Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

The new dual anions solvent-free nickel complex based on the pyridine-4-carbohydrazide ligand

Contents

Experimental

Caution!

Some of the studied compounds have the potential to be energetic materials that are heat, friction, and impact sensitive. To safeguard personal safety throughout the whole experiment, appropriate protective equipment (goggles, safety shields, rubber gloves, etc.) must be used.

Materials and Equipment

The analytical grade reagents used in the experiment were bought from Aladdin and Azov and utilized without additional purification. The analytical grade reagents used in the experiment were bought from Aladdin and Azov and utilized without additional purification.

Differential scanning calorimetry (TGA/DSC2, METTLER TOLEDO) was used to study the thermal behavior of synthesized compound under a nitrogen environment and a heating rate of 5 $^{\circ}C \cdot min^{-1}$.

Infrared (IR) spectra were measured on a Nicolet Is10 spectrometer with a measurement range of 4000 - 400 cm^{-1}. On an elemental analyzer (Vario EL Cube, Germany), elemental analyses (C, H, N or C, H, N, O) were performed.

By using a BAM DFH-10 device with a weight drop of 5 kg, the standard step approach of the drop weight device was used to assess the mechanical sensitivities of the material, including impact sensitivity and friction sensitivity.

Enthalpy of Formation Calculation

In this research, calculations of enthalpy of formation are performed based on its definition. Taking the compound $C_aH_bN_cO_d$ as an example, the corresponding general equation for its formation reaction is as follows:

$$aC + \frac{b}{2}H_2 + \frac{c}{2}N_2 + \frac{d}{2}O_2 + M_e \rightarrow C_aH_bN_cO_dM_e$$

And the atomization reaction is employed to derive the enthalpy of formation according to the Hess law:

$$C_aH_bN_cO_dM_e \rightarrow aC + bH + cN + dO + eM$$

For the formation reaction, the gas-phase heat of reaction at 298 K can be calculated from the following equation:

$$\Delta_f H(C_aH_bN_cO_dM_e) = a\Delta_f H(C) + b\Delta_f H(H) + c\Delta_f H(N) + d\Delta_f H(O) + e\Delta_f H(M) - \Delta H$$

Where Δ_fH(C), Δ_fH(H), Δ_fH(N), Δ_fH(O) and $\Delta_f H(M)$ are experimental gas phase enthalpies of formation of C, H, N and O atoms; $\Delta H_{atomization}$ is standard reaction enthalpy for atomization reaction, which can be can be calculated by the following equation:

$$\Delta H_{atomization} = aH(C) + bH(H) + cH(N) + dH(O) + eH(M) - H(C_aH_bN_cO_d)$$

According to Hess law, the solid-phase enthalpy of formation can be obtained from the gas-phase enthalpy of formation of and the enthalpy of sublimation as follows:

$$\Delta H_{solid} = \Delta H_{gas} - \Delta H_{sublimation}$$

In this work, we obtained the enthalpy of sublimation using the method of ref. S1:

$$\Delta H_{sublimation} = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + \mathrm{c}$$

Where SA is molecular surface area, υ is equilibrium constant of positive and negative electrostatic potentials at the surface of the molecule and σ_{tot} is variance of total surface electrostatic potential. The details of heats of formation calculation are listed in **Table S1**.

References

[S1] P. Politzer, J. S. Murray, M. Edward Grice, M. Desalvo, E. Miller, Molecular Physics 1997, 91, 923-928.

