479.93(w). Elemental analysis (CHN), C<sub>114</sub>H<sub>124</sub>N<sub>42</sub>Ni<sub>8</sub>O<sub>15</sub>, (corresponding to Ni<sub>8</sub>L<sub>6</sub>(NO<sub>3</sub>)<sub>4</sub>·(DMF)<sub>2</sub>·H<sub>2</sub>O), calculated (%): C 49.04, H 4.48, N 21.07; found (%): C 49.30, H 4.90, N 21.28.

{[Ni<sub>8</sub>L<sub>6</sub>(HCO<sub>2</sub>)<sub>2</sub>(DEF)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O}<sub>n</sub> (**7**). A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (14.2 mg, 0.04 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DEF/ethanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h. Dark green blocklike crystals were obtained (5.7 mg, 39.5%, based on Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). IR spectrum (KBr pellets, cm<sup>-1</sup>): 3426.76(m), 3022.52(w), 2918.64(w), 2843.21(w), 1654.88(m), 1614.07(vs), 1488.22(m), 1437.60(m), 1399.14(m), 1339.37(m), 1285.89(m), 1221.22(w), 1194.62(w), 1139.25(m), 1093.45(m), 1056.52(m), 972.57(m), 929.54(w), 885.06(w), 851.15(m), 790.96(w), 738.94(w), 692.40(w), 663.63(w), 622.99(w), 605.89(w), 551.47(w), 488.55(w), 450.26(w). Elemental analysis (CHN), (C<sub>120</sub>H<sub>134</sub>Cl<sub>2</sub>N<sub>38</sub>Ni<sub>8</sub>O<sub>15</sub>), (corresponding to {[Ni<sub>8</sub>L<sub>6</sub>(HCO<sub>2</sub>)<sub>2</sub>(DEF)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O)<sub>n</sub>), calculated (%): C 49.89, H 4.68, N 18.42; found (%): C 49.42, H 4.38, N 18.83.

[Ni<sub>8</sub>L<sub>6</sub>(N<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O·DMF]<sub>n</sub> (**8**). A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (14.2 mg, 0.04 mmol), NaN<sub>3</sub> (6.5 mg, 0.1 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h. Dark green rodlike crystals were obtained (6.6 mg, 50.0%, based on Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). IR spectrum (KBr pellets, cm<sup>-1</sup>): 3424.74(m), 3021.20(w), 2916.19(w), 2832.95(w), 2085.76(vs), 2045.25(vs), 1665.43(m), 1614.26(vs), 1490.54(m), 1477.87(m), 1437.28(m), 1400.04(m), 1337.79(m), 1285.55(s), 1219.08(w), 1195.21(w), 1138.57(m), 1092.58(w), 1054.63(m), 974.42(m), 882.84(w), 851.45(m), 793.96(w), 739.60(w), 694.68(w), 664.11(w), 602.81(w), 552.00(m), 500.09(w), 476.56(w). Elemental analysis (CHN), (C<sub>111</sub>H<sub>117</sub>N<sub>49</sub>Ni<sub>8</sub>O<sub>2</sub>)<sub>n</sub>, (corresponding to [Ni<sub>8</sub>L<sub>6</sub>(N<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O·DMF]<sub>n</sub>), calculated (%): C 50.52, H 4.47, N 26.01; found (%): C 50.18, H 4.41, N 25.73.

[Ni<sub>8</sub>L<sub>6</sub>(N(CN)<sub>2</sub>)<sub>4</sub>·H<sub>2</sub>O·0.5DMF]<sub>n</sub> (**9**). A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (14.2 mg, 0.04 mmol), NaN(CN)<sub>2</sub> (8.9 mg, 0.1 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF (2.5 mL) was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h. Dark green blocklike crystals were obtained (5.4 mg, 40.0%, based on Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). IR spectrum (KBr pellets, cm<sup>-1</sup>): 3465.09(m), 3021.74(w), 2917.14(w), 2839.92(w), 2159.57(vs), 1654.61(w), 1613.91(vs), 1477.34(m), 1438.77(m), 1399.73(m), 1340.43(m), 1285.37(s), 1285.37(w), 1218.37(w), 1195.55(w), 1138.31(s), 1092.70(w), 1054.56(m), 973.74(m), 881.22(w), 850.24(m), 794.87(w), 739.41(w), 692.87(w), 664.15(m), 603.42(w), 551.82(m), 517.94(w), 476.81(w). Elemental analysis (CHN), (C<sub>117.5</sub>H<sub>113.5</sub>N<sub>48.5</sub>Ni<sub>8</sub>O<sub>1.5</sub>)<sub>n</sub>, (corresponding to [Ni<sub>8</sub>L<sub>6</sub>(N(CN)<sub>2</sub>)<sub>4</sub>·H<sub>2</sub>O·0.5DMF]<sub>n</sub>), calculated (%): C 52.30, H 4.24, N 25.17; found (%): C 51.92, H 4.21, N 25.68.

