Supporting Information

Energetic coordination compounds: self-assembled from the nitrogen-rich energetic C-C bonded pyrazole and triazole

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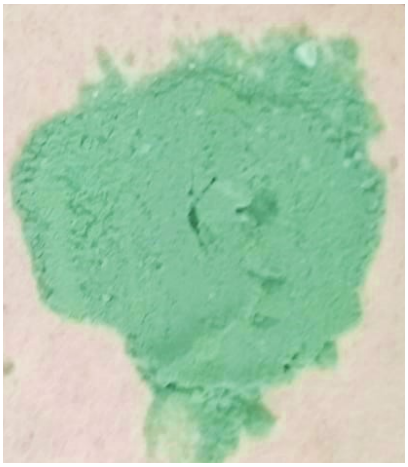
Experimental Section

Caution! All the compounds investigated are potentially explosive, energetic materials. Although we have experienced no difficulties in the syntheses and characterization of these compounds, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be always worn.

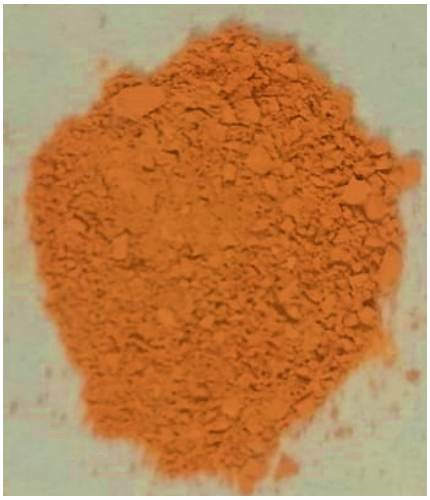
Materials and Methods:

Reagents were purchased from Ak Scientifics, Acros Organics or Aldrich as analytical grade and were used as received. Melting and Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and at heating rate of 10 °C min^{-1} on a differential scanning calorimeter (SDT650). IR spectra were recorded using Zn-Se pellets with ECO-ATR spectrometer (Bruker Alpha II). The powder X-ray diffraction (PXRD) data measurements were collected using a Rigaku MiniFlex 600 diffractometer. Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fall hammer and a BAM friction tester. The single-crystal X-ray data collection was carried out using Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[1]. the structure was solved with the olex2.solve[2] structure solution program using Charge Flipping and refined with the SHELXL[3] refinement package using Least Squares minimisation. The non-covalent interactions and molecular drawings were studied using the Diamond program.[4] The surface morphology of compounds **1–6** was examined using Scanning electron microscopy (SEM) (CARL ZEISS EVO 50). Samples were prepared by coating with a thin gold layer in a vacuum prior to examination.

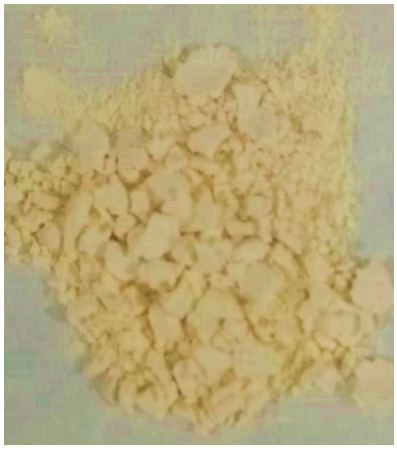
Synthesis of 1: A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (58 mg, 0.2 mmol) was taken in 5 mL of methanol and added dropwise to a mixed stirred solution (1:1, H_2O:MeOH) of NPTA (39 mg, 0.2 mmol) at room temperature. Immediate precipitate was observed. The mixture was stirred for further 2 hrs at same temperature, formed solid precipitate was filtered and washed 2−3 times with DI water, methanol and air-dried to obtain the powder samples. The filtrate was slowly evaporated at room temperature and green block-shaped single crystals of **1** were grown in 5 days to obtain the crystal product. Yield: 70%. T_d (onset): 316 °C. IR (ATR ZnSe): 3459, 3352, 3237, 3149, 1644, 1482, 1399, 1325, 1275, 1187, 1118, 1043, 1022, 986, 914, 868, 825, 747 cm^{-1}.



Synthesis of 2: Complex **2** was synthesized by the method described as **1** using $Co(NO_3)_2 \cdot 6H_2O$ (58 mg, 0.2 mmol) instead of $Ni(NO_3)_2 \cdot 6H_2O$. Dark pink block-shaped single crystals of **2** were grown in 7 days by slow evaporation of filtrate at room temperature. Yield: 66%. T_d (onset): 331 °C. IR (ATR ZnSe): 3470, 3263, 2986, 2886, 2819, 2352, 1770, 1709, 1596, 1487, 1391, 1334, 1278, 1181, 1123, 967, 924, 834, 752 cm^{-1}.

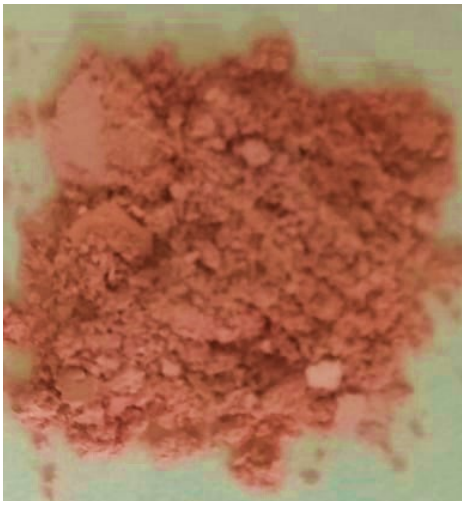


Synthesis of 3: Complex **3** was obtained using the same method as **1**. $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 0.2 mmol) instead of $Ni(NO_3)_2 \cdot 6H_2O$. Colourless block-shaped single crystals of **3** were obtained in 7 days by slow evaporation of filtrate at room temperature. Yield: 76%. T_d (onset): 351 °C. IR (ATR ZnSe): 3496, 3263, 2989, 2886, 2819, 2352, 1779, 1712, 1632, 1594, 1480, 1382, 1290, 1123, 1084, 975, 929, 830, 752 cm^{-1}.

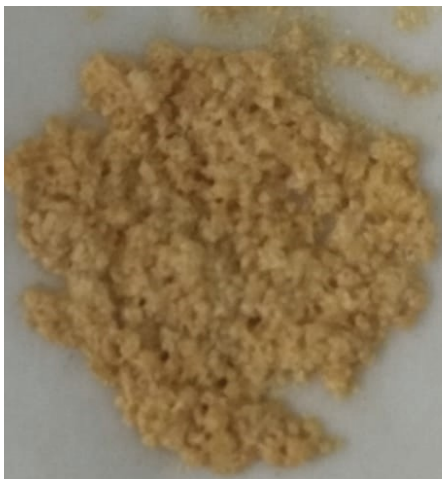


Synthesis of 4: 10 mL aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (58 g, 0.2 mmol) was added to the 10 mL mixed solvent solution of NPTN (48 mg, 0.2 mmol) in water and methanol (1:1) and stirred the reaction mixture for 6 hrs at room temperature and observed the light green coloured precipitate. The formed precipitate was filtered off, washed with water, methanol and air-dried. The powder compound was dissolved in DMF and kept for crystallization at room temperature. Light green coloured block-shaped single crystals of **4** were obtained in 15 days by slow evaporation of the solvent. Yield: 66%. T_d (onset): 375 ^oC. IR (ATR ZnSe): 3360, 3303, 3145, 1648, 1602, 1532, 1469, 1415, 1358, 1305, 1255, 1206, 1145, 1102, 1026, 985, 942, 835, 746 cm^{-1}.

Synthesis of 5: Complex **5** was obtained using the same method as **4**. $Co(NO_3)_2 \cdot 6H_2O$ (58 mg, 0.2 mmol) was used instead of $Ni(NO_3)_2 \cdot 6H_2O$. Pink-coloured block-shaped crystals of **5** were gained in 15 days by slow evaporation of solution at room temperature. Yield: 64%. T_d (onset): 216 ^oC. IR (ATR ZnSe): 3317, 3271, 3127, 1738, 1524, 1465, 1354, 1308, 1248, 1197, 1142, 1097, 1062, 973, 959, 934, 828, 739 cm^{-1}.



Synthesis of 6: Complex **6** was obtained using the same method used for **4**. $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 0.2 mmol) was used instead of $Ni(NO_3)_2 \cdot 6H_2O$. Light, yellow-coloured block-shaped crystals of **6** were obtained in 10 days by slow evaporation of solution at room temperature. Yield: 70%. T_d (onset): 333 ^oC. IR (ATR ZnSe): 3378, 3158, 3114, 2961, 1752, 1613, 1523, 1459, 1343, 1200, 1111, 1011, 946, 844, 802, 737 cm^{-1}.



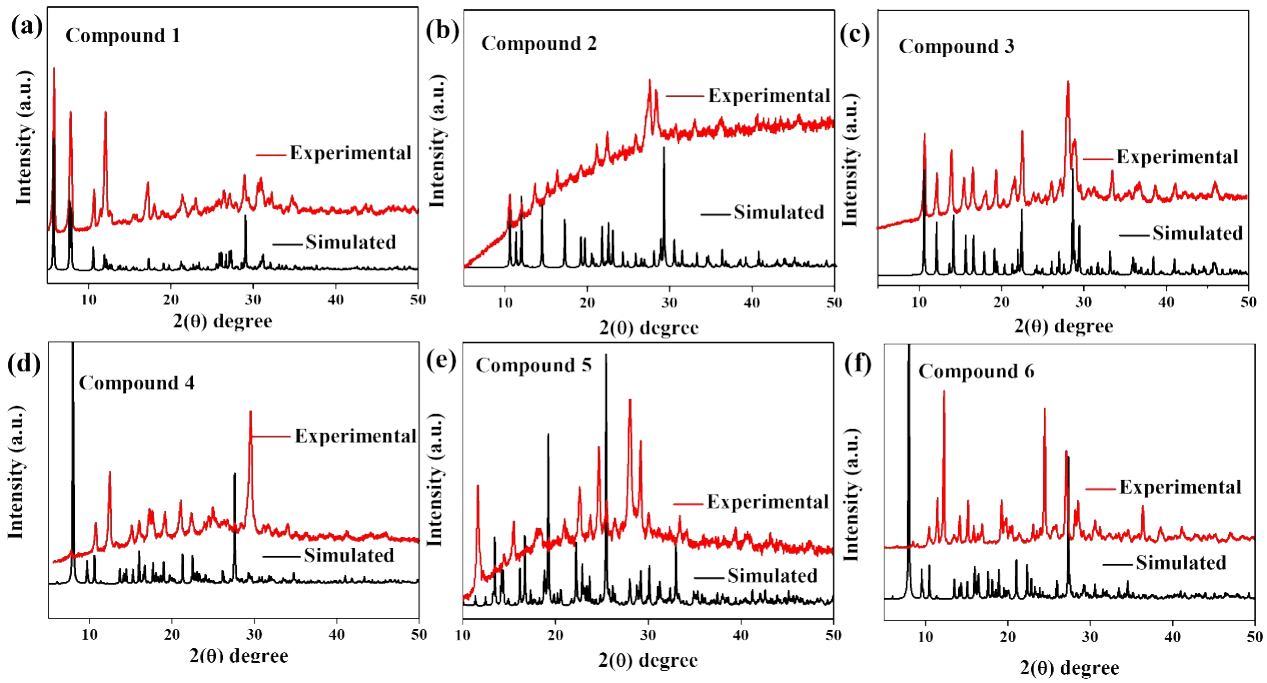


Figure S1. PXRD spectra of compounds **1–6**.