Supplementary Figures S1-S8

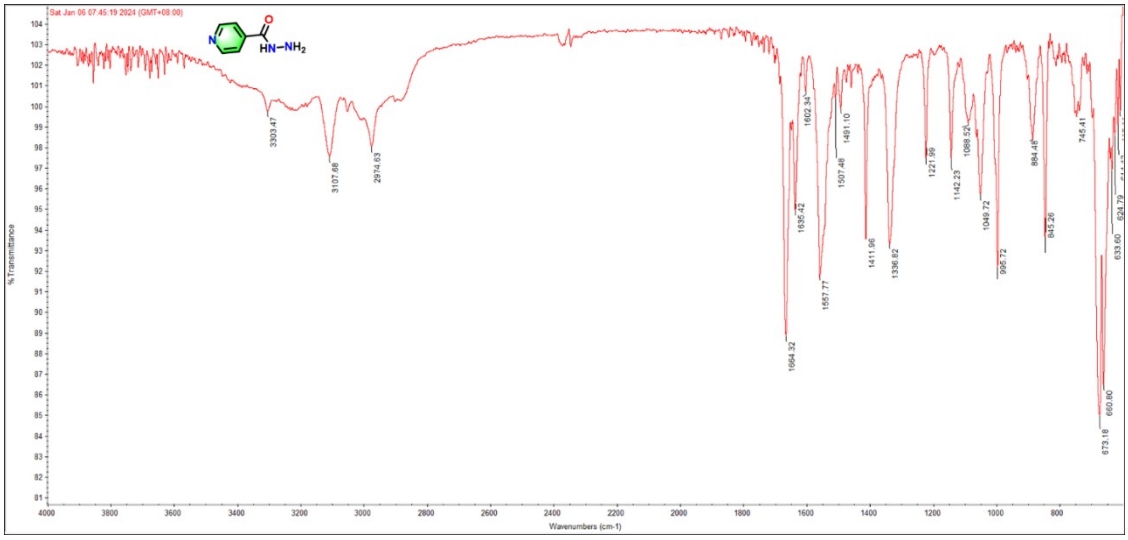

Figure S1 IR of **4-PDCA**.

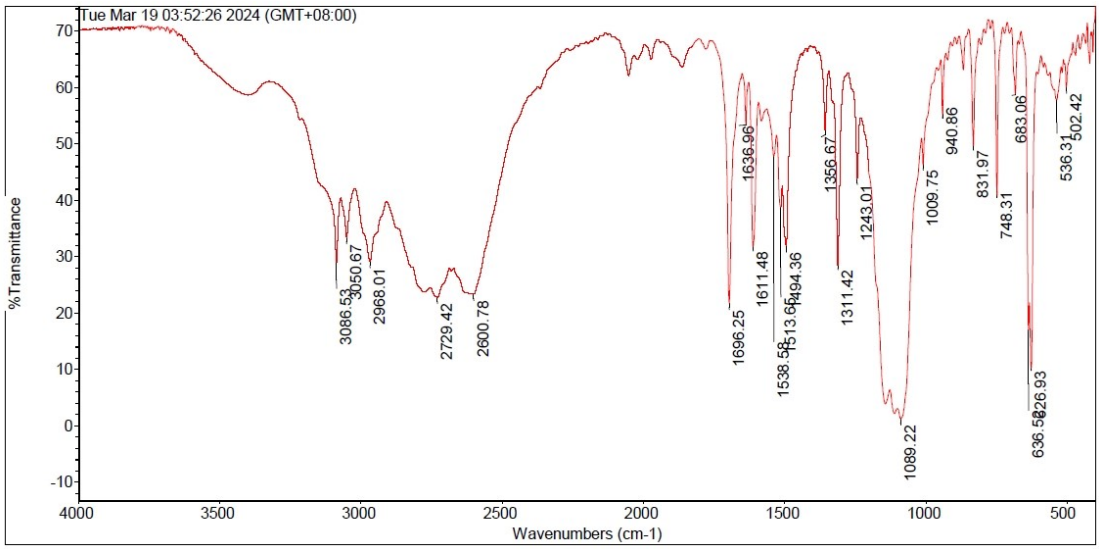

Figure S2 IR of **4-PDCA·2HClO$_4$·H$_2$O**.

