Supplementary Material (ESI) for New Journal of Chemistry


# Solvothermal syntheses, characterizations and properties of three transition-metal ($Ni^{II}$, $Co^{II}$) imino-carboxylate-diphosphonates

**Kuirong Ma,[a,b] Jianing Xu,[a] Lirong Zhang,[a] Jing Shi,[a] Daojun Zhang,[a] Yulan Zhu,[b] Yong Fan,[a]* Tianyong Song[a]***

***[a] State Key Laboratory of Inorgnic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, Jilin / P. R. China, E-mail: mrfy@jlu.edu.cn.***
***[b] Jiangsu key laboratory for chemistry of low-dimensional materials, Department of Chemistry, Huaiyin Teachers College, Huaian, Jiangsu / P. R. China.***

**Fig. SA1.** One-dimensional O−H···O hydrogen-bonded chain of **1** down the *c* axis. State the Ni-centred octahedra are shaded in green and that the hydrogen atoms are in white. Hydrogen bonds are drawn as dotted blue lines.

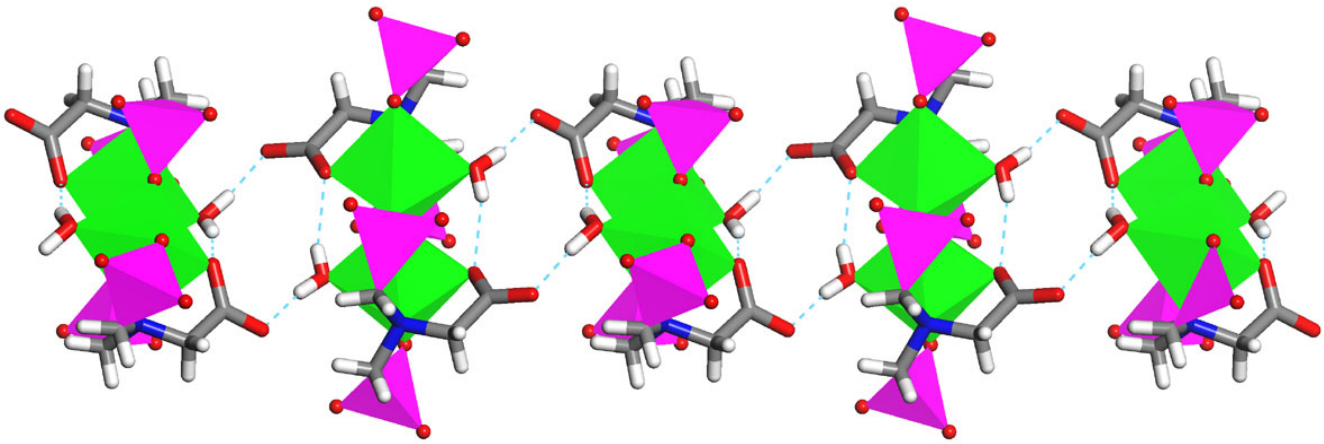


**Fig. SA2.** Three-dimensional O−H···N ($NH_4^+$) hydrogen-bonded network of **1** down the *x* axis. Hydrogen bonds are drawn as dotted blue lines. 1,3-PDA cations are omitted for clarity.

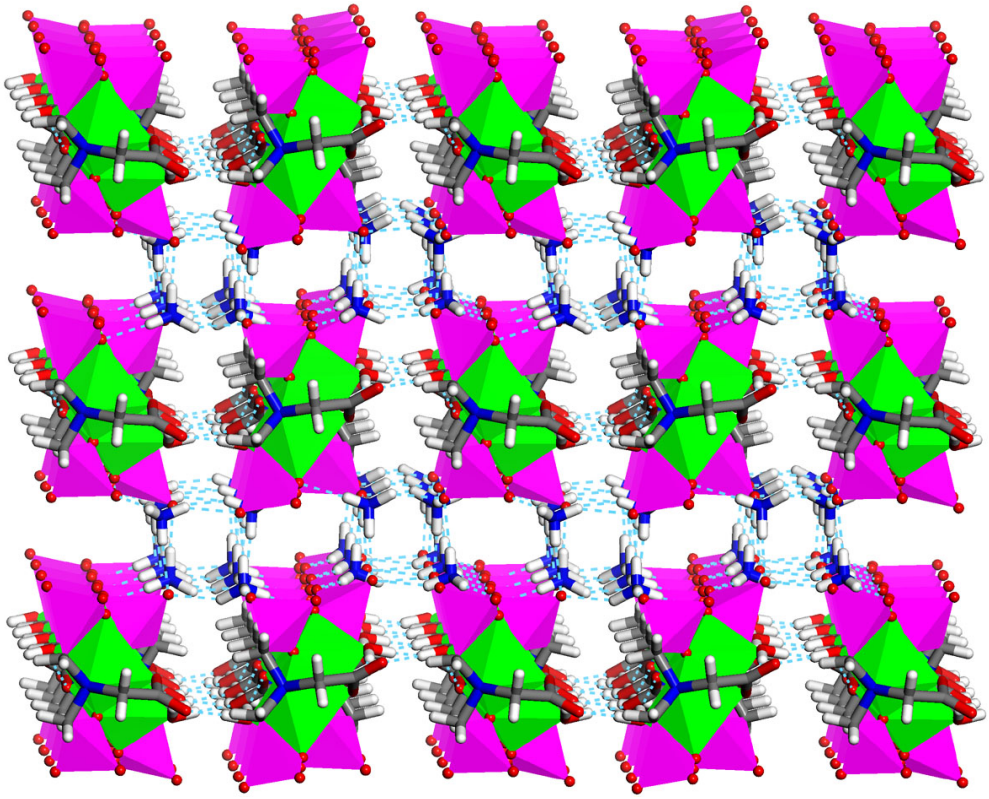


**Fig. SA3** One-dimensional O−H···O hydrogen-bonded chain in the crystal structure of **2** down the *b* axis. Hydrogen bonds are drawn as dotted blue lines. State the Ni-centred octahedra are shaded in green and that the hydrogen atoms are in white.