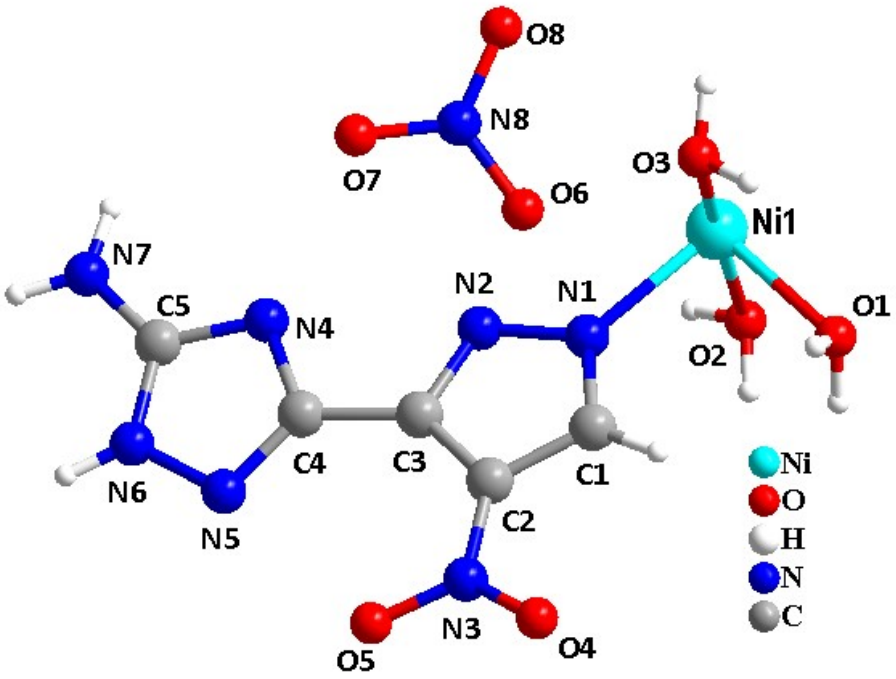


Figure S2. The asymmetric unit of compound **1**.

Table S1. Crystal data and structure refinement for 1.

CCDC No.	2258463
Identification code	1
Empirical formula	$C_{10}H_{20}N_{16}Ni_2O_{16}$
Formula weight	737.84
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.215(2)
b/Å	10.564(2)
c/Å	13.351(3)
α/°	90
β/°	109.349(7)
γ/°	90
Volume/Å^3	1226.3(5)
Z	2
ρ_{calc}g/cm^3	1.998
μ/mm^{-1}	1.647
F(000)	752.0
Crystal size/mm^3	0.22 × 0.2 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.032 to 56.694
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	17031
Independent reflections	3003 [R_{int} = 0.0874, R_{sigma} = 0.0612]
Data/restraints/parameters	3003/1/200
Goodness-of-fit on F^2	1.185
Final R indexes [I>=2σ (I)]	R_1 = 0.0995, wR_2 = 0.2754
Final R indexes [all data]	R_1 = 0.1080, wR_2 = 0.2830
Largest diff. peak/hole / e Å^{-3}	3.61/-1.26

Table S2. Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O1	2.151(4)	O8	N8	1.258(8)
Ni1	O3	2.065(5)	N4	C5	1.345(8)
Ni1	N1	2.054(6)	N4	C4	1.370(8)
Ni1	O2	2.098(5)	N2	C3	1.342(8)
Ni1	N4^1	2.066(5)	N3	C2	1.403(8)
Ni1	N2^1	2.079(5)	N6	N5	1.374(8)
O7	N8	1.245(8)	N6	C5	1.339(9)
N1	N2	1.377(7)	C1	C2	1.383(9)
N1	C1	1.338(8)	N5	C4	1.315(8)
O6	N8	1.281(8)	N7	C5	1.346(9)

Table S2. Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O5	N3	1.250(7)	C3	C4	1.471(8)
O4	N3	1.230(8)	C3	C2	1.405(8)

[1]1-X,1-Y,1-Z

Table S3. Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Ni1	O1	84.27(18)	C3	N2	N1	108.5(5)
O3	Ni1	O2	172.6(2)	O5	N3	C2	118.0(6)
O3	Ni1	N4[1]	90.1(2)	O4	N3	O5	123.0(6)
O3	Ni1	N2[1]	96.5(2)	O4	N3	C2	119.0(6)
N1	Ni1	O1	91.17(19)	C5	N6	N5	110.6(5)
N1	Ni1	O3	88.9(2)	O7	N8	O6	119.6(6)
N1	Ni1	O2	88.9(2)	O7	N8	O8	120.9(6)
N1	Ni1	N4[1]	177.5(2)	O8	N8	O6	119.4(6)
N1	Ni1	N2[1]	99.6(2)	N1	C1	C2	109.9(6)
O2	Ni1	O1	88.72(18)	C4	N5	N6	102.2(5)
N4[1]	Ni1	O1	91.00(19)	N2	C3	C4	114.3(5)
N4[1]	Ni1	O2	92.4(2)	N2	C3	C2	108.6(5)
N4[1]	Ni1	N2[1]	78.2(2)	C2	C3	C4	137.1(6)
N2[1]	Ni1	O1	169.2(2)	N4	C5	N7	125.6(6)
N2[1]	Ni1	O2	90.8(2)	N6	C5	N4	109.1(5)
N2	N1	Ni1	125.3(4)	N6	C5	N7	125.3(6)
C1	N1	Ni1	126.8(4)	N4	C4	C3	115.4(5)
C1	N1	N2	107.9(5)	N5	C4	N4	115.0(6)
C5	N4	Ni1[1]	141.2(4)	N5	C4	C3	129.6(6)
C5	N4	C4	103.0(5)	N3	C2	C3	129.7(6)
C4	N4	Ni1[1]	115.2(4)	C1	C2	N3	125.1(6)
N1	N2	Ni1[1]	134.5(4)	C1	C2	C3	105.1(5)
C3	N2	Ni1[1]	116.5(4)				

[1]1-X,1-Y,1-Z

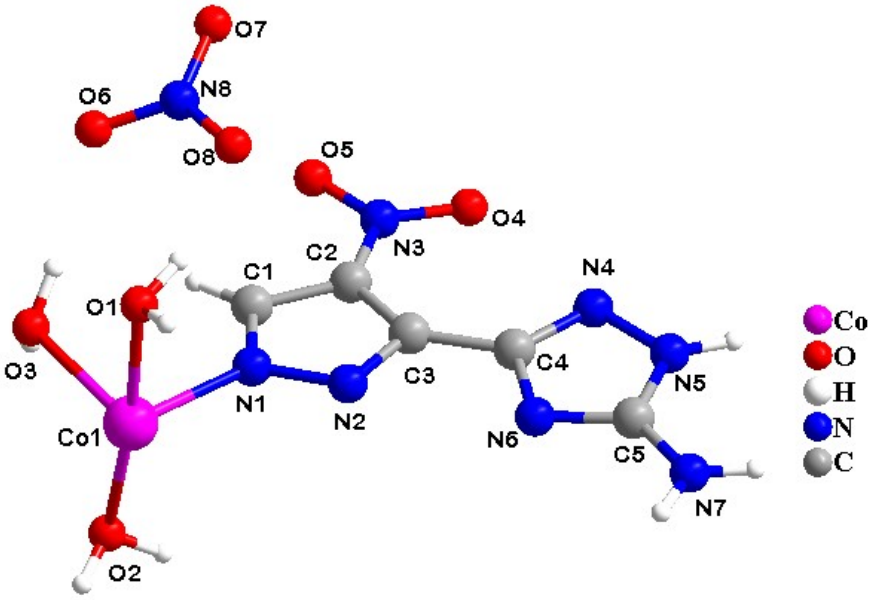


Figure S3. The asymmetric unit of compound **2**.

Table S4. Crystal data and structure refinement for 2.

CCDC No.	2258459
Identification code	2
Empirical formula	$C_{10}H_{20}Co_2N_{16}O_{16}$
Formula weight	738.28
Temperature/K	100
Crystal system	triclinic
Space group	*P-1*
a/Å	8.822(4)
b/Å	9.267(4)
c/Å	9.384(4)
α/°	94.197(14)
β/°	108.760(13)
γ/°	116.565(12)
Volume/Å^3	628.0(5)
Z	1
ρ_{calc}g/cm^3	1.952
μ/mm^{-1}	1.430
F(000)	374.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.742 to 56.912
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-12 \le l \le 12$
Reflections collected	11056
Independent reflections	3130 [R_{int} = 0.0646, R_{sigma} = 0.0589]
Data/restraints/parameters	3130/0/203

Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.1458
Final R indexes [all data]	R_1 = 0.0754, wR_2 = 0.1597
Largest diff. peak/hole / e $Å^{-3}$	1.30/-1.26

Table S5. Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O3	2.150(2)	N2	C3	1.347(4)
Co1	O2	2.107(3)	N6	C4	1.366(4)
Co1	O1	2.085(3)	N6	C5	1.331(4)
Co1	N2[1]	2.115(3)	N1	C1	1.334(4)
Co1	N6[1]	2.089(3)	N3	C2	1.410(4)
Co1	N1	2.101(3)	N5	N4	1.385(4)
O8	N8	1.255(4)	N5	C5	1.340(4)
O4	N3	1.233(4)	N4	C4	1.325(4)
O5	N3	1.241(4)	N7	C5	1.348(5)
O6	N8	1.242(4)	C4	C3	1.451(5)
O7	N8	1.263(4)	C3	C2	1.396(4)
N2	N1	1.365(4)	C1	C2	1.398(5)