{[Ni<sub>8</sub>L<sub>6</sub>(C(CN)<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O·0.5DMF}<sub>n</sub> (**10**). A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (14.2 mg, 0.04 mmol), KC(CN)<sub>3</sub> (12.9 mg, 0.1 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/ethanol mixed solvent (3 mL, 2:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h. Dark green polyhedron-like crystals were obtained (6.3 mg, 44.8%, based on Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). IR spectrum (KBr, pellets, cm<sup>-1</sup>): 3424.57(m), 3020.87(w), 2915.51(w), 2848.84(w), 2214.72(s),

2180.89(s), 1614.47(vs), 1492.76(m), 1476.96(m), 1438.94(m), 1399.19(m), 1384.62(m), 1341.82(m), 1286.32(s), 1238.52(w), 1221.96(w), 1196.56(w), 1139.07(s), 1121.02(m), 1100.21(s), 975.35(m), 884.13(w), 850.53(m), 794.07(w), 739.13(w), 694.93(w), 664.03(w), 623.19(w), 602.57(w), 552.22(w), 518.61(w). Elemental analysis (CHN), (C<sub>117.5</sub>H<sub>113.5</sub>Cl<sub>2</sub>N<sub>42.5</sub>Ni<sub>8</sub>O<sub>9.5</sub>)<sub>n</sub>, (corresponding to {[Ni<sub>8</sub>L<sub>6</sub>(C(CN)<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O·0.5DMF}<sub>n</sub>), calculated (%): C 50.14, H 4.21, N 21.11; found (%): C 50.96, H 4.27, N 21.22.

{[Ni<sub>8</sub>L<sub>6</sub>(HCO<sub>2</sub>)<sub>2</sub>(DMF)<sub>2</sub>][Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]-H<sub>2</sub>O·2DMF}<sub>n</sub> (**11**). A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (18.3 mg, 0.05 mmol), dimercaptomaleonitrile disodium salt (Na<sub>2</sub>C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>, 3.7 mg, 0.02 mmol), and 1 mL of DMF was added to a 5 mL glass bottle; the mixed solution was stirred for 30 min at room temperature. Then, the 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), 1 mL of DMF, and 0.5 mL of methanol were added to the above solution. The final solution was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h. Both dark green (complex **7**) and brown blocklike crystals (complex **11**) were obtained. If the mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (18.3 mg, 0.05 mmol), dimercaptomaleonitrile disodium salt (Na<sub>2</sub>C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>, 3.7 mg, 0.02 mmol), 5-methyl-1H-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), and DMF/methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 h and cooled to room temperature at a rate of 5 °C/h, only brown blocklike crystals of **11** were obtained (5.2 mg, 30.0%, based on Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). IR spectrum (KBr pellets, cm<sup>-1</sup>): 3434.37(m), 3022.44(w), 2920.66(w), 2852.19(w), 2192.05(m), 1655.45(m), 1613.51(vs), 1479.99(m), 1438.26(m), 1400.51(m), 1341.27(m), 1285.72(s), 1219.94(w), 1196.06(w), 1139.32(s), 1093.41(w), 1055.93(m), 974.01(m), 881.49(w), 850.82(m), 795.09(w), 739.14(w), 692.11(w), 664.18(w), 603.81(w), 551.96(m), 511.89(w). Elemental analysis (CHN), (C<sub>130</sub>H<sub>140</sub>N<sub>44</sub>Ni<sub>9</sub>O<sub>9</sub>S<sub>4</sub>)<sub>n</sub>, (corresponding to {[Ni<sub>8</sub>L<sub>6</sub>(HCO<sub>2</sub>)<sub>2</sub>·(DMF)<sub>2</sub>][Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]-H<sub>2</sub>O·2DMF}<sub>n</sub>), calculated (%): C 50.06, H 4.52, N 19.76, S 4.11; found (%): C 50.43, H 4.32, N 19.51, S 4.35.