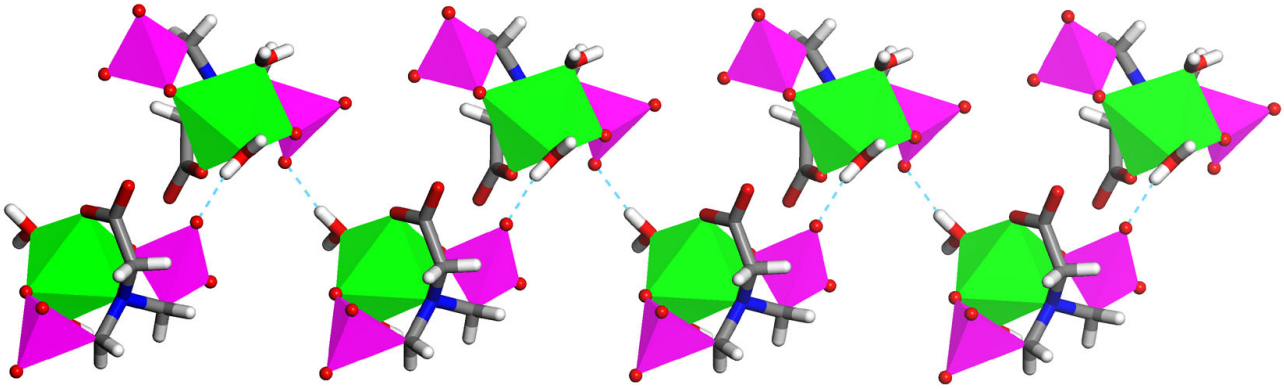


**Fig. SA4** Two-dimensional O−H···O hydrogen-bonded network in the crystal structure of **2** in the *ac* plane. Hydrogen bonds are drawn as dotted blue lines.

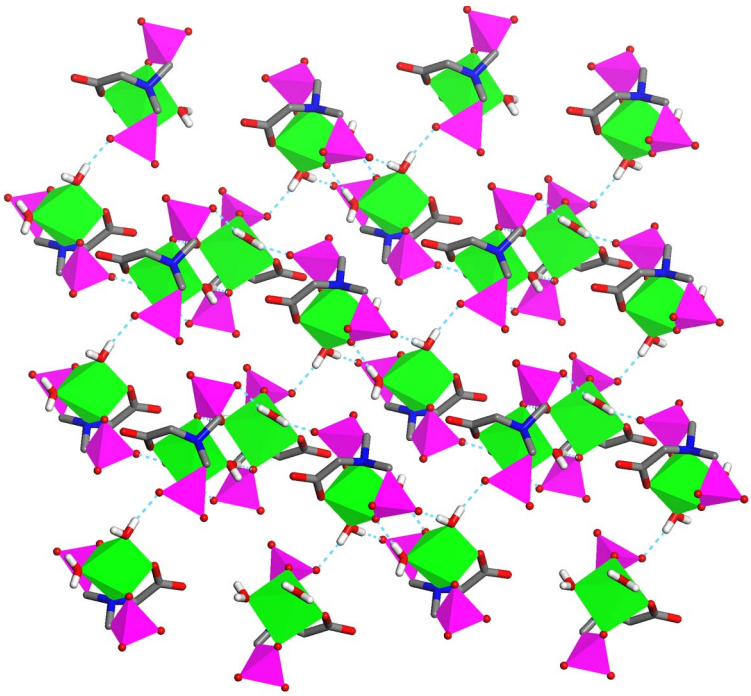


**Fig. SA5**. Two-dimensional network built from water chains of **2**. Hydrogen bonds are drawn as dotted blue lines.

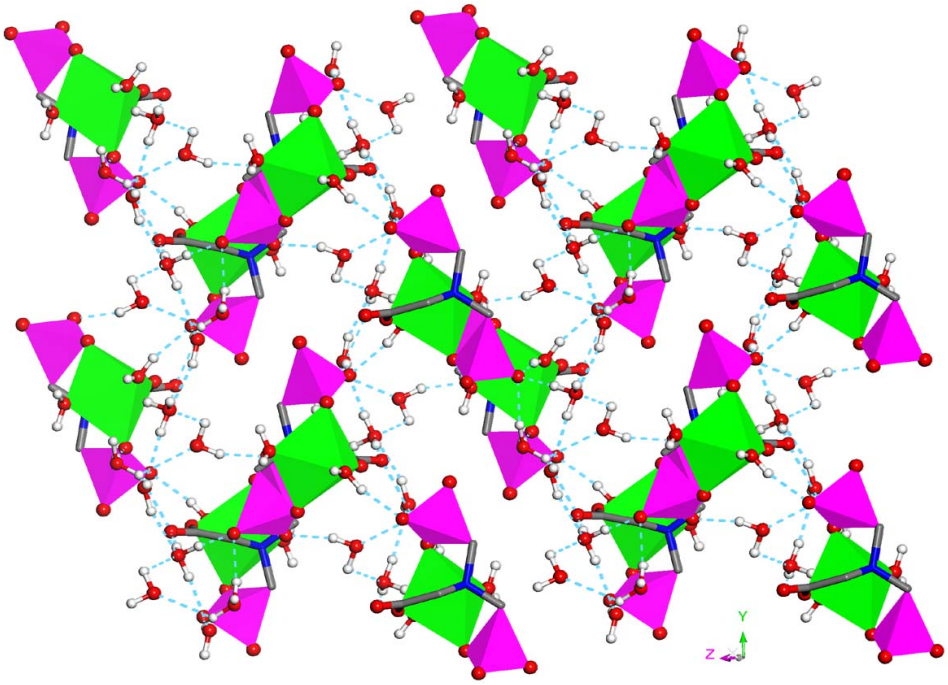


**Fig. SA6** One-dimensional O−H···O hydrogen-bonded chain in the crystal structure of **3** down the *b* axis. Hydrogen bonds are drawn as dotted blue lines. State the Co-centred octahedra are shaded in green and that the hydrogen atoms are in white.