[1]2-X,1-Y,1-Z

Table S6. Bond Angles for 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Co1	O3	89.31(10)	C1	N1	N2	108.4(3)
O2	Co1	N2[1]	97.01(11)	O4	N3	O5	123.5(3)
O1	Co1	O3	83.61(10)	O4	N3	C2	119.1(3)
O1	Co1	O2	172.79(10)	O5	N3	C2	117.5(3)
O1	Co1	N2[1]	89.50(11)	O8	N8	O7	119.2(3)
O1	Co1	N6[1]	91.19(11)	O6	N8	O8	120.8(3)
O1	Co1	N1	90.45(11)	O6	N8	O7	119.9(3)
N2[1]	Co1	O3	163.85(10)	C5	N5	N4	110.8(3)
N6[1]	Co1	O3	89.48(10)	C4	N4	N5	101.5(3)
N6[1]	Co1	O2	87.38(11)	N6	C4	C3	115.1(3)
N6[1]	Co1	N2[1]	76.04(11)	N4	C4	N6	114.7(3)
N6[1]	Co1	N1	178.34(11)	N4	C4	C3	130.2(3)
N1	Co1	O3	90.56(11)	N2	C3	C4	114.5(3)
N1	Co1	O2	90.96(10)	N2	C3	C2	107.5(3)
N1	Co1	N2[1]	104.12(11)	C2	C3	C4	137.9(3)
N1	N2	Co1[1]	133.3(2)	N1	C1	C2	108.7(3)

Table S6. Bond Angles for 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	N2	Co1[1]	117.2(2)	C3	C2	N3	129.4(3)
C3	N2	N1	109.3(3)	C3	C2	C1	106.0(3)
C4	N6	Co1[1]	117.0(2)	C1	C2	N3	124.6(3)
C5	N6	Co1[1]	138.8(2)	N6	C5	N5	109.1(3)
C5	N6	C4	103.9(3)	N6	C5	N7	126.3(3)
N2	N1	Co1	122.2(2)	N5	C5	N7	124.6(3)
C1	N1	Co1	129.2(2)				

[1]2-X,1-Y,1-Z

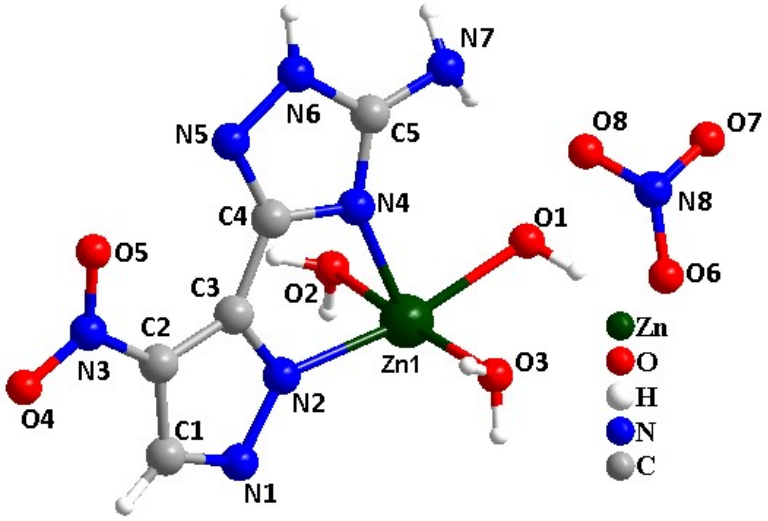


Figure S4. The asymmetric unit of compound **3**.

Table S7. Crystal data and structure refinement for 3.

CCDC No.	2258462
Identification code	3
Empirical formula	$C_5H_{10}N_8O_8Zn$
Formula weight	375.58
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.841(3)
b/Å	13.320(5)
c/Å	10.831(4)
α/°	90
β/°	99.819(9)

γ/°	90
Volume/Å^3	1256.8(7)
Z	4
ρ_{calc}g/cm^3	1.985
μ/mm^{-1}	2.018
F(000)	760.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.118 to 56.752
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 17$, $-14 \le l \le 14$
Reflections collected	19003
Independent reflections	3132 [R_{int} = 0.0675, R_{sigma} = 0.0437]
Data/restraints/parameters	3132/0/203
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.0839
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.0920
Largest diff. peak/hole / e Å^{-3}	0.68/-0.63

Table S8. Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1	2.123(2)	N4	C5	1.332(3)
Zn1	O3	2.176(2)	N1	N2	1.372(3)
Zn1	O2	2.182(2)	N1	C1	1.334(3)
Zn1	N4[1]	2.095(2)	N3	C2	1.421(3)
Zn1	N1	2.060(2)	N5	N6	1.384(3)
Zn1	N2[1]	2.161(2)	N5	C4	1.316(3)
O7	N8	1.261(3)	N2	C3	1.347(3)
O5	N3	1.232(3)	N6	C5	1.353(3)
O4	N3	1.241(3)	N7	C5	1.347(4)
O6	N8	1.249(3)	C4	C3	1.462(4)
O8	N8	1.260(3)	C1	C2	1.394(4)
N4	C4	1.373(3)	C2	C3	1.404(4)

[1]1-X,1-Y,1-Z

Table S9. Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Zn1	O3	84.54(8)	O4	N3	C2	117.3(2)
O1	Zn1	O2	90.51(8)	C4	N5	N6	102.1(2)
O1	Zn1	N2[1]	164.57(8)	N1	N2	Zn1[1]	135.06(16)

Table S9. Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Zn1	O2	173.40(8)	C3	N2	Zn1[1]	115.70(18)
N4[1]	Zn1	O1	88.97(8)	C3	N2	N1	109.1(2)
N4[1]	Zn1	O3	95.00(9)	C5	N6	N5	110.2(2)
N4[1]	Zn1	O2	89.27(9)	O6	N8	O7	120.6(2)
N4[1]	Zn1	N2[1]	76.60(9)	O6	N8	O8	120.4(2)
N1	Zn1	O1	92.26(8)	O8	N8	O7	119.0(2)
N1	Zn1	O3	87.41(8)	N4	C4	C3	116.0(2)
N1	Zn1	O2	88.42(9)	N5	C4	N4	114.9(2)
N1	Zn1	N4[1]	177.39(9)	N5	C4	C3	128.9(2)
N1	Zn1	N2[1]	102.38(9)	N4	C5	N6	109.0(2)
N2[1]	Zn1	O3	91.19(8)	N4	C5	N7	126.3(3)
N2[1]	Zn1	O2	94.70(9)	N7	C5	N6	124.6(3)
C4	N4	Zn1[1]	115.99(18)	N1	C1	C2	108.6(2)
C5	N4	Zn1[1]	137.90(19)	C1	C2	N3	123.9(2)
C5	N4	C4	103.7(2)	C1	C2	C3	106.3(2)
N2	N1	Zn1	122.13(15)	C3	C2	N3	129.8(2)
C1	N1	Zn1	129.09(19)	N2	C3	C4	114.8(2)
C1	N1	N2	108.6(2)	N2	C3	C2	107.4(2)
O5	N3	O4	123.5(2)	C2	C3	C4	137.8(2)
O5	N3	C2	119.2(2)				

[1]1-X,1-Y,1-Z

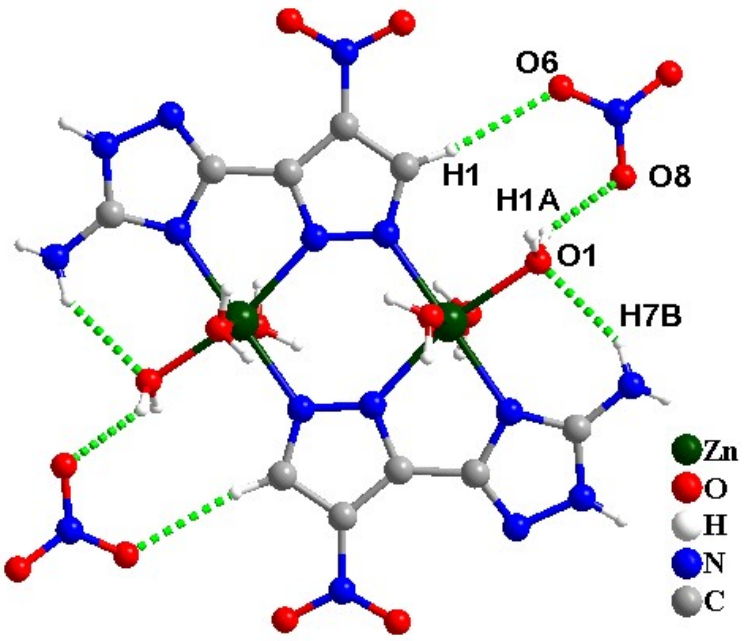


Figure S5. Inter/Intramolecular hydrogen bonding interaction in **3**.

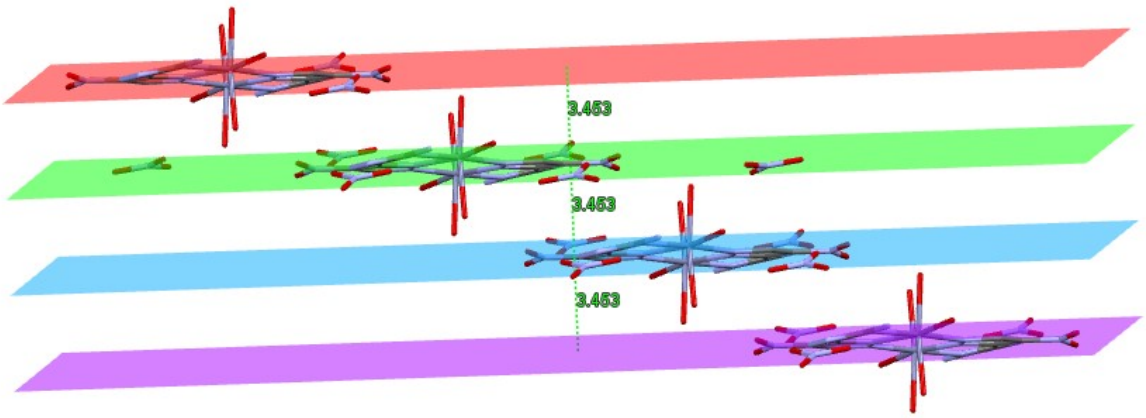


Figure S6. Interplanar distance present in **3**.