**Caution!** In the syntheses of complexes **1–11**, the volume of the solution should not exceed one-third of the volume of the glass tubes to avoid overloading. Be careful to avoid potential empyrosis and incised wound when flame-sealing and opening the glass tubes.

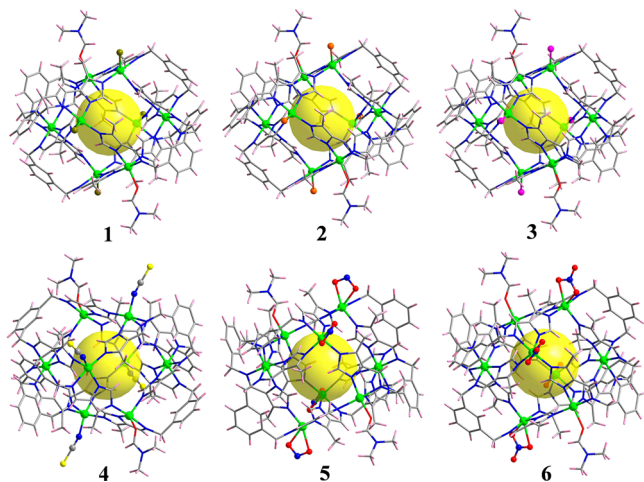
**Crystal Structure Determination.** One of the single crystals of complexes **1–11** suitable for diffraction analysis was mounted with glue at the end of a glass fiber. Data collection was performed with an Oxford Diffraction Gemini E instrument (Cu X-ray source, K $\alpha$ ,  $\lambda$  = 1.54056 Å; Mo X-ray source, K $\alpha$ ,  $\lambda$  = 0.71073 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd.). Crystals of **1–11** were measured at 293 K. The data were processed using CrysAlis<sup>Pro</sup>. The structures were solved by direct methods and refined by full-matrix least-squares refinements based on  $F^2$ . Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were conducted using the SHELXL-97 programs. The treatment for the guest molecules in the cavities of **1**, **3**, **4**, **6**, **7**, **8**, **9**, **10**, and **11** involves the use of the SQUEEZE program of PLATON. A summary of crystal data and structure refinement parameters is listed in Tables S1–S4 (see the Supporting Information). CCDC nos. 1417505–1417515.

## RESULTS AND DISCUSSION

All compounds in this work were synthesized by the solvothermal *subcomponent self-assembly* of *m*-xylylenediamine, 5-methyl-4-formylimidazole, nickel(II) salts, and respective inorganic anions. These multicomponent reactions as described in the **Experimental Section** can be easily performed under solvothermal conditions (DMF or DEF–MeOH or EtOH mixture as solvent, heating at 120 °C for 3 days). The most important merit of applying the solvothermal subcomponent self-assembly technology is direct growth of single crystals of

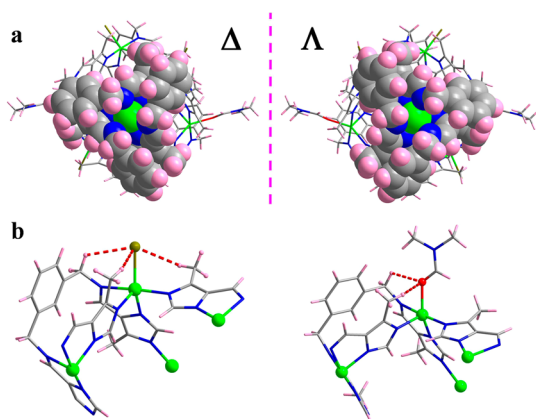
the target compounds, convenient for obtaining suitable single crystals for X-ray diffraction measurement.