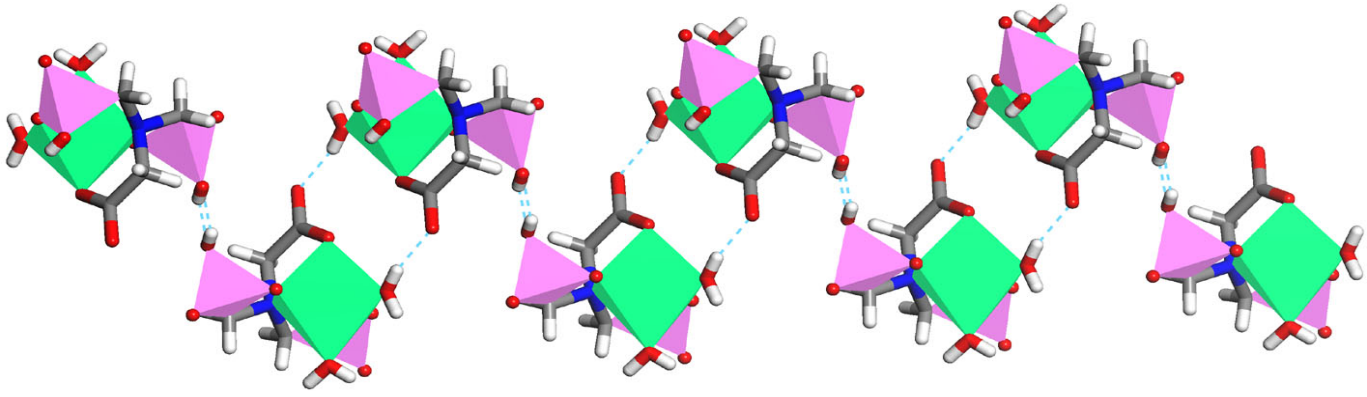


**Fig. SA7** Two-dimensional O−H···O hydrogen-bonded network in the crystal structure of **3** in the *ab* plane. Lattice waters are omitted for clarity. Hydrogen bonds are drawn as dotted blue lines.

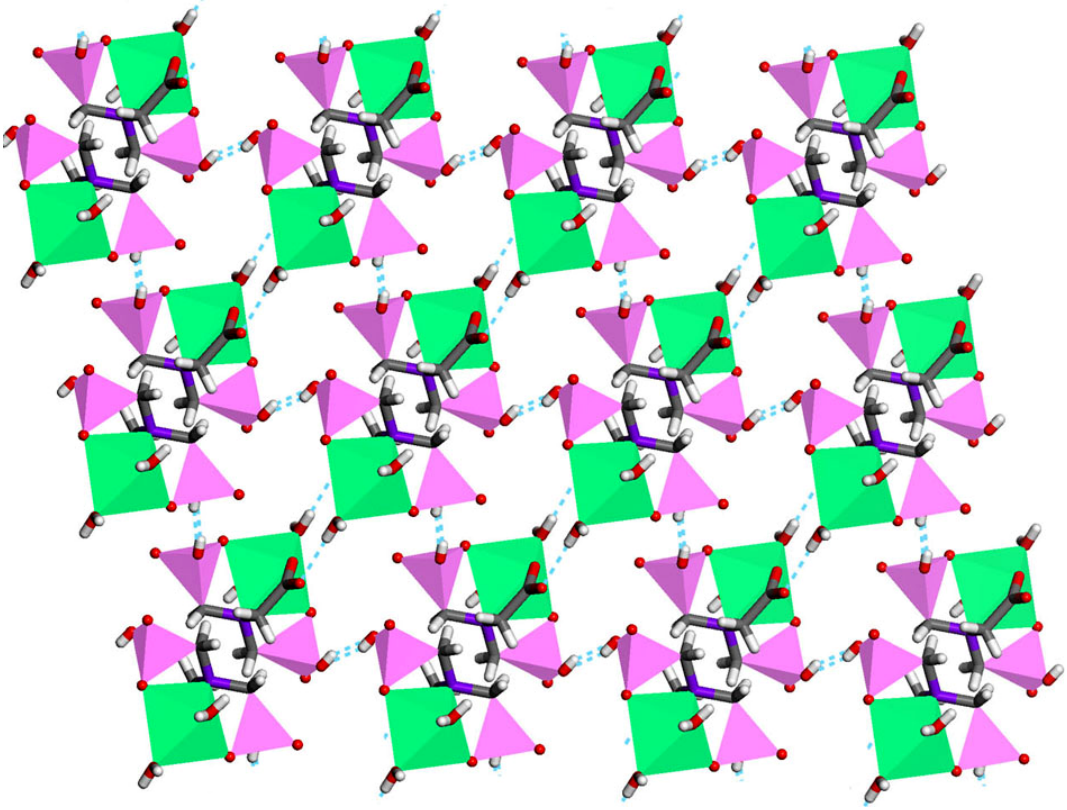
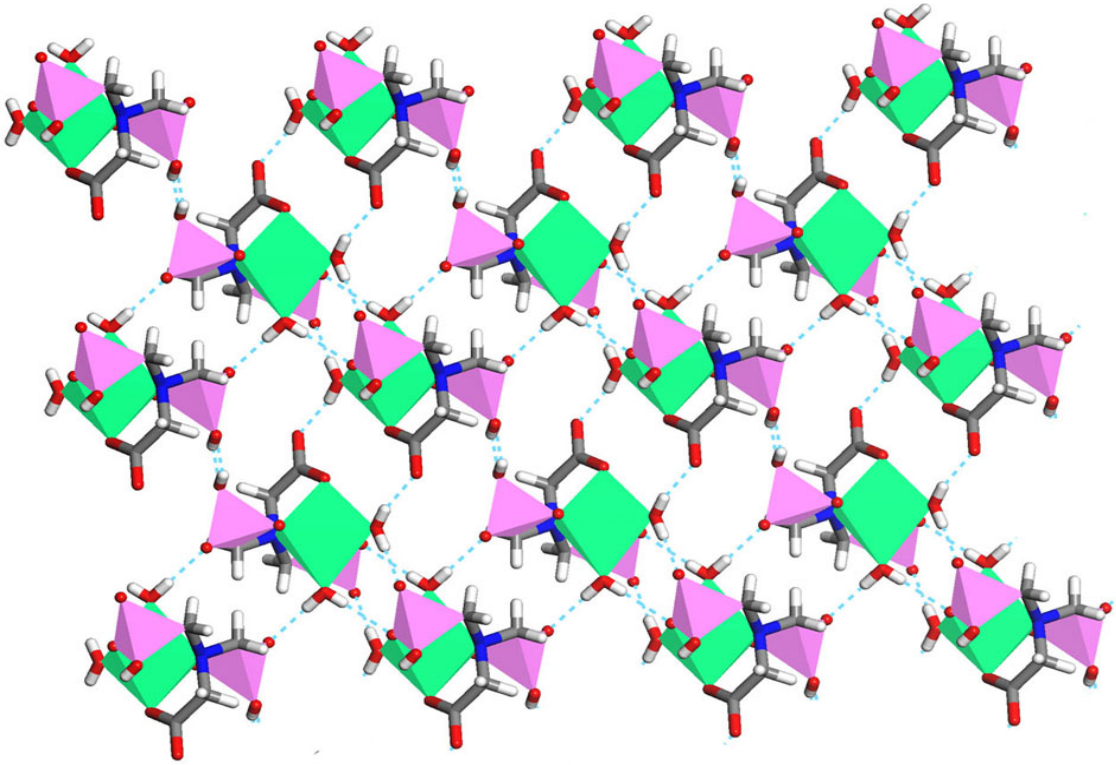