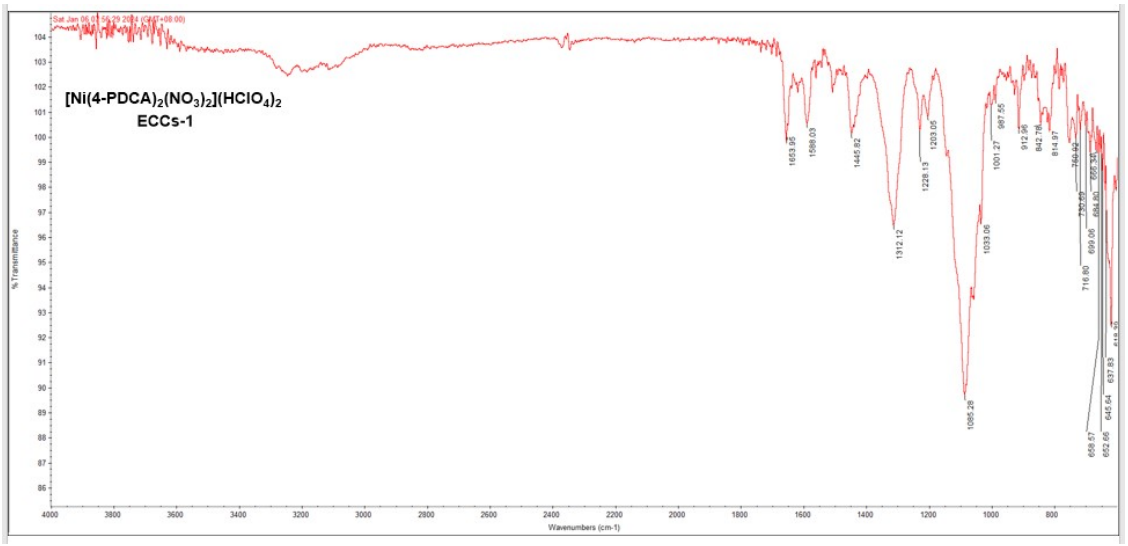

Figure S3 IR of **ECCs-1**.

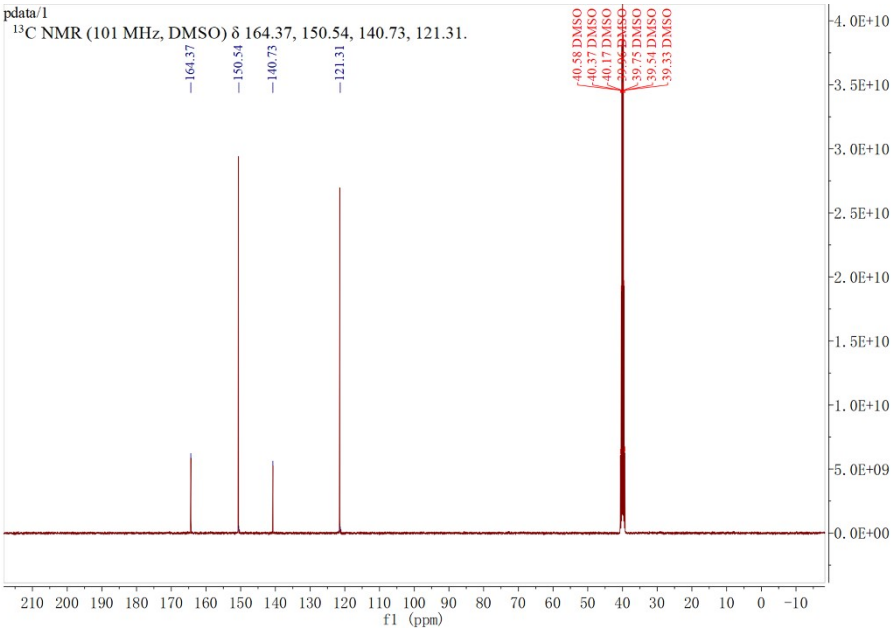

Figure S4 ^{13}C NMR of **4-PDCA**.