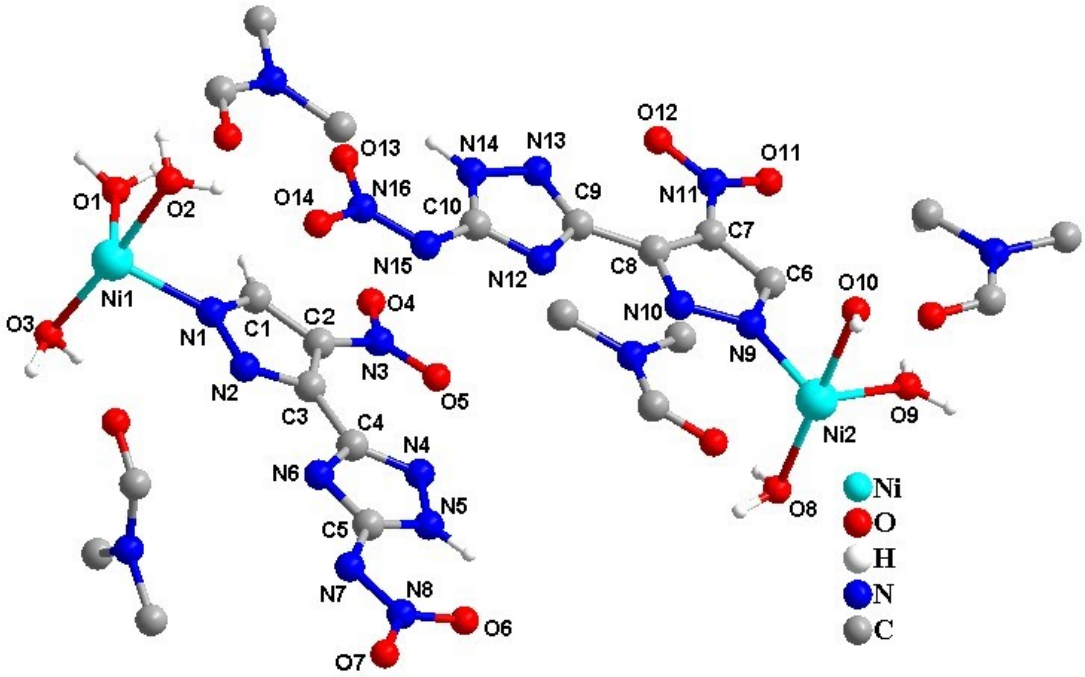


Figure S7. The asymmetric unit of **4**.

Table S10. Crystal data and structure refinement for 4.

CCDC No.	2258464
Identification code	4
Empirical formula	$C_{10}H_{16}N_{16}Ni_2O_{14}$
Formula weight	701.81
Temperature/K	100
Crystal system	triclinic
Space group	*P-1*
a/Å	11.6407(7)
b/Å	12.0947(7)
c/Å	15.6754(9)
α/°	68.215(2)
β/°	87.615(2)
γ/°	85.471(2)
Volume/Å^3	2042.8(2)

[1]-X,2-Y,1-Z; [2]1-X,1-Y,2-Z

Table S11. Bond Lengths for 4.

Atom	Atom	Length/ Å	Atom	Atom	Length/ Å
Ni1	O2	2.105(4)	N10	C8	1.333(7)
Ni1	O3	2.101(4)	N12	C9	1.366(7)
Ni1	O1	2.092(4)	N12	C10	1.322(6)
Ni1	N61	2.076(4)	N2	C3	1.333(7)
Ni1	N1	2.033(4)	N9	C6	1.337(7)
Ni1	N21	2.103(4)	N3	C2	1.382(7)
Ni2	O10	2.115(4)	N15	N16	1.308(6)
Ni2	O9	2.096(4)	N15	C10	1.373(7)
Ni2	O8	2.102(4)	N7	N8	1.309(6)
Ni2	N102	2.083(4)	N7	C5	1.403(7)
Ni2	N122	2.076(4)	N14	N13	1.370(6)
Ni2	N9	2.037(4)	N14	C10	1.353(7)
O7	N8	1.274(6)	O11	N11	1.251(6)
O14	N16	1.251(6)	N13	C9	1.312(7)
O13	N16	1.264(6)	N4	N5	1.387(6)
O6	N8	1.256(6)	N4	C4	1.343(6)
O5	N3	1.245(6)	N5	C5	1.332(7)
N6	C4	1.320(7)	N11	C7	1.407(7)
N6	C5	1.329(6)	C3	C2	1.419(7)
O12	N11	1.218(6)	C3	C4	1.468(7)
O4	N3	1.235(6)	C2	C1	1.389(7)
N1	N2	1.360(6)	C8	C9	1.462(7)
N1	C1	1.346(7)	C8	C7	1.397(7)
N10	N9	1.345(6)	C6	C7	1.387(7)

[1]-X,2-Y,1-Z; [2]1-X,1-Y,2-Z

Table S12. Bond Angles for 4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Ni1	O2	176.21(15)	C6	N9	Ni2	125.6(4)
O3	Ni1	N2[1]	91.72(17)	C6	N9	N10	109.5(4)
O1	Ni1	O2	93.23(15)	O5	N3	C2	118.5(4)
O1	Ni1	O3	86.27(16)	O4	N3	O5	121.9(5)
O1	Ni1	N2[1]	167.38(15)	O4	N3	C2	119.6(4)
N6[1]	Ni1	O2	90.15(16)	N16	N15	C10	118.0(4)
N6[1]	Ni1	O3	86.09(17)	N8	N7	C5	116.3(4)
N6[1]	Ni1	O1	89.48(15)	C10	N14	N13	109.9(4)
N6[1]	Ni1	N2[1]	77.95(16)	O7	N8	N7	116.8(4)
N1	Ni1	O2	91.27(17)	O6	N8	O7	120.7(4)
N1	Ni1	O3	92.51(17)	O6	N8	N7	122.5(5)
N1	Ni1	O1	93.13(16)	O14	N16	O13	119.5(4)
N1	Ni1	N6[1]	176.95(17)	O14	N16	N15	118.5(4)
N1	Ni1	N2[1]	99.40(17)	O13	N16	N15	122.0(4)

N21	Ni1	O2	87.95(15)	C9	N13	N14	103.3(4)
O9	Ni2	O10	91.88(17)	C4	N4	N5	100.7(4)
O9	Ni2	O8	88.93(18)	C5	N5	N4	110.8(4)
O8	Ni2	O10	178.62(16)	O12	N11	O11	123.6(5)
N10[2]	Ni2	O10	89.15(16)	O12	N11	C7	119.7(4)
N10[2]	Ni2	O9	166.48(16)	O11	N11	C7	116.7(4)
N10[2]	Ni2	O8	89.80(17)	N2	C3	C2	108.6(4)
N12[2]	Ni2	O10	91.43(16)	N2	C3	C4	114.6(5)
N12[2]	Ni2	O9	88.13(16)	C2	C3	C4	136.8(5)
N12[2]	Ni2	O8	87.48(18)	N3	C2	C3	131.4(5)
N12[2]	Ni2	N10[2]	78.36(17)	N3	C2	C1	124.3(5)
N9	Ni2	O10	88.80(17)	C1	C2	C3	104.3(4)
N9	Ni2	O9	93.62(17)	N6	C4	N4	114.6(4)
N9	Ni2	O8	92.26(18)	N6	C4	C3	117.2(4)
N9	Ni2	N10[2]	99.88(17)	N4	C4	C3	128.1(5)
N9	Ni2	N12[2]	178.23(17)	N10	C8	C9	114.8(4)
C4	N6	Ni1[1]	115.0(3)	N10	C8	C7	108.4(4)
C4	N6	C5	105.6(4)	C7	C8	C9	136.7(5)
C5	N6	Ni1[1]	139.0(4)	N12	C9	C8	116.3(4)
N2	N1	Ni1	125.1(3)	N13	C9	N12	113.4(5)
C1	N1	Ni1	127.0(4)	N13	C9	C8	130.3(5)
C1	N1	N2	107.9(4)	N1	C1	C2	109.8(4)
N9	N10	Ni2[2]	135.3(3)	N12	C10	N15	119.6(5)
C8	N10	Ni2[2]	116.1(3)	N12	C10	N14	108.5(4)
C8	N10	N9	108.6(4)	N14	C10	N15	131.9(5)
C9	N12	Ni2[2]	114.2(3)	N6	C5	N7	119.6(5)
C10	N12	Ni2[2]	140.4(4)	N6	C5	N5	108.3(5)
C10	N12	C9	105.0(4)	N5	C5	N7	131.8(5)
N1	N2	Ni1[1]	135.5(3)	N9	C6	C7	108.0(5)
C3	N2	Ni1[1]	115.1(3)	C8	C7	N11	129.9(5)
C3	N2	N1	109.4(4)	C6	C7	N11	124.6(5)
N10	N9	Ni2	124.8(3)	C6	C7	C8	105.5(5)

[1]-X,2-Y,1-Z; [2]1-X,1-Y,2-Z

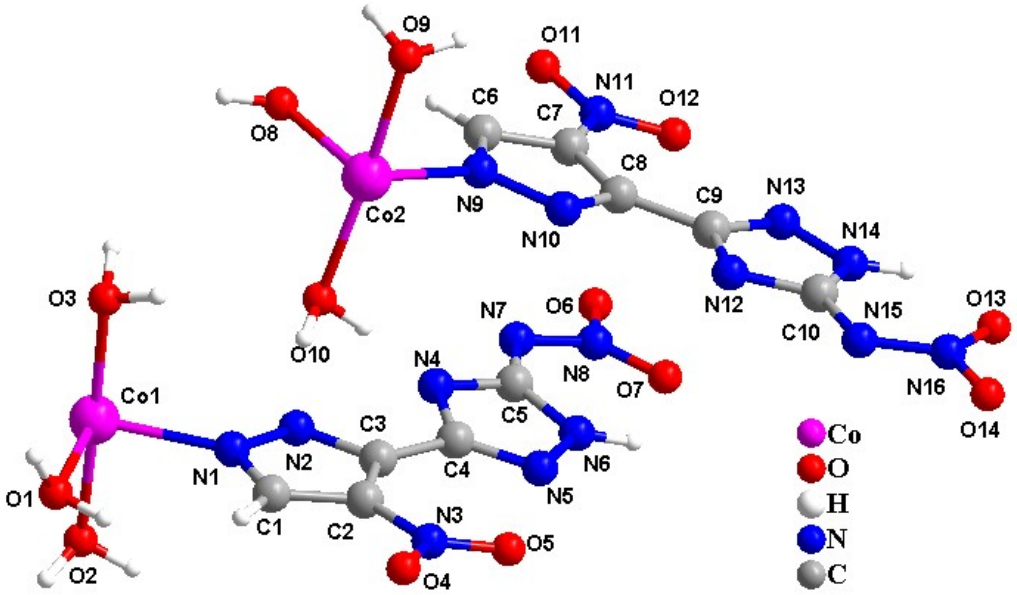


Figure S8. The asymmetric unit of **5**.

Table S13. Crystal data and structure refinement for 5.