**Fig. SA8** Two-dimensional O−H···O hydrogen-bonded network in the crystal structure of **3** in the *bc* plane. Lattice waters are omitted for clarity. Hydrogen bonds are drawn as dotted blue lines.



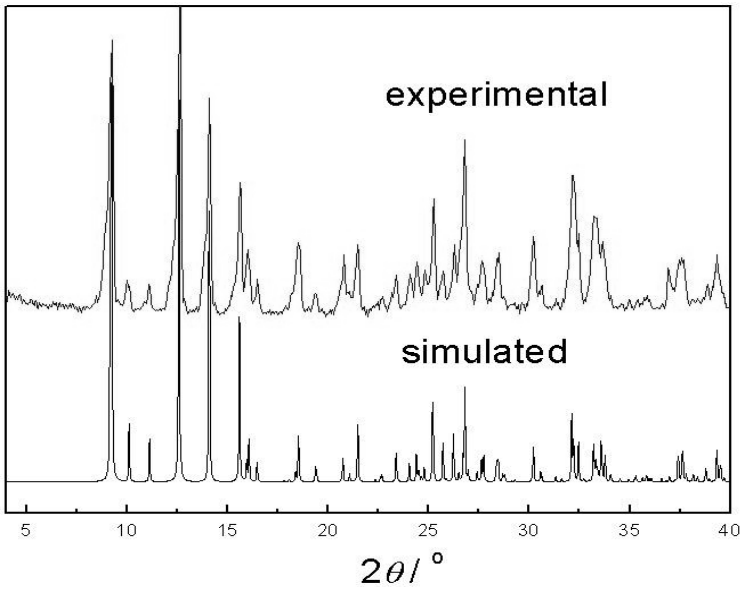



**Fig. SB1** Experimental and simulated powder X-ray diffraction patterns of compound **1**.

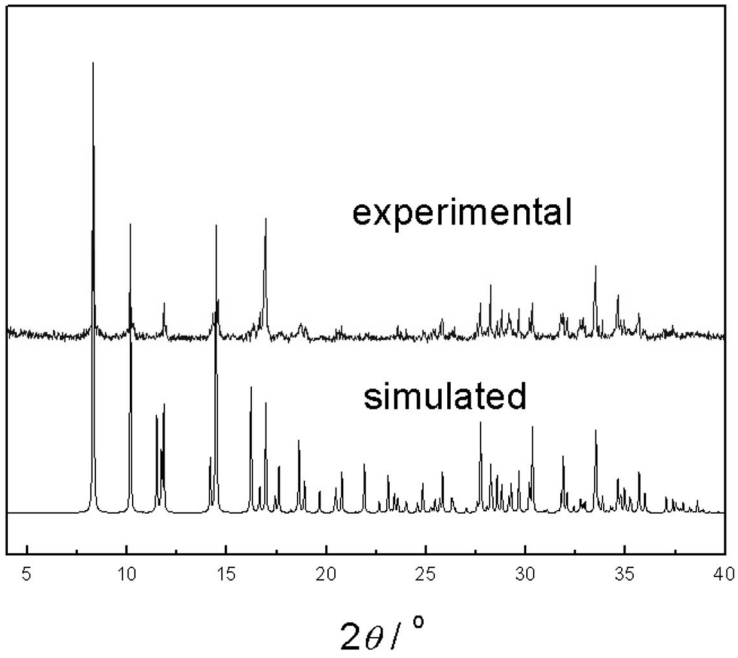



**Fig. SB2** Experimental and simulated powder X-ray diffraction patterns of compound **2**.

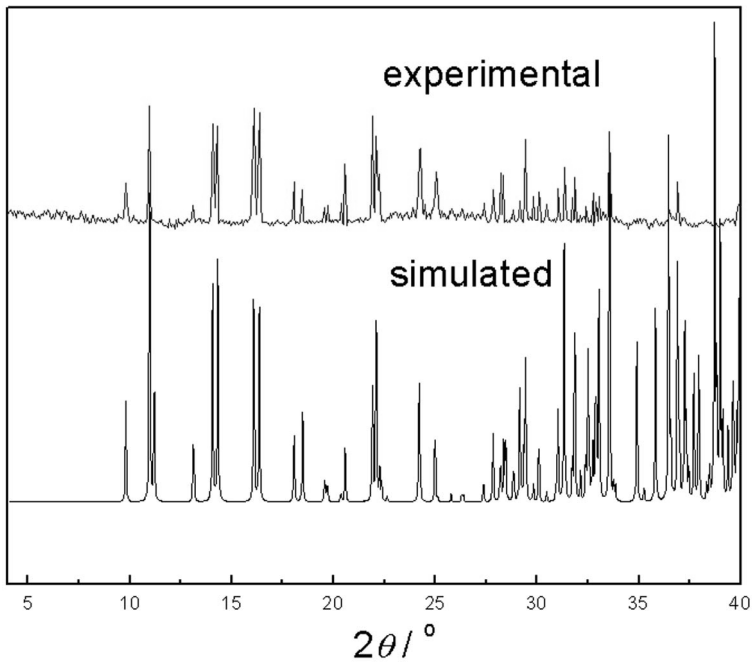



**Fig. SB3** Experimental and simulated powder X-ray diffraction patterns of compound **3**.

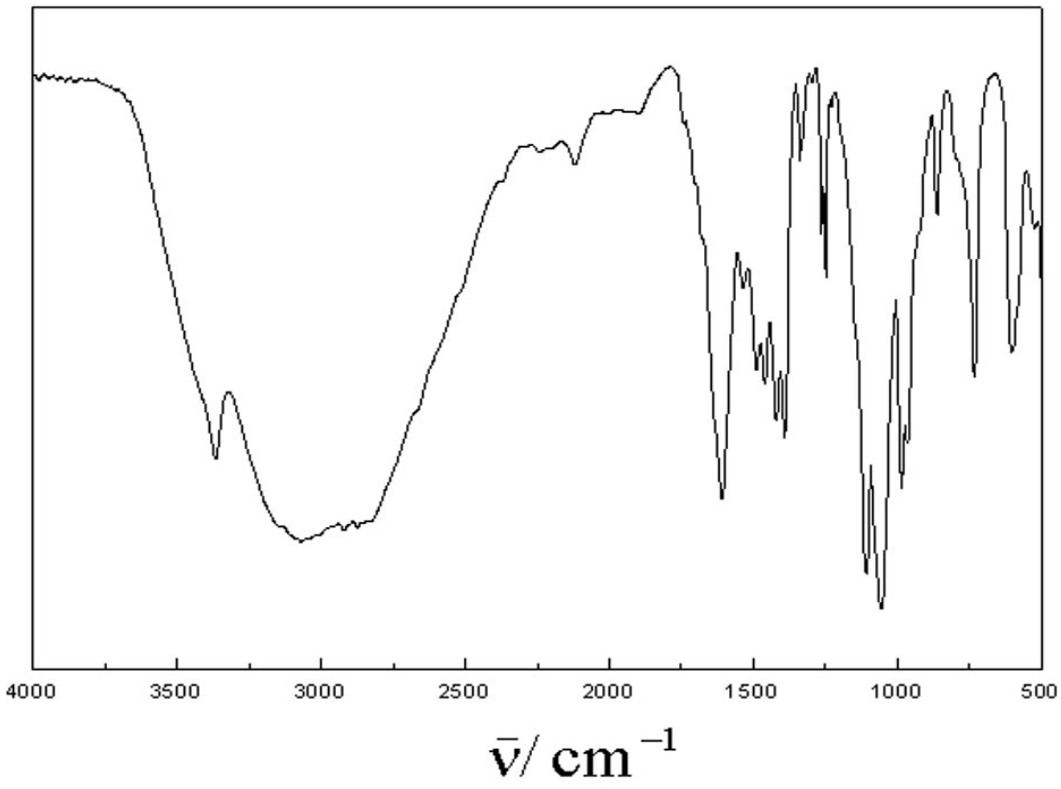



**Fig. SC1** FTIR spectrum of the compound **1.**

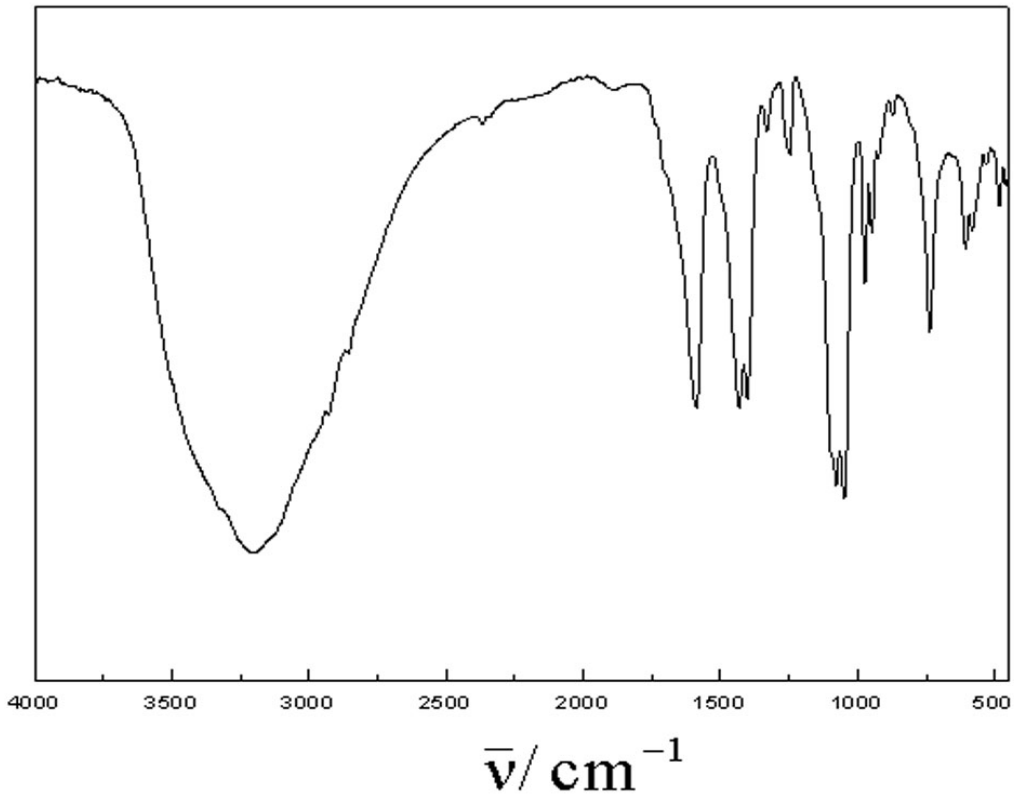



**Fig. SC2** FTIR spectrum of the compound **2**.

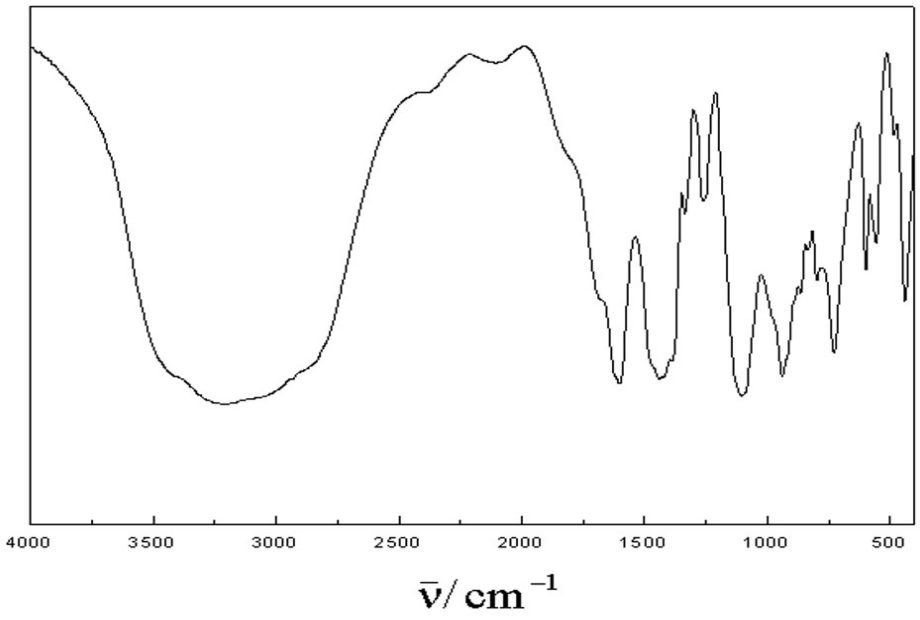



**Fig. SC3** FTIR spectrum of the compound **3**.

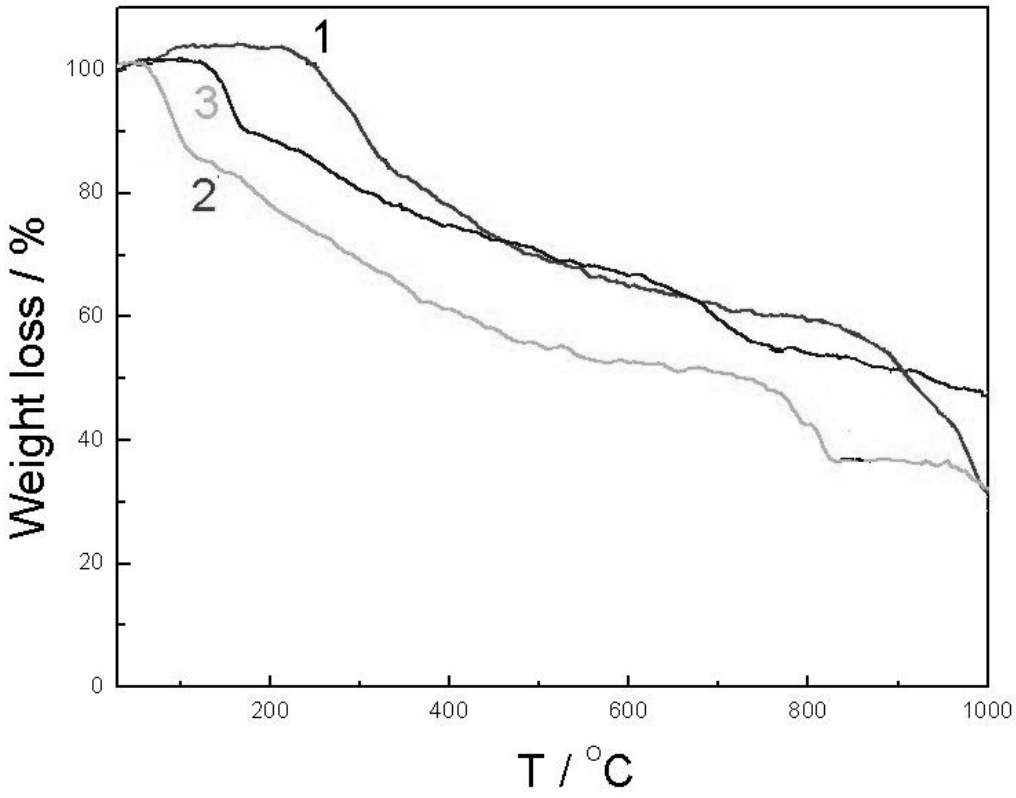



**Fig. SD** TGA curves of compounds **1**−**3**.

**Table S1.** Selected Bond Lengths [Å] and Angles [°] of Compounds **1**−**3**.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Compound **1** | | | | | | | |
| Ni(1)-O(1)$^{\#1}$ | 2.037(2) | Ni(1)-O(9) | 2.102(2) | P(1)-O(1) | 1.534(2) | P(2)-O(4) | 1.537(2) |