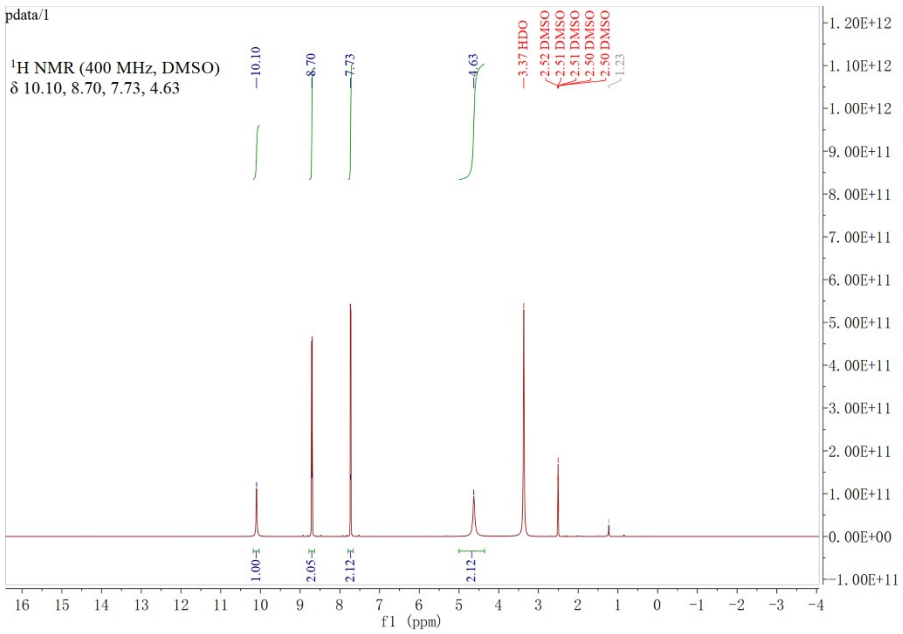

Figure S5 ^{1}H NMR of **4-PDCA**.

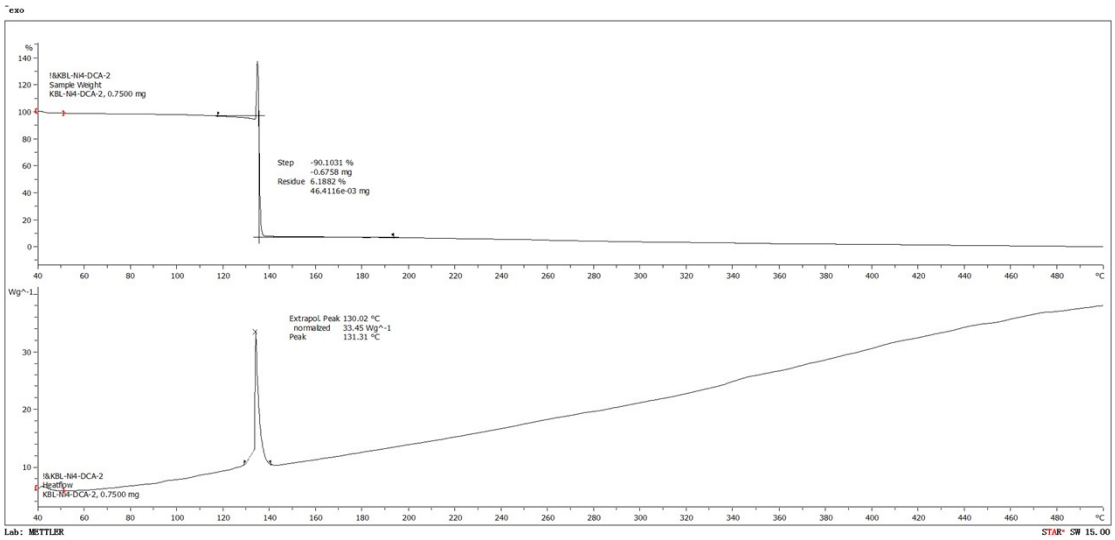

Figure S6 TG-DSC of **ECCs-1**.