Structures of compounds **1–6** feature an 8-nuclear cubic cage and crystallize in the same monoclinic space group ( $P2_1/n$ ). Because of the similar structures (Figure 1), the structure of



**Figure 1.** X-ray crystal structures of cubic Ni-imidazolate cages **1–6** (the yellow ball representing the inner cavity). Color codes: Ni, green; Cl, brown; Br, orange; I, purple; S, yellow; O, red; N, blue; C, gray; H, pink.

**1** will be described in detail. As shown in Figure 1, cubic Ni-imidazolate cage **1** contains 8 Ni<sup>II</sup>, 6 L, 4 Cl<sup>−</sup>, and 2 DMF molecules. The Ni<sup>II</sup> centers act as the vertices of the cubic cage. In **1**, two Ni<sup>II</sup> ions adopt an octahedral coordination geometry, and each Ni<sup>II</sup> ion is chelated by three L (Figure 2a). The other



**Figure 2.** Two octahedral Ni<sup>II</sup> vertices featuring opposite asymmetric arrangements ( $\Delta$  and  $\Lambda$ , respectively, a) in **1**, and the surrounding environment of trigonal-bipyramidal Ni<sup>II</sup> vertices (red dotted lines for the short distances of C–H $\cdots$ X (X = Cl and O), b). Color codes: Ni, green; Cl, brown; O, red; N, blue; C, gray; H, pink.

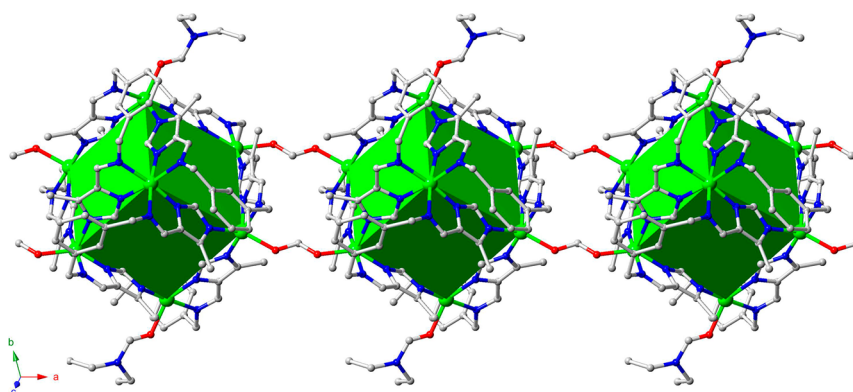
six Ni<sup>II</sup> ions adopt a trigonal-bipyramidal coordination geometry and are coordinated by four nitrogen atoms and one chlorine anion or one oxygen atom (Figure 2b). The N–Ni bond lengths range from 2.001(7) to 2.184(7) Å, which are similar to those in our previously reported Ni-imidazolate cubic cage.<sup>37</sup> The side of the cage is the imidazolate group coming from the *in situ* formed L. The successful formation of L is further documented by IR spectra (C=N feature absorbance peak at around 1615 cm<sup>−1</sup>, Figure S2). The Ni $\cdots$

Ni distances range from 6.079 to 6.237 Å, and the volume of cage **1** is about 227.0 Å<sup>3</sup>. A water molecule is confined in the cage cavity as a guest (Figure S1).