| Ni(1)-O(1) | 2.094(2) | Ni(1)-N(1) | 2.098(2) | P(1)-O(2) | 1.521(2) | P(2)-O(5) | 1.518(2) |
| Ni(1)-O(4) | 2.043(2) | P(1)-C(1) | 1.831(2) | P(1)-O(3) | 1.510(2) | P(2)-O(6) | 1.518(2) |
| Ni(1)-O(7) | 2.051(2) | P(2)-C(2) | 1.837(2) | O(4)-Ni(1)-N(1) | 84.27(6) | O(1)-P(1)-C(1) | 102.33(9) |
| O(1)$^{\#1}$-Ni(1)-O(4) | 103.81(6) | O(7)-Ni(1)-N(1) | 84.44(7) | O(3)-P(1)-O(1) | 112.48(9) | O(3)-P(1)-O(2) | 112.61(9) |
| O(1)$^{\#1}$-Ni(1)-O(7) | 86.65(7) | O(1)-Ni(1)-N(1) | 87.70(6) | O(2)-P(1)-O(1) | 111.98(9) | O(6)-P(2)-O(4) | 111.61(1) |
| O(4)-Ni(1)-O(7) | 94.05(7) | O(1)$^{\#1}$-Ni(1)-O(9) | 88.75(7) | O(3)-P(1)-C(1) | 111.21(1) | C(3)-N(1)-Ni(1) | 105.25(1) |
| O(1)$^{\#1}$-Ni(1)-O(1) | 84.55(6) | O(4)-Ni(1)-O(9) | 90.45(7) | O(2)-P(1)-C(1) | 105.53(1) | C(1)-N(1)-Ni(1) | 107.68(1) |
| O(4)-Ni(1)-O(1) | 171.48(6) | O(7)-Ni(1)-O(9) | 174.22(7) | P(2)-O(4)-Ni(1) | 117.53(9) | C(2)-N(1)-Ni(1) | 108.61(1) |
| O(7)-Ni(1)-O(1) | 88.00(6) | O(1)-Ni(1)-O(9) | 88.07(7) | Ni(1)$^{\#1}$-O(1)-Ni(1) | 95.45(6) | P(1)-O(1)-Ni(1)$^{\#1}$ | 146.66(9) |
| O(1)$^{\#1}$-Ni(1)-N(1) | 168.39(6) | N(1)-Ni(1)-O(9) | 99.64(7) | C(4)-O(7)-Ni(1) | 113.85(1) | P(1)-O(1)-Ni(1) | 115.71(8) |
| | | | | | | O(6)-P(2)-O(5) | 113.66(1) |
| Compound **2** | | | | | | | |