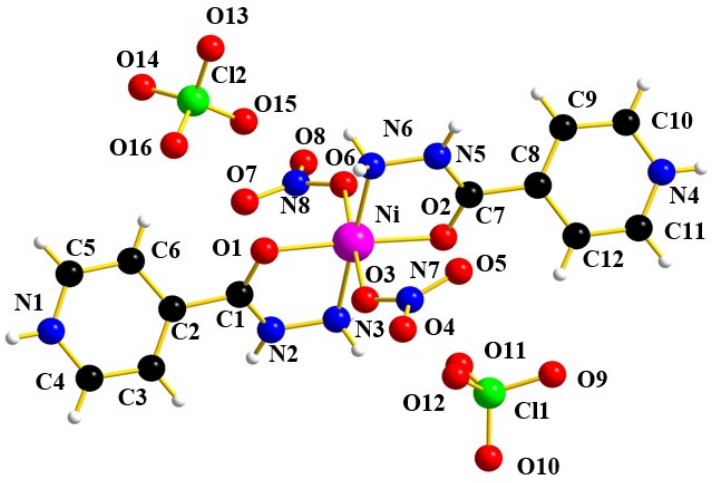

Figure S7. The single crystal of **ECCs-1**.

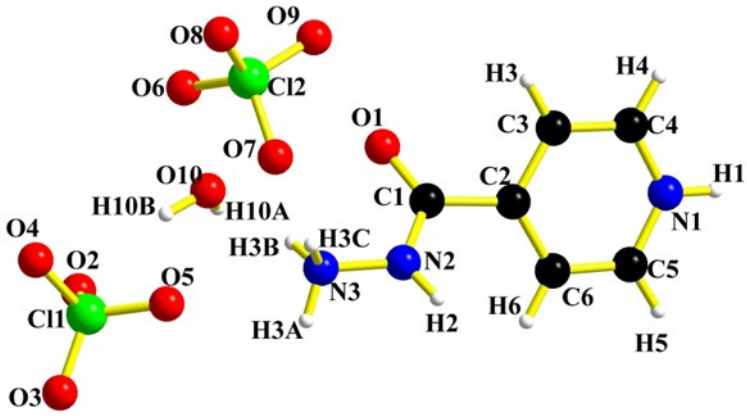

Figure S8. The single crystal of **4-PDCA·2HClO$_4$·H$_2$O**.

Supplementary Table S1-S3

Table S1: Details of heats of formation calculation of ECCs-1

Electronic energy / Hartree	-4536.5986191
ZPE / Hartree	0.239010
ZPE scale factor	0.9887
H_{cor} / Hartree	0.2568911
H_f (gas) / kJ mol^{-1}	-259.1
Area / Å^2	524.34415
$\nu\sigma_{tot}^2$ / kcal mol^{-1}	138.83029
H_{sub} / kJ mol^{-1}	157.8
H_f (solid) / kJ mol^{-1}	-452.9