CCDC No.	2258460
Identification code	5
Empirical formula	$C_{10}H_{16}Co_2N_{16}O_{14}$
Formula weight	702.25
Temperature/K	100
Crystal system	triclinic
Space group	*P-1*
a/Å	11.507(4)
b/Å	12.980(5)
c/Å	14.249(5)
α/°	72.344(11)
β/°	75.743(12)
γ/°	71.317(10)
Volume/Å^3	1894.7(12)
Z	2
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.941
F(000)	708.0
Crystal size/mm^3	0.12 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.374 to 57.192
Index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-19 \le l \le 19$
Reflections collected	28328

Independent reflections	9391 [R_{int} = 0.0853, R_{sigma} = 0.0935]
Data/restraints/parameters	9391/1/388
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0910, wR_2 = 0.2701
Final R indexes [all data]	R_1 = 0.1198, wR_2 = 0.2982
Largest diff. peak/hole / e $Å^{-3}$	1.82/-1.14

Table S14. Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co2	O9	2.137(4)	N4	C5	1.354(7)
Co2	O8	2.141(4)	N4	C4	1.382(7)
Co2	O10	2.120(4)	N13	N14	1.381(6)
Co2	$N12^1$	2.122(5)	N13	C9	1.325(7)
Co2	$N10^1$	2.123(4)	O5	N3	1.246(7)
Co2	N9	2.115(5)	N6	C5	1.361(7)
Co1	O3	2.118(4)	N14	C10	1.341(7)
Co1	O2	2.148(4)	N9	C6	1.333(7)
Co1	O1	2.131(4)	N15	N16	1.321(7)
Co1	$N4^2$	2.142(5)	N15	C10	1.379(7)
Co1	$N2^2$	2.135(5)	O4	N3	1.228(7)
Co1	N1	2.103(5)	N2	N1	1.369(6)
O6	N8	1.268(6)	N2	C3	1.359(7)
O14	N16	1.279(7)	N7	N8	1.331(7)
O7	N8	1.259(7)	N7	C5	1.361(8)
O11	N11	1.257(7)	N11	C7	1.418(7)
N12	C10	1.354(7)	N1	C1	1.338(8)
N12	C9	1.368(7)	N3	C2	1.432(8)
N10	N9	1.385(6)	C4	C3	1.483(8)
N10	C8	1.356(7)	C3	C2	1.403(8)
N5	N6	1.374(6)	C1	C2	1.404(8)
N5	C4	1.323(8)	C9	C8	1.471(8)
O12	N11	1.246(7)	C7	C8	1.413(8)
O13	N16	1.233(7)	C7	C6	1.416(8)

[1]-X,2-Y,1-Z; [2]1-X,1-Y,-Z

Table S15. Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O9	Co2	O8	92.02(18)	N16	N15	C10	115.8(5)
O10	Co2	O9	174.20(16)	N1	N2	$Co1^2$	134.3(4)
O10	Co2	O8	89.12(18)	C3	N2	$Co1^2$	116.6(4)
O10	Co2	$N12^1$	87.11(18)	C3	N2	N1	108.9(4)
O10	Co2	$N10^1$	90.20(17)	N8	N7	C5	116.4(5)
$N12^1$	Co2	O9	87.23(18)	O14	N16	N15	117.0(5)

Table S15. Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N12[1]	Co2	O8	88.59(18)	O13	N16	O14	118.4(5)
N12[1]	Co2	N10[1]	77.39(18)	O13	N16	N15	124.5(5)
N10[1]	Co2	O9	87.31(17)	O11	N11	C7	118.6(5)
N10[1]	Co2	O8	165.98(17)	O12	N11	O11	122.5(5)
N9	Co2	O9	92.54(18)	O12	N11	C7	118.9(5)
N9	Co2	O8	93.62(17)	O6	N8	N7	116.0(5)
N9	Co2	O10	93.06(18)	O7	N8	O6	121.4(5)
N9	Co2	N12[1]	177.78(18)	O7	N8	N7	122.6(5)
N9	Co2	N10[1]	100.40(18)	N2	N1	Co1	122.5(4)
O3	Co1	O2	178.46(18)	C1	N1	Co1	128.4(4)
O3	Co1	O1	91.12(19)	C1	N1	N2	109.0(5)
O3	Co1	N4[2]	86.32(19)	O5	N3	C2	117.9(5)
O3	Co1	N2[2]	90.14(19)	O4	N3	O5	124.1(5)
O1	Co1	O2	89.71(18)	O4	N3	C2	118.0(5)
O1	Co1	N4[2]	87.49(18)	N4	C5	N6	108.1(5)
O1	Co1	N2[2]	164.34(19)	N4	C5	N7	119.4(5)
N4[2]	Co1	O2	92.42(18)	N7	C5	N6	132.5(5)
N2[2]	Co1	O2	88.70(18)	N5	C4	N4	113.5(5)
N2[2]	Co1	N4[2]	77.01(18)	N5	C4	C3	130.9(5)
N1	Co1	O3	91.9(2)	N4	C4	C3	115.6(5)
N1	Co1	O2	89.36(19)	N12	C10	N15	119.1(5)
N1	Co1	O1	92.70(19)	N14	C10	N12	108.5(5)
N1	Co1	N4[2]	178.2(2)	N14	C10	N15	132.3(5)
N1	Co1	N2[2]	102.86(18)	N2	C3	C4	115.3(5)
C10	N12	Co2[1]	140.7(4)	N2	C3	C2	107.4(5)
C10	N12	C9	104.3(5)	C2	C3	C4	137.3(5)
C9	N12	Co2[1]	114.9(4)	N1	C1	C2	108.3(5)
N9	N10	Co2[1]	135.1(3)	N12	C9	C8	116.4(5)
C8	N10	Co2[1]	116.1(4)	N13	C9	N12	113.7(5)
C8	N10	N9	108.7(4)	N13	C9	C8	129.8(5)
C4	N5	N6	103.5(5)	C8	C7	N11	130.1(5)
C5	N4	Co1[2]	139.4(4)	C8	C7	C6	105.1(5)
C5	N4	C4	104.3(5)	C6	C7	N11	124.8(5)
C4	N4	Co1[2]	115.3(4)	C3	C2	N3	129.0(5)
C9	N13	N14	103.0(5)	C3	C2	C1	106.3(5)
C5	N6	N5	110.5(5)	C1	C2	N3	124.8(6)
C10	N14	N13	110.6(4)	N10	C8	C9	115.1(5)
N10	N9	Co2	124.5(3)	N10	C8	C7	108.2(5)
C6	N9	Co2	126.9(4)	C7	C8	C9	136.7(5)
C6	N9	N10	108.6(5)	N9	C6	C7	109.3(5)

[1]-X,2-Y,1-Z; [2]1-X,1-Y,-Z

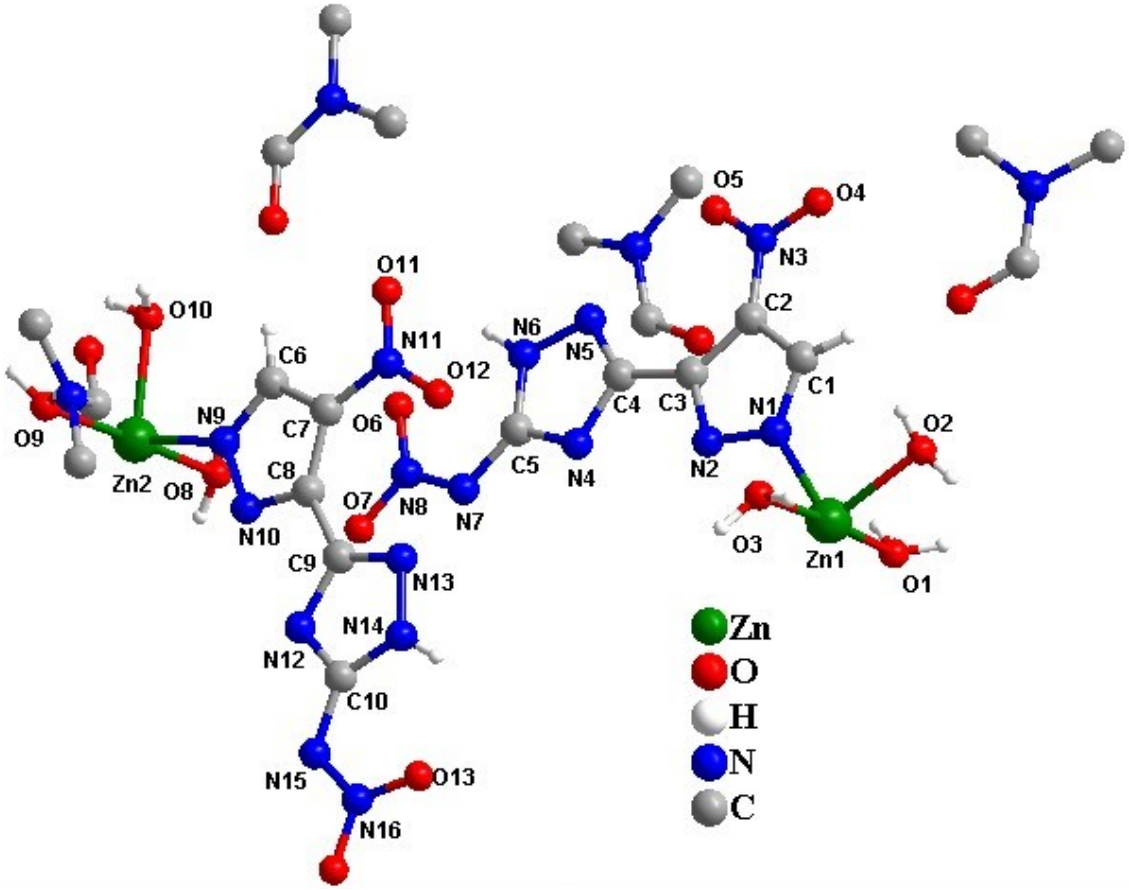


Figure S9. The asymmetric unit of **6**.

Table S16. Crystal data and structure refinement for 6.