| Ni(1)-O(1) | 2.038(2) | Ni(1)-O(10) | 2.115(2) | P(1)-O(1) | 1.544(2) | P(2)-O(4) | 1.539(2) |
| Ni(1)-O(4) | 2.042(2) | Ni(1)-N(1) | 2.125(2) | P(1)-O(2) | 1.517(2) | P(2)-O(5) | 1.522(2) |
| Ni(1)-O(7) | 2.055(2) | P(1)-C(1) | 1.828(3) | P(1)-O(3) | 1.524(2) | P(2)-O(6) | 1.517(2) |
| Ni(1)-O(9) | 2.086(2) | P(2)-C(2) | 1.828(3) | | | | |
| O(7)-Ni(1)-O(10) | 178.23(8) | O(9)-Ni(1)-N(1) | 173.76(8) | O(2)-P(1)-O(1) | 111.84(1) | O(5)-P(2)-O(4) | 113.67(1) |
| O(7)-Ni(1)-O(9) | 90.43(8) | O(1)-Ni(1)-N(1) | 85.82(7) | O(3)-P(1)-O(1) | 111.59(1) | P(1)-O(1)-Ni(1) | 116.17(1) |
| O(10)-Ni(1)-O(9) | 91.33(8) | O(7)-Ni(1)-O(4) | 92.34(8) | O(2)-P(1)-C(1) | 109.33(1) | P(2)-O(4)-Ni(1) | 113.92(1) |
| O(7)-Ni(1)-O(1) | 92.69(8) | O(10)-Ni(1)-O(4) | 87.46(8) | O(3)-P(1)-C(1) | 106.75(1) | C(4)-O(7)-Ni(1) | 115.03(2) |
| O(10)-Ni(1)-O(1) | 87.28(8) | O(9)-Ni(1)-O(4) | 92.04(8) | O(1)-P(1)-C(1) | 103.72(1) | C(3)-N(1)-Ni(1) | 107.03(2) |
| O(9)-Ni(1)-O(1) | 95.59(8) | O(1)-Ni(1)-O(4) | 170.83(7) | O(6)-P(2)-O(5) | 112.71(1) | C(1)-N(1)-Ni(1) | 106.53(1) |
| O(7)-Ni(1)-N(1) | 83.42(8) | N(1)-Ni(1)-O(4) | 87.15(7) | O(6)-P(2)-O(4) | 111.47(1) | C(2)-N(1)-Ni(1) | 107.89(2) |
| O(10)-Ni(1)-N(1) | 94.81(8) | O(2)-P(1)-O(3) | 113.04(1) | | | | |