Table S2. Crystallographic data for **ECCs-1.**

Bond	Bond length/Å	Bond	Bond length /Å	Bond	Bond length /Å
Ni1-O1	1.966(2)	O6-N8	1.284(4)	C1-C2	1.489(4)
Ni1-O2	1.963(2)	O7-N8	1.236(4)	C2-C3	1.395(5)
Ni1-O3	2.380(2)	O8-N8	1.240(4)	C2-C6	1.392(4)
Ni1-O6	2.373(2)	N1-C5	1.336(5)	C3-C4	1.376(6)
Ni1-N3	2.022(3)	N1-C4	1.336(4)	C5-C6	1.378(6)
Ni1-N6	2.014(3)	N2-N3	1.417(4)	C7-C8	1.486(4)
Cl1-O12	1.423(4)	N2-C1	1.321(4)	C8-C9	1.398(5)
Cl1-O9	1.403(5)	N4-C11	1.342(5)	C8-C12	1.391(4)
Cl1-O10	1.447(3)	N4-C10	1.341(5)	C9-C10	1.371(6)
Cl1-O11	1.419(3)	N5-N6	1.422(4)	C11-C12	1.372(6)
Cl2-O14	1.420(3)	N5-C7	1.323(4)	C3-H3	0.93
Cl2-O15	1.414(3)	N1-H1	0.86	C4-H4	0.93
Cl2-O16	1.424(4)	N2-H2	0.86	C5-H5A	0.93
Cl2-O13	1.420(3)	N3-H3A	0.9	C6-H6	0.93
O1-C1	1.251(4)	N3-H3B	0.9	C9-H9	0.93
O2-C7	1.248(4)	N4-H4A	0.86	C10-H10	0.93
O3-N7	1.265(4)	N5-H5	0.86	C11-H11	0.93
O4-N7	1.255(4)	N6-H6B	0.9	C12-H12	0.93
O5-N7	1.237(4)	N6-H6A	0.9		

Bond	Bond angle/°	Bond	Bond angle/°	Bond	Bond angle/°
O1-Ni1-O2	176.47(10)	N3-N2-C1	116.3(3)	C3-C2-C6	120.0(3)
O1-Ni1-O3	80.82(9)	Ni1-N3-N2	106.2(2)	C1-C2-C3	121.8(3)
O1-Ni1-O6	100.38(9)	C10-N4-C11	122.8(3)	C1-C2-C6	118.1(3)
O1-Ni1-N3	82.78(11)	N6-N5-C7	116.4(3)	C2-C3-C4	118.9(3)
O1-Ni1-N6	97.96(11)	Ni1-N6-N5	106.5(2)	N1-C4-C3	119.4(3)
O2-Ni1-O3	95.73(9)	O3-N7-O4	117.7(3)	N1-C5-C6	119.8(3)
O2-Ni1-O6	83.07(9)	O3-N7-O5	121.2(3)	C2-C6-C5	118.6(3)
O2-Ni1-N3	96.48(11)	O4-N7-O5	121.1(3)	O2-C7-C8	118.8(3)

O2-Ni1-N6	82.74(11)	O6-N8-O7	119.2(3)	N5-C7-C8	119.0(3)
O3-Ni1-O6	178.80(8)	O7-N8-O8	122.6(3)	O2-C7-N5	122.2(3)
O3-Ni1-N3	89.40(10)	O6-N8-O8	118.3(3)	C9-C8-C12	120.0(3)
O3-Ni1-N6	90.05(10)	C5-N1-H1	118	C7-C8-C12	118.2(3)
O6-Ni1-N3	90.83(10)	C4-N1-H1	118	C7-C8-C9	121.6(3)
O6-Ni1-N6	89.71(10)	N3-N2-H2	122	C8-C9-C10	118.8(3)
N3-Ni1-N6	178.99(12)	C1-N2-H2	122	N4-C10-C9	119.8(4)
O9-Cl1-O10	108.32(19)	Ni1-N3-H3A	110	N4-C11-C12	120.0(3)
O9-Cl1-O11	111.7(2)	N2-N3-H3A	111	C8-C12-C11	118.7(3)
O9-Cl1-O12	109.7(2)	N2-N3-H3B	111	C2-C3-H3	121
O10-Cl1-O11	109.70(16)	Ni1-N3-H3B	110	C4-C3-H3	121
O10-Cl1-O12	109.64(19)	H3A-N3-H3B	109	N1-C4-H4	120
O11-Cl1-O12	107.84(18)	C11-N4-H4A	119	C3-C4-H4	120
O13-Cl2-O14	109.7(2)	C10-N4-H4A	119	C6-C5-H5A	120
O13-Cl2-O16	107.7(2)	N6-N5-H5	122	N1-C5-H5A	120
O14-Cl2-O15	108.36(18)	C7-N5-H5	122	C2-C6-H6	121
O14-Cl2-O16	109.2(2)	N5-N6-H6A	110	C5-C6-H6	121
O15-Cl2-O16	111.2(2)	Ni1-N6-H6A	110	C8-C9-H9	121
O13-Cl2-O15	110.6(2)	N5-N6-H6B	110	C10-C9-H9	121
Ni1-O1-C1	111.3(2)	H6A-N6-H6B	109	N4-C10-H10	120
Ni1-O2-C7	111.9(2)	Ni1-N6-H6B	110	C9-C10-H10	120
Ni1-O3-N7	129.12(19)	N2-C1-C2	117.9(3)	N4-C11-H11	120
Ni1-O6-N8	126.66(19)	O1-C1-N2	122.8(3)	C12-C11-H11	120
C4-N1-C5	123.3(3)	O1-C1-C2	119.3(3)	C11-C12-H12	121