CCDC No.	2258461
Identification code	6
Empirical formula	$C_{10}H_{16}N_{16}O_{14}Zn_2$
Formula weight	715.13
Temperature/K	100
Crystal system	triclinic
Space group	*P-1*
a/Å	11.7885(4)
b/Å	12.0697(4)
c/Å	15.7929(6)
α/°	68.2650(10)
β/°	87.1700(10)
γ/°	84.8060(10)
Volume/Å3	2078.44(13)
Z	2
ρcalcg/cm3	1.143
μ/mm-1	1.214
F(000)	720.0
Crystal size/mm3	0.2 × 0.18 × 0.12

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.408 to 56.714
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	34339
Independent reflections	10339 [Rint = 0.0379, Rsigma = 0.0396]
Data/restraints/parameters	10339/0/386
Goodness-of-fit on F2	1.109
Final R indexes [I>=2σ (I)]	R1 = 0.0493, wR2 = 0.1555
Final R indexes [all data]	R1 = 0.0577, wR2 = 0.1623
Largest diff. peak/hole / e Å-3	0.78/-0.70

Table S17. Bond Lengths for 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn2	O8	2.153(3)	N12	C9	1.345(4)
Zn2	O10	2.128(2)	O4	N3	1.239(4)
Zn2	O9	2.167(3)	N10	N9	1.373(4)
Zn2	N121	2.117(3)	N10	C8	1.337(4)
Zn2	N101	2.174(3)	N5	N6	1.371(4)
Zn2	N9	2.054(3)	N5	C4	1.316(4)
Zn1	O1	2.183(3)	N9	C6	1.334(4)
Zn1	O3	2.198(3)	N1	N2	1.366(4)
Zn1	O2	2.108(3)	N1	C1	1.330(4)
Zn1	N42	2.132(3)	N6	C5	1.348(4)
Zn1	N1	2.041(3)	N14	N13	1.376(4)
Zn1	N22	2.146(3)	N14	C10	1.341(4)
O14	N16	1.263(4)	N7	N8	1.311(4)
O6	N8	1.251(4)	N7	C5	1.377(4)
O7	N8	1.257(4)	N11	C7	1.406(4)
O5	N3	1.222(4)	N2	C3	1.340(4)
O13	N16	1.245(4)	N3	C2	1.424(4)
O11	N11	1.240(4)	N13	C9	1.326(4)
O12	N11	1.230(4)	C9	C8	1.467(4)
N4	C4	1.354(4)	C4	C3	1.470(4)
N4	C5	1.333(4)	C3	C2	1.401(4)
N15	N16	1.314(4)	C8	C7	1.413(4)
N15	C10	1.383(4)	C7	C6	1.394(5)
N12	C10	1.340(4)	C2	C1	1.387(4)

[1]2-X,-Y,1-Z; [2]1-X,1-Y,-Z

Table 18. Bond Angles for 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O8	Zn2	O9	175.38(10)	C1	N1	N2	108.9(3)
O8	Zn2	N10[1]	88.43(10)	O14	N16	N15	117.0(3)
O10	Zn2	O8	93.71(10)	O13	N16	O14	120.6(3)
O10	Zn2	O9	86.66(10)	O13	N16	N15	122.4(3)

O10	Zn2	N10[1]	164.35(10)	C5	N6	N5	110.5(3)
O9	Zn2	N10[1]	89.99(10)	C10	N14	N13	111.1(3)
N12[1]	Zn2	O8	89.82(10)	N8	N7	C5	117.3(3)
N12[1]	Zn2	O10	88.52(10)	O11	N11	C7	117.7(3)
N12[1]	Zn2	O9	85.58(11)	O12	N11	O11	122.7(3)
N12[1]	Zn2	N10[1]	75.97(10)	O12	N11	C7	119.6(3)
N9	Zn2	O8	91.33(11)	N1	N2	Zn1[2]	134.8(2)
N9	Zn2	O10	94.40(10)	C3	N2	Zn1[2]	116.3(2)
N9	Zn2	O9	93.24(11)	C3	N2	N1	108.9(3)
N9	Zn2	N12[1]	176.78(11)	O6	N8	O7	120.8(3)
N9	Zn2	N10[1]	101.06(10)	O6	N8	N7	122.0(3)
O1	Zn1	O3	176.50(11)	O7	N8	N7	117.2(3)
O2	Zn1	O1	93.47(11)	O5	N3	O4	123.9(3)
O2	Zn1	O3	89.21(12)	O5	N3	C2	119.6(3)
O2	Zn1	N4[2]	87.19(10)	O4	N3	C2	116.5(3)
O2	Zn1	N2[2]	163.55(10)	C9	N13	N14	101.4(3)
N4[2]	Zn1	O1	91.39(10)	N12	C10	N15	119.1(3)
N4[2]	Zn1	O3	86.48(11)	N12	C10	N14	108.0(3)
N4[2]	Zn1	N2[2]	76.45(10)	N14	C10	N15	132.8(3)
N1	Zn1	O1	88.95(11)	N12	C9	C8	117.2(3)
N1	Zn1	O3	93.10(12)	N13	C9	N12	114.9(3)
N1	Zn1	O2	94.46(11)	N13	C9	C8	127.9(3)
N1	Zn1	N4[2]	178.30(11)	N4	C4	C3	116.8(3)
N1	Zn1	N2[2]	101.90(11)	N5	C4	N4	114.3(3)
N2[2]	Zn1	O1	88.63(10)	N5	C4	C3	128.9(3)
N2[2]	Zn1	O3	88.16(11)	N4	C5	N6	108.2(3)
C4	N4	Zn1[2]	115.2(2)	N4	C5	N7	119.5(3)
C5	N4	Zn1[2]	139.7(2)	N6	C5	N7	132.3(3)
C5	N4	C4	104.6(3)	N2	C3	C4	115.0(3)
N16	N15	C10	116.4(3)	N2	C3	C2	107.5(3)
C10	N12	Zn2[1]	139.0(2)	C2	C3	C4	137.5(3)
C10	N12	C9	104.5(3)	N10	C8	C9	114.8(3)
C9	N12	Zn2[1]	116.1(2)	N10	C8	C7	107.9(3)
N9	N10	Zn2[1]	135.0(2)	C7	C8	C9	137.4(3)
C8	N10	Zn2[1]	115.9(2)	N11	C7	C8	130.1(3)
C8	N10	N9	109.1(3)	C6	C7	N11	124.4(3)
C4	N5	N6	102.4(3)	C6	C7	C8	105.5(3)
N10	N9	Zn2	123.9(2)	C3	C2	N3	129.6(3)
C6	N9	Zn2	127.6(2)	C1	C2	N3	124.1(3)
C6	N9	N10	108.5(3)	C1	C2	C3	106.3(3)

[1]2-X,-Y,1-Z; [2]1-X,1-Y,-Z

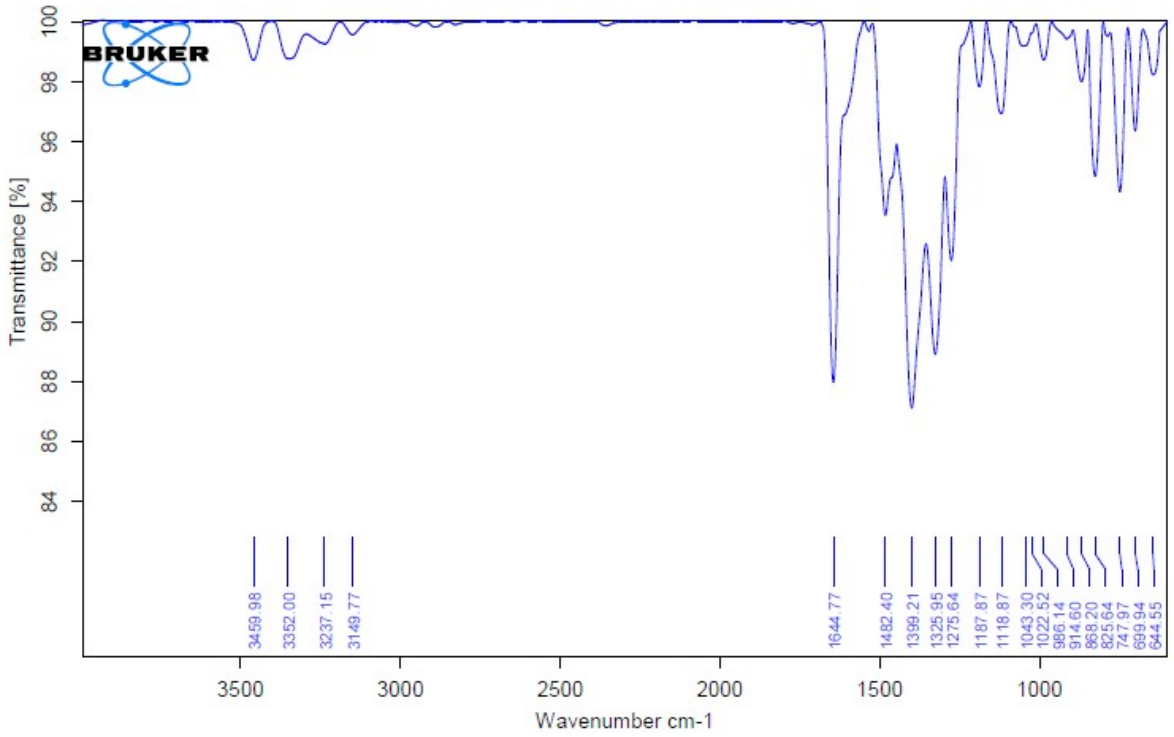


Figure S10. IR spectrum of compound **1**.

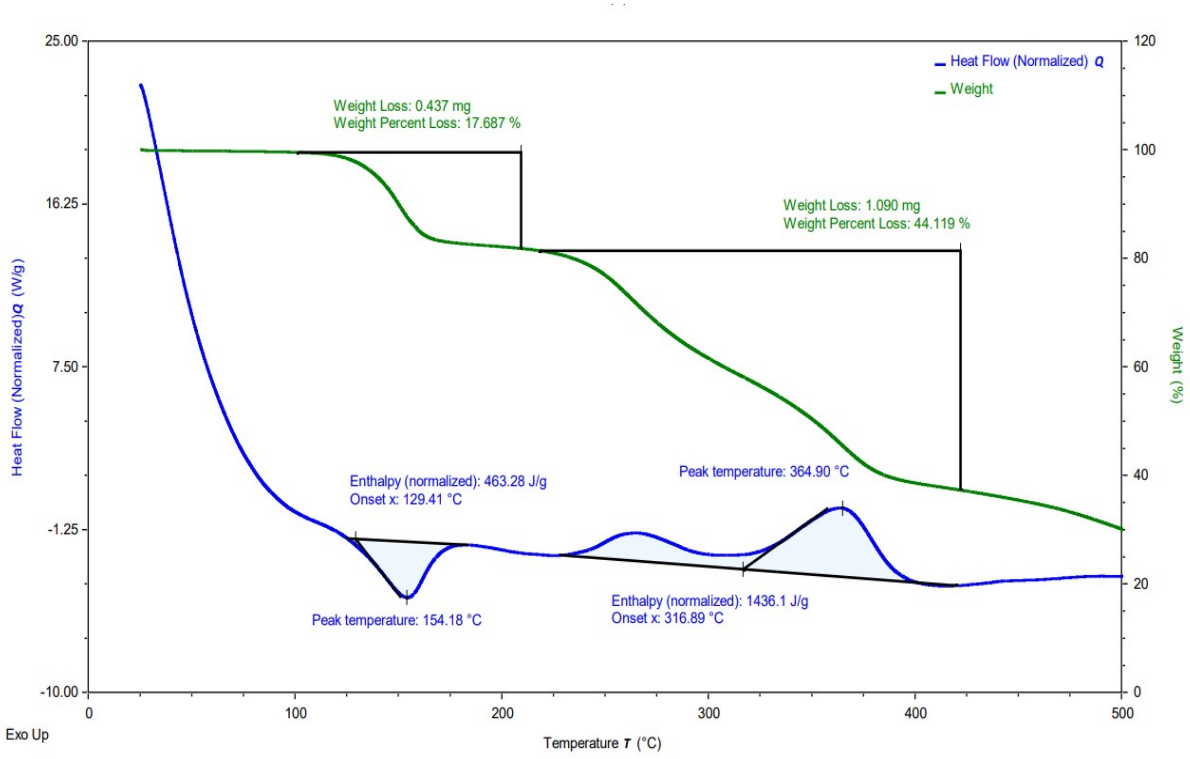


Figure S11. TGA-DSC spectra of compound **1**.