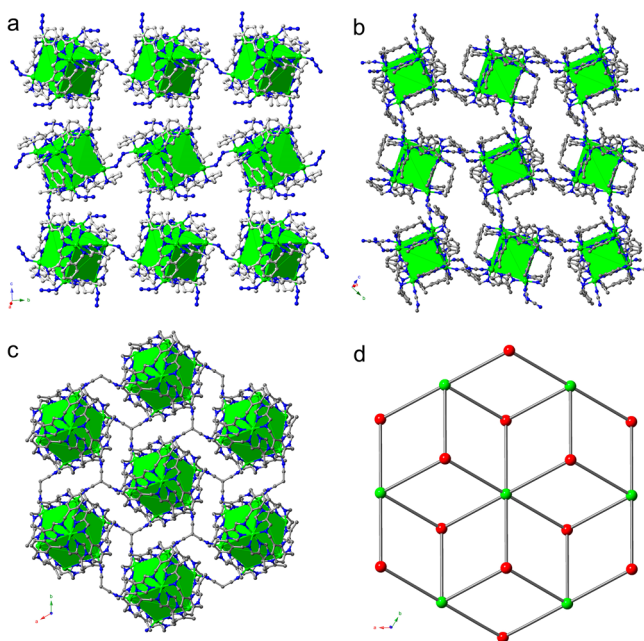
Interestingly, in cage **1**, each of the Ni<sup>II</sup> centers is chelated by three L with an octahedral coordination geometry and the Ni<sup>II</sup> centers adopt opposite asymmetric arrangements ( $\Delta$  and  $\Lambda$ , respectively, Figure 2a), similar to those of the previously reported Co<sup>III</sup> atoms.<sup>39</sup> This structural feature makes that the cubic cage as a whole is a mesomer. There are two types of Ni<sup>II</sup> atoms in the six trigonal-bipyramidal Ni<sup>II</sup> centers for each cage (ratio: 4:2). One binds with four nitrogen atoms and one Cl<sup>−</sup> (four Ni atoms) and the other with four nitrogen atoms and one oxygen atom of the DMF molecule (two Ni atoms). The Cl<sup>−</sup> anions and O atoms are surrounded by methyl and methylene groups, and the weak C–H $\cdots$ X (X = Cl and O) hydrogen bonds possibly exist (H $\cdots$ Cl 2.806–2.986 Å, and H $\cdots$ O 2.364–2.649 Å, Figure 2b).

An important structural feature in **1–6** is that the anions (Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, SCN<sup>−</sup>, NO<sub>2</sub><sup>−</sup>, and NO<sub>3</sub><sup>−</sup>, respectively) coordinate to Ni<sup>II</sup> centers; therefore, all cages are neutral. Trials using perchlorate salts as weaker coordination anions to obtain a positive Ni-imidazolate cage like that of the cobalt cage<sup>39</sup> failed. Instead, a polymeric compound (**7**) based on Ni-imidazolate cages and formate was obtained by reacting Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 5-methyl-1H-imidazole-4-carbaldehyde, and *m*-xylylenediamine in the mixture solvent of DEF/ethanol under solvothermal conditions. Compound **7** crystallizes in triclinic  $P\bar{1}$  space group. Similar to those in **1–6**, a cubic 8-nuclear Ni-imidazolate cage composed of eight Ni<sup>II</sup> centers and 6 L was successfully yielded. Notably, the Ni-imidazolate cages are bridged by formate to form an extended one-dimensional coordination polymer. In **7**, six five-coordinated Ni<sup>II</sup> centers for each cage are coordinated by four formate anions and two DEF molecules (Figure 3). Although varied one-dimensional coordination polymers based on coordination cages have been reported,<sup>19,40</sup> the ladder-like coordination polymer in **7** containing Ni-imidazolate cages bridged by double formate is unusual. In **7**, each formate anion links two cages with four positive charges each; therefore, the extended one-dimensional coordination polymer is positive, balanced by ClO<sub>4</sub><sup>−</sup> anions. This result indicates that the Ni-imidazolate cages can be used as building blocks to construct coordination polymers through judiciously choosing bridging anions.

N<sub>3</sub><sup>−</sup>, (CN)<sub>2</sub>N<sup>−</sup>, and (CN)<sub>3</sub>C<sup>−</sup> are well-known good bridging anions for constructing coordination polymers. They are chosen as anionic linkers to bridge the Ni-imidazolate cages to form extended coordination polymers. Three two-dimensional coordination polymers **8**, **9**, and **10** were obtained by *subcomponent self-assembly* under the solvothermal reaction conditions similar to the syntheses for **1–6**, respectively. The IR spectra of these complexes show the same strong absorptions around 1610 cm<sup>−1</sup> and absorptions around 2100 cm<sup>−1</sup> (2045–2215 cm<sup>−1</sup>, Figures S8–S10), which indicate that the dynamic imine bonds (C=N) are formed and the anions (N<sub>3</sub><sup>−</sup>, (CN)<sub>2</sub>N<sup>−</sup>, and (CN)<sub>3</sub>C<sup>−</sup>) are involved in these compounds. **8–10** crystallize in monoclinic  $C2/c$ ,  $P2_1/n$ , and hexagonal  $R\bar{3}$  space groups, respectively, featuring two-dimensional structures. Similar to **1–7**, the Ni-imidazolate cages are also found in **8–10** with slightly different cage sizes (Ni $\cdots$ Ni, 6.081(7)–6.233(7) Å in **8**; 6.051(1)–6.199(1) Å in **9**; and 6.053(1)–6.159(1) Å in **10**, respectively). As shown in Figure 4a, in **8**, each Ni-imidazolate cage unit connects to another four Ni<sup>II</sup>-imidazolate cage units to form an extended



**Figure 3.** Ladder-like coordination polymer in **7** based on Ni–imidazole cages (Color codes: Ni, green; O, red; N, blue; C, gray; H atoms are omitted for clarity).