Dihedral angle	Bond angle /°	Dihedral angle	Bond angle /°	Dihedral angle	Bond angle /°
O3-Ni1-O1-C1	-95.4(2)	O1-Ni1-N6-N5	172.41(19)	N6-N5-C7-C8	177.2(3)
O6-Ni1-O1-C1	84.7(2)	O2-Ni1-N6-N5	-4.10(19)	C7-N5-N6-Ni1	3.4(3)
N3-Ni1-O1-C1	-4.8(2)	O3-Ni1-N6-N5	91.7(2)	O1-C1-C2-C6	36.6(4)

N6-Ni1-O1-C1	175.9(2)	O6-Ni1-N6-N5	-87.2(2)	N2-C1-C2-C3	39.6(4)
O3-Ni1-O2-C7	-84.8(2)	Ni1-O1-C1-C2	179.3(2)	N2-C1-C2-C6	-145.3(3)
O6-Ni1-O2-C7	95.1(2)	Ni1-O1-C1-N2	1.3(4)	O1-C1-C2-C3	-138.5(3)
N3-Ni1-O2-C7	-174.8(2)	Ni1-O2-C7-C8	179.1(2)	C6-C2-C3-C4	0.3(4)
N6-Ni1-O2-C7	4.5(2)	Ni1-O2-C7-N5	-4.0(4)	C1-C2-C6-C5	-176.0(3)
O1-Ni1-O3-N7	-149.7(3)	Ni1-O3-N7-O4	172.27(19)	C3-C2-C6-C5	-0.8(4)
O2-Ni1-O3-N7	31.1(3)	Ni1-O3-N7-O5	-7.3(4)	C1-C2-C3-C4	175.3(3)
N3-Ni1-O3-N7	127.6(3)	Ni1-O6-N8-O7	16.9(4)	C2-C3-C4-N1	0.2(4)
N6-Ni1-O3-N7	-51.6(3)	Ni1-O6-N8-O8	-162.8(2)	N1-C5-C6-C2	0.8(4)
O1-Ni1-O6-N8	-25.7(3)	C5-N1-C4-C3	-0.2(5)	O2-C7-C8-C12	-38.6(4)
O2-Ni1-O6-N8	153.6(3)	C4-N1-C5-C6	-0.3(5)	O2-C7-C8-C9	136.6(3)
N3-Ni1-O6-N8	57.1(3)	N3-N2-C1-O1	5.3(5)	N5-C7-C8-C12	144.4(3)
N6-Ni1-O6-N8	-123.7(3)	N3-N2-C1-C2	-172.8(3)	N5-C7-C8-C9	-40.4(4)
O1-Ni1-N3-N2	6.92(19)	C1-N2-N3-Ni1	-8.5(3)	C12-C8-C9-C10	0.7(4)
O2-Ni1-N3-N2	-176.6(2)	C11-N4-C10-C9	-1.2(5)	C7-C8-C9-C10	-174.4(3)
O3-Ni1-N3-N2	87.7(2)	C10-N4-C11-C12	0.7(6)	C7-C8-C12-C11	174.2(3)
O6-Ni1-N3-N2	-93.4(2)	N6-N5-C7-O2	0.3(5)	C9-C8-C12-C11	-1.1(5)
C8-C9-C10-N4	0.4(5)	N4-C11-C12-C8	0.4(5)		