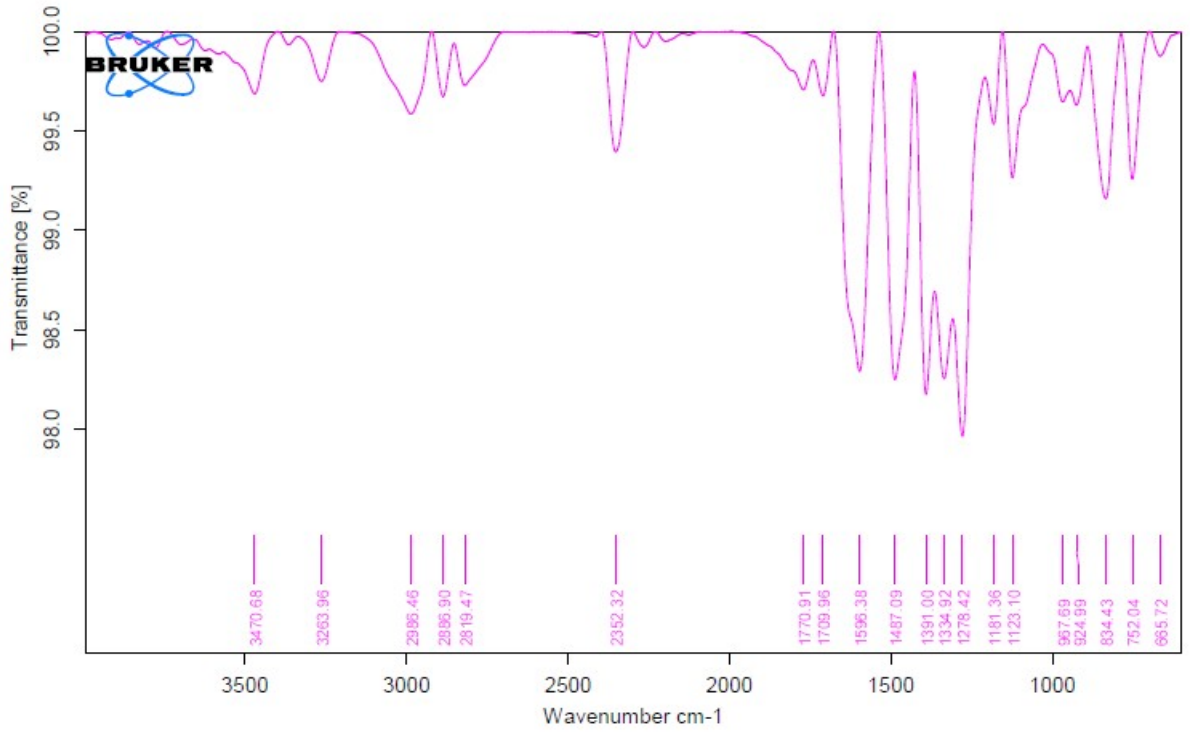


Figure S12. IR spectrum of compound **2.**

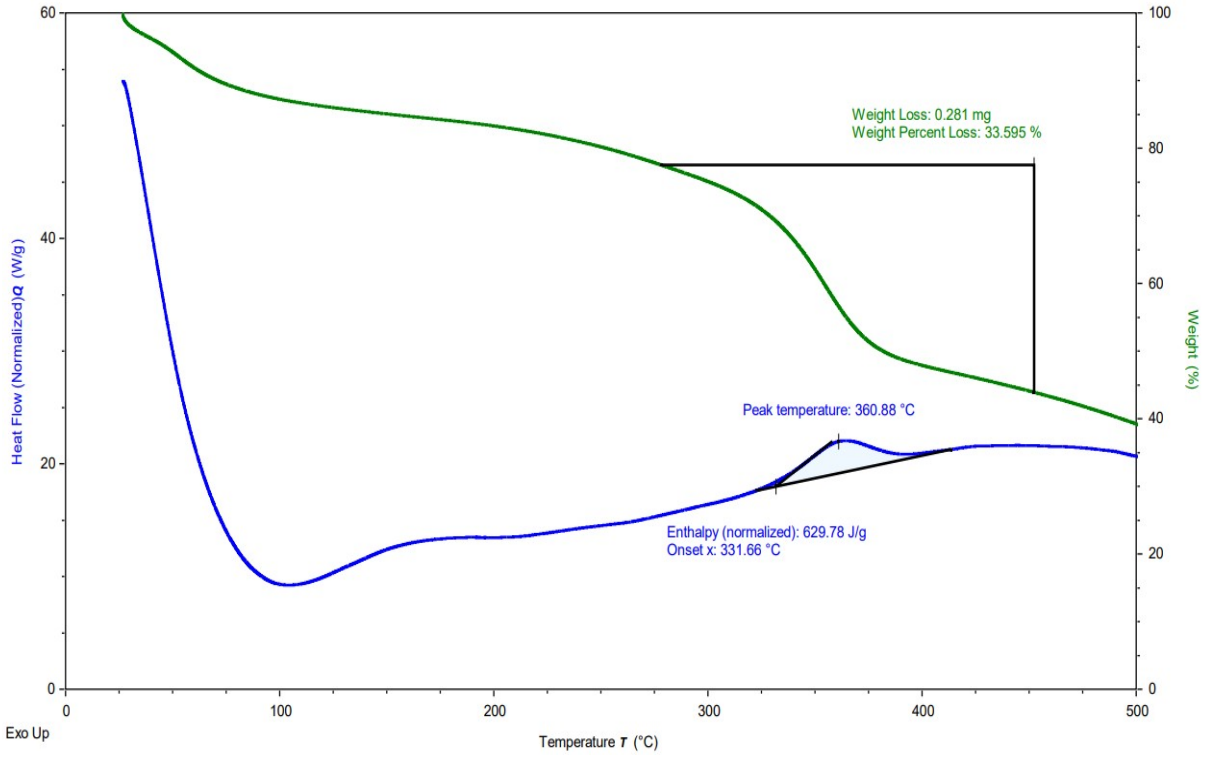


Figure S13. TGA-DSC spectra of compound **2**.