| \Compound **3** | | | | | | | |
| Co(1)-O(1) | 2.084(2) | Co(1)-O(6) | 2.128(2) | P(1)-O(3) | 1.521(2) | P(2)-O(4) | 1.508(2) |
| Co(1)-O(2) | 2.051(2) | Co(1)-N(1) | 2.183(2) | P(1)-O(8) | 1.539(2) | P(2)-O(6) | 1.528(2) |
| Co(1)-O(3) | 2.115(2) | P(2)-C(1) | 1.823(2) | P(1)-O(9) | 1.496(2) | P(2)-O(7) | 1.543(2) |
| Co(1)-O(5) | 2.082(2) | P(1)-C(2) | 1.824(2) | | | | |
| O(2)-Co(1)-O(5) | 91.50(8) | O(5)-Co(1)-O(6) | 93.04(8) | O(6)-Co(1)-N(1) | 84.21(7) | C(3)-O(2)-Co(1) | 116.33(1) |
| O(2)-Co(1)-O(1) | 179.01(8) | O(1)-Co(1)-O(6) | 92.16(8) | O(9)-P(1)-O(3) | 113.96(1) | P(1)-O(3)-Co(1) | 116.10(9) |
| O(5)-Co(1)-O(1) | 88.46(9) | O(3)-Co(1)-O(6) | 169.57(6) | O(9)-P(1)-O(8) | 112.42(1) | C(2)-N(1)-Co(1) | 106.95(1) |
| O(2)-Co(1)-O(3) | 89.66(8) | O(2)-Co(1)-N(1) | 81.97(7) | O(3)-P(1)-O(8) | 111.38(1) | C(1)-N(1)-Co(1) | 106.01(1) |
| O(5)-Co(1)-O(3) | 97.32(8) | O(5)-Co(1)-N(1) | 172.95(8) | O(4)-P(2)-O(6) | 113.27(1) | C(4)-N(1)-Co(1) | 106.95(1) |
| O(1)-Co(1)-O(3) | 89.37(8) | O(1)-Co(1)-N(1) | 98.12(8) | O(4)-P(2)-O(7) | 111.77(1) | P(2)-O(6)-Co(1) | 116.18(9) |
| O(2)-Co(1)-O(6) | 88.83(7) | O(3)-Co(1)-N(1) | 85.36(7) | O(6)-P(2)-O(7) | 112.15(1) | | |

Symmetry transformations used to generate equivalent atoms:

$^{\#}1$ -x+1, -y+1, -z $^{\#}2$ -x+1/2, y-1/2, z

**Table S2.** Hydrogen Bonds [Å] and Angles [°] for Compounds **1**−**3**.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| Compound **1** | | | | |
| N(2)-H(4)...O(3)#1 | 0.89 | 1.94 | 2.821(2) | 171.7 |
| N(2)-H(5)...O(6)#3 | 0.89 | 1.88 | 2.752(2) | 165.6 |
| N(2)-H(6)...O(4) | 0.89 | 2.25 | 2.894(2) | 129.1 |
| N(2)-H(6)...O(5) | 0.89 | 2.39 | 3.190(3) | 149.1 |
| O(9)-H(1)...O(7)#1 | 0.74(3) | 2.14(3) | 2.849(2) | 161(3) |
| O(9)-H(2)...O(8)#4 | 0.93(4) | 1.81(4) | 2.732(3) | 171(3) |
| N(3)-H(7)...O(2)#2 | 0.85(3) | 2.03(3) | 2.879(2) | 177(3) |
| N(3)-H(8)...O(2) | 0.99(3) | 1.95(3) | 2.833(2) | 147(3) |
| N(3)-H(9)...O(4)#4 | 0.88(3) | 1.84(3) | 2.696(2) | 164(3) |
| N(3)-H(10)...O(5)#5 | 1.00(3) | 1.74(3) | 2.740(2) | 175(3) |
| N(4)-H(11)...O(3)#1 | 0.87(3) | 1.97(3) | 2.832(2) | 169(3) |
| N(4)-H(12)...O(2)#6 | 0.86(3) | 1.96(3) | 2.809(2) | 169(3) |
| N(4)-H(13)...O(6)#7 | 0.95(4) | 1.86(4) | 2.799(2) | 170(3) |
| N(4)-H(14)...O(5)#2 | 0.90(4) | 2.05(4) | 2.878(2) | 152(3) |
| Compound **2** | | | | |
| O(9)-H(9A)...O(6)#1 | 0.880(2) | 1.86(2) | 2.730(3) | 168(4) |
| O(9)-H(9B)...O(3)#2 | 0.861(2) | 1.92(2) | 2.770(3) | 168(4) |
| O(10)-H(10A)...O(7W)#3 | 0.884(2) | 1.761(2) | 2.642(3) | 174(4) |
| O(10)-H(10B)...O(1)#2 | 0.880(2) | 1.84(2) | 2.714(3) | 175(4) |
| O(1W)-H(1A)...O(6)#4 | 0.92(2) | 1.80(2) | 2.709(4) | 171(5) |
| O(1W)-H(1B)...O(3W)#5 | 0.91(2) | 2.20(3) | 3.035(6) | 152(5) |
| O(2W)-H(2A)...O(2) | 0.911(2) | 1.85(2) | 2.735(4) | 162(4) |
| O(3W)-H(3A)...O(8) | 0.940(2) | 1.79(2) | 2.727(4) | 177(5) |
| O(3W)-H(3B)...O(1W)#4 | 0.932(2) | 2.35(3) | 3.276(8) | 165(5) |
| O(3W)-H(3C)...O(3)#4 | 0.922(2) | 1.82(2) | 2.720(4) | 163(4) |
| O(4W)-H(4A)...O(2) | 0.880(2) | 1.81(2) | 2.685(3) | 177(5) |
| O(4W)-H(4B)...O(5)#6 | 0.89(2) | 1.92(2) | 2.801(4) | 179(5) |
| O(5W)-H(5B)...O(8)#7 | 0.969(2) | 2.39(3) | 3.206(4) | 142(4) |
| O(5W)-H(5B)...O(2W)#7 | 0.969(2) | 2.38(4) | 3.055(4) | 126(3) |
| O(5W)-H(5C)...O(3)#2 | 0.954(2) | 1.94(2) | 2.882(3) | 170(4) |
| O(6W)-H(6A)...O(1) | 0.958(2) | 1.88(2) | 2.824(3) | 170(4) |
| O(6W)-H(6B)...O(5)#6 | 0.96(2) | 2.10(3) | 3.007(3) | 156(4) |
| O(6W)-H(6C)...O(4)#1 | 0.949(2) | 1.91(2) | 2.848(3) | 172(4) |
| O(7W)-H(7A)...O(8)#7 | 0.891(2) | 1.86(2) | 2.736(3) | 166(3) |
| O(7W)-H(7A)...O(7)#7 | 0.891(2) | 2.53(3) | 3.221(3) | 135(3) |
| O(7W)-H(7B)...O(5) | 0.910(2) | 1.80(2) | 2.705(3) | 171(4) |
| Compound **3** | | | | |
| O(5)-H(10)...O(11)#5 | 0.76(4) | 1.98(4) | 2.718(3) | 166(4) |
| O(5)-H(11)...O(4)#3 | 0.81(4) | 1.93(4) | 2.725(3) | 168(4) |
| O(1)-H(7)...O(9)#4 | 0.877(2) | 1.80(2) | 2.666(3) | 167(3) |
| O(1)-H(8)...O(6)#3 | 0.864(2) | 1.89(2) | 2.725(3) | 164(3) |
| O(12W)-H(16)...O(7)#2 | 0.99(4) | 1.88(4) | 2.855(3) | 169(3) |
| O(13W)-H(19)...O(13W)#1 | 0.81(3) | 2.01(3) | 2.818(7) | 178(4) |

Symmetry transformations used to generate equivalent atoms:

Compound **1.** #1 -x+1, -y+1, -z #2 -x+1, y, -z+1/2 #3 -x+3/2, -y+1/2,-z #4 x, -y+1, z+1/2 #5 -x+3/2, y+1/2, -z+1/2 #6 x-1/2, y-1/2, z #7 x-1, y, z

Compound **2.** #1 -x+3/2, y-1/2, -z+1/2 #2 -x+1, -y, -z #3 -x+1, -y+1, -z #4 -x+2, -y, -z #5 x-1/2, -y-1/2, z-1/2 #6 x, y-1, z #7 -x+3/2, y+1/2, -z+1/2

Compound **3.** #1 -x+2, -y+1, -z #2 x+1, y, z #3 -x+1, -y, -z #4 -x+1, -y+1, -z #5 -x+1, -y, -z+1