Table S3. Crystallographic data for **4-PDCA·2HClO$_4$·H$_2$O.**

Bond	Bond length/Å	Bond	Bond length /Å	Bond	Bond length /Å
Cl1-O5	1.425(4)	O10-H10B	0.85(2)	C1-C2	1.502(6)
Cl1-O2	1.424(3)	N1-C4	1.338(6)	C2-C3	1.405(5)
Cl1-O3	1.403(4)	N1-C5	1.338(6)	C2-C6	1.397(6)
Cl1-O4	1.470(4)	N2-N3	1.417(5)	C3-C4	1.372(6)
Cl2-O6	1.441(3)	N2-C1	1.335(5)	C5-C6	1.377(6)
Cl2-O7	1.453(3)	N1-H1	0.88	C3-H3	0.95
Cl2-O8	1.437(3)	N2-H2	0.88	C4-H4	0.95
Cl2-O9	1.429(3)	N3-H3C	0.91	C5-H5	0.95
O1-C1	1.227(5)	N3-H3B	0.91	C6-H6	0.95
O10-H10A	0.85(3)	N3-H3A	0.91		

Bond	Bond angle/°	Bond	Bond angle/°	Bond	Bond angle/°
O2-Cl1-O4	106.0(2)	N3-N2-C1	117.7(3)	C1-C2-C6	123.2(4)
O2-Cl1-O5	111.6(2)	C4-N1-H1	118	C1-C2-C3	117.4(3)
O3-Cl1-O4	108.3(2)	C5-N1-H1	118	C3-C2-C6	119.4(4)
O3-Cl1-O5	111.8(2)	N3-N2-H2	121	C2-C3-C4	119.6(4)
O4-Cl1-O5	107.6(2)	C1-N2-H2	121	N1-C4-C3	118.7(4)
O2-Cl1-O3	111.3(2)	N2-N3-H3C	109	N1-C5-C6	119.5(4)
O6-Cl2-O8	109.09(17)	H3A-N3-H3B	110	C2-C6-C5	118.8(4)
O6-Cl2-O9	110.9(2)	H3B-N3-H3C	109	C4-C3-H3	120
O6-Cl2-O7	108.76(15)	N2-N3-H3B	109	C2-C3-H3	120
O7-Cl2-O9	108.94(18)	H3A-N3-H3C	110	N1-C4-H4	121
O8-Cl2-O9	110.0(2)	N2-N3-H3A	109	C3-C4-H4	121
O7-Cl2-O8	109.17(16)	N2-C1-C2	115.9(3)	C6-C5-H5	120
H10A-O10-H10B	108(3)	O1-C1-N2	123.4(4)	N1-C5-H5	120
C4-N1-C5	124.1(4)	O1-C1-C2	120.7(4)	C5-C6-H6	121
C2-C6-H6	121				

Dihedral angle	Bond angle /°	Dihedral angle	Bond angle /°	Dihedral angle	Bond angle /°
C5-N1-C4-C3	-1.4(7)	O1-C1-C2-C6	-138.2(4)	C1-C2-C6-C5	176.2(4)
C4-N1-C5-C6	0.9(7)	N2-C1-C2-C3	-142.2(4)	C3-C2-C6-C5	-1.0(6)
N3-N2-C1-O1	4.9(6)	N2-C1-C2-C6	40.5(5)	C2-C3-C4-N1	0.6(6)
N3-N2-C1-C2	-173.8(3)	C1-C2-C3-C4	-176.8(4)	N1-C5-C6-C2	0.3(7)
O1-C1-C2-C3	39.0(5)	C6-C2-C3-C4	0.6(6)		