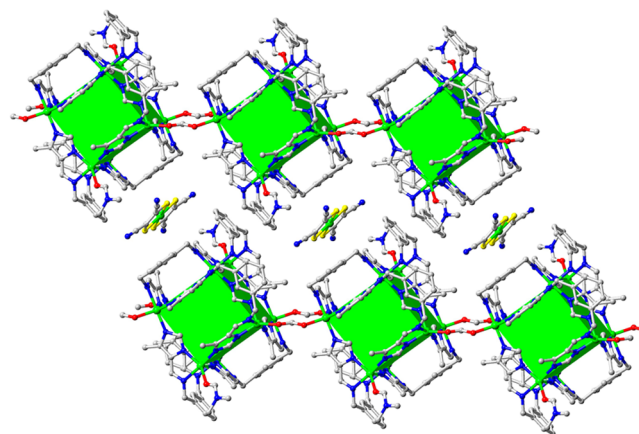
**Figure 4.** Crystal structures of two-dimensional coordination polymers **8** (a), **9** (b), and **10** (c) based on Ni–imidazole cages and  $\text{N}_3^-$ ,  $(\text{CN})_2\text{N}^-$ , and  $(\text{CN})_3\text{C}^-$ , respectively. Color codes: Ni, green; O, red; N, blue; C, gray; H atoms are omitted for clarity. (d) The **kgd** topologic network of **10**.

gridlike two-dimensional coordination polymer through four  $\text{N}_3^-$  ions. The Ni···Ni distance between two  $\text{N}_3^-$ -linked cages is about 6.0 Å (5.931(7) and 6.008(7) Å). The  $\text{N}_3^-$  ions adopt a *trans*-coordination model interacting with  $\text{Ni}^{\text{II}}$  (Figure 4a). There are another two pendant  $\text{N}_3^-$  ions coordinated with the left two five-coordinated  $\text{Ni}^{\text{II}}$  centers, which balance the positive charges of the Ni–imidazole cages. The structure of **9** is similar to that of **8**, except the bridging ions of  $(\text{CN})_2\text{N}^-$  than  $\text{N}_3^-$  in **8**. Because of the longer ion of  $(\text{CN})_2\text{N}^-$  (N···N distance, 4.385(1) Å), the Ni···Ni distance between the adjacent two Ni–imidazole cages are 8.062(2) Å, longer than that in **8** (Figure 4b). In the crystal structure of **10**, each  $\text{Ni}^{\text{II}}$ –imidazole cage unit is linked with the adjacent six cage units by six  $(\text{CN})_3\text{C}^-$  ions, and each  $(\text{CN})_3\text{C}^-$  links to three cages, resulting in an extended two-dimensional network, as shown in Figure 4c. In the network of **10**, the Ni–imidazole cage can be simplified as a 6-connected node, and the  $(\text{CN})_3\text{C}^-$  can be treated as a 3-connected node. The 3,6-connected

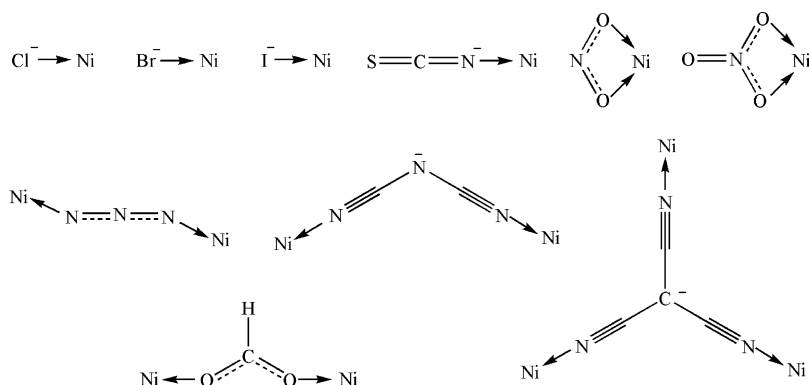
network can be rationalized as a **kgd** topology with a Vertex symbol of  $(4^3)(4^6 \cdot 6^6 \cdot 8^3)$  (Figure 4d).<sup>45</sup> In the **kgd** network, the mole ratio between the Ni–imidazole cage and  $(\text{CN})_3\text{C}^-$  is 1:2, and each  $\text{Ni}^{\text{II}}$ –imidazole cage has 4+ charges. Therefore, the network is positive, which is balanced by  $\text{ClO}_4^-$ .

To further investigate the self-assembly chemistry of the Ni–imidazole cages with anions, we employ a metal complex anion  $[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]^{2-}$  ( $\text{C}_4\text{N}_2\text{S}_2$  = dimercaptomaleonitrile) as linker.  $[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]^{2-}$ , prepared by the reaction of  $\text{Ni}^{2+}$  and dimercaptomaleonitrile disodium salt, reacted with 5-methyl-1*H*-imidazole-4-carbaldehyde, *m*-xylenediamine, and  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  under solvothermal conditions, yielding single crystals of **11**. The product is a ladder-like coordination polymer containing  $\text{Ni}^{\text{II}}$ –imidazole cages and formate, which is identical with that of **7** except for the coordinating solvent molecules (DEF, DMF for **7**, **11**, respectively). The complex  $[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]^{2-}$  anions do not coordinate with the  $\text{Ni}^{2+}$  and act as counteranions to balance the positive charge of the ladder-like coordination polymer (Figure 5). This may be due to the weaker coordination ability of  $[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]^{2-}$  compared with the *in situ* formed formate.

The thermogravimetric analyses (TGA) of **1–11** found that they have a good thermal stability (decomposing temperature > 300 °C), as shown in Figures S24–S34. Complex **4** shows interesting thermogravimetric behavior. As shown in Figure S27, it has two weight loss steps and begins to decompose at



**Figure 5.** Single-crystal structure of one-dimensional coordination polymer **11**. Color codes: Ni, green; O, red; N, blue; C, gray; S, yellow (H atoms are omitted for clarity).

Scheme 2. Binding Modes of Anions to Ni<sup>II</sup> Centers of the Cubic Ni–Imidazolate Cage

around 410 °C. The first weight loss of 5.2% at the range of 96–162 °C could be attributed to the loss of the guest DMF molecules (calculated 5.0%). The next step at 162–225 °C with a 5.5% weight loss is probably due to the loss of the coordinated DMF molecules and encapsulated guest water molecule (calculated 5.6%).

## CONCLUSIONS

We successfully constructed a series of Ni<sup>II</sup>–imidazolate cubic cages and their coordination polymers by solvothermal *subcomponent self-assembly*. Solvothermal reactions of Ni<sup>II</sup>, 5-methyl-4-formylimidazole, and *m*-xylenediamine can produce markedly different product structures of Ni<sup>II</sup>–imidazolate cages when combined with varied anions. The anions with different sizes and coordination properties (Scheme 2) as linkers can tune the assembly of the Ni<sup>II</sup>–imidazolate cages, providing a successful strategy of bridging the metal–organic cages to extended coordination polymers. This work further documented that the solvothermal *subcomponent self-assembly* technology is green and efficient for synthesizing metal organic cages and their coordination polymers. We anticipate that plenty of coordination polymers or metal–organic frameworks with interesting structures and advanced functions can be constructed by this technology and approach.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01844.

Experimental details, FT-IR spectra, powder X-ray diffraction patterns, and TGA plots of 1–11 (PDF)  
Crystallographic data of 1–11 (CIF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work is financially supported by the National Basic Research Program of China (973 Program, 2012CB821706, and 2013CB834803), the National Natural Science Foundation of China (91222202, 21171114, 21101103, and 21371113),

Guangdong Natural Science Funds for Distinguished Young Scholars, (2014A030306042), the Training Program for Excellent Young College Teacher of Guangdong Province, and Shantou University.

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