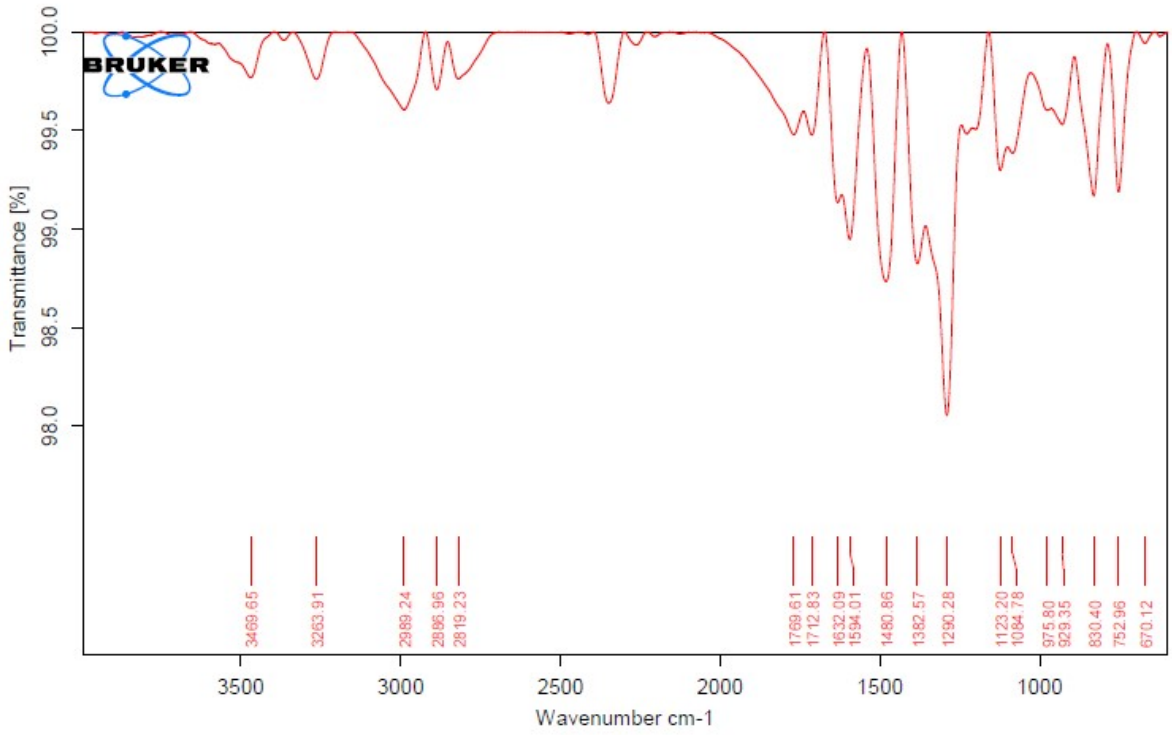


Figure S14. IR spectrum of compound **3.**

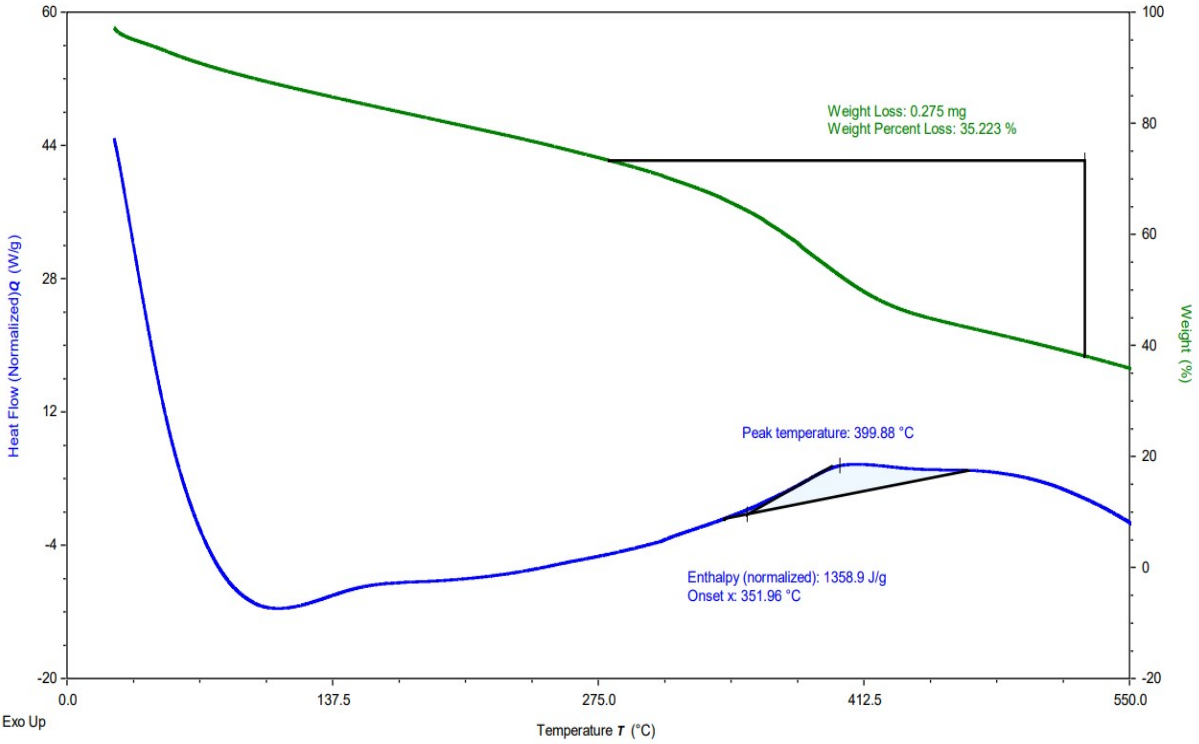


Figure S15. TGA-DSC spectra of compound **3**.

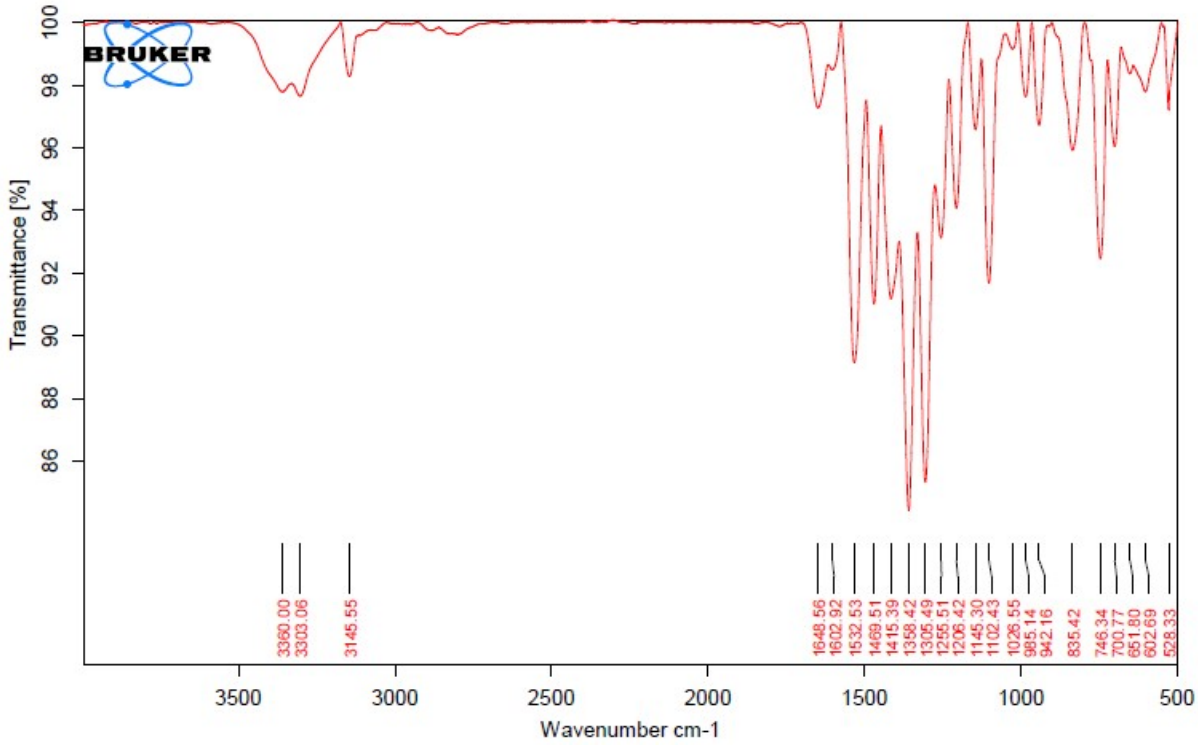


Figure S16. IR spectrum of compound **4.**

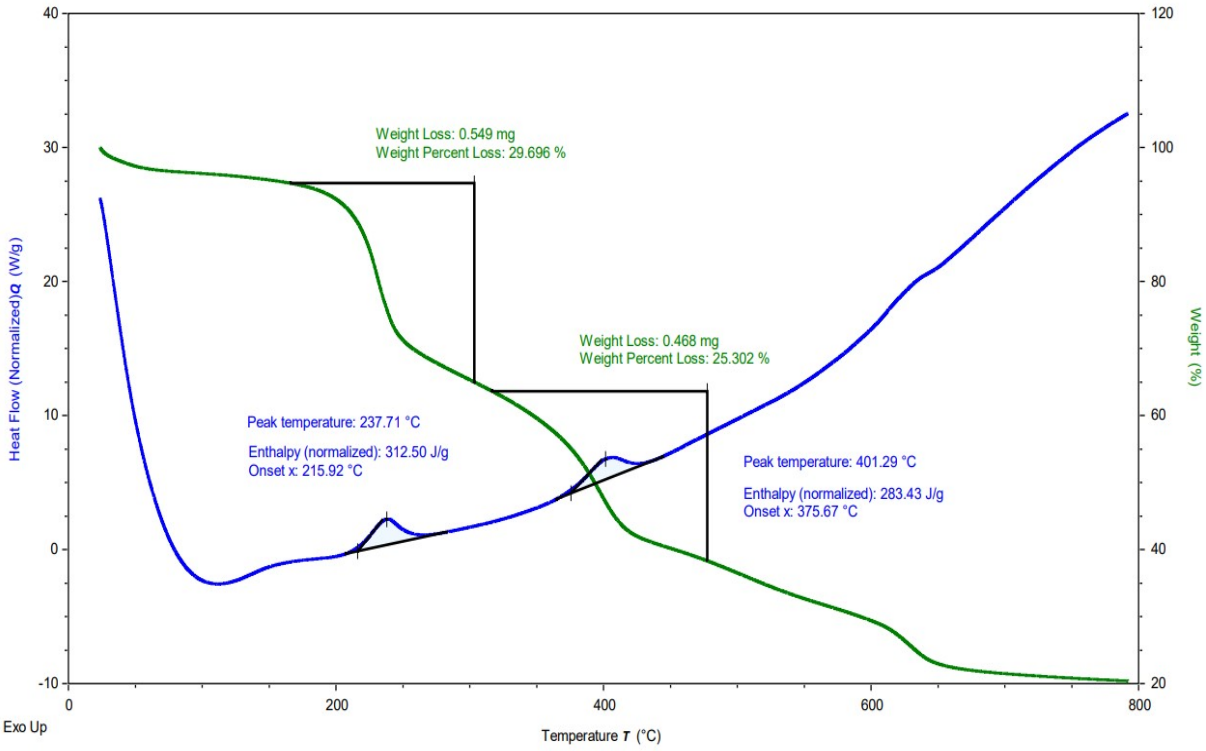


Figure S17. TGA-DSC spectra of compound **4**.

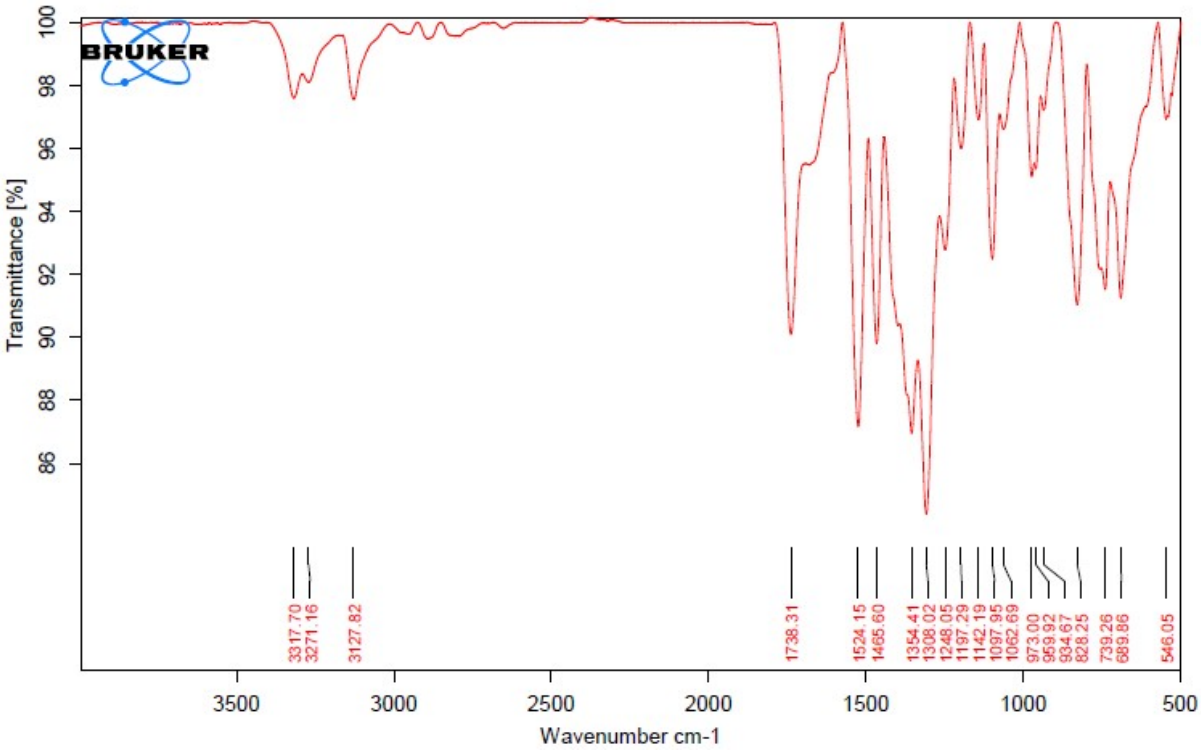


Figure S18. IR spectrum of compound **5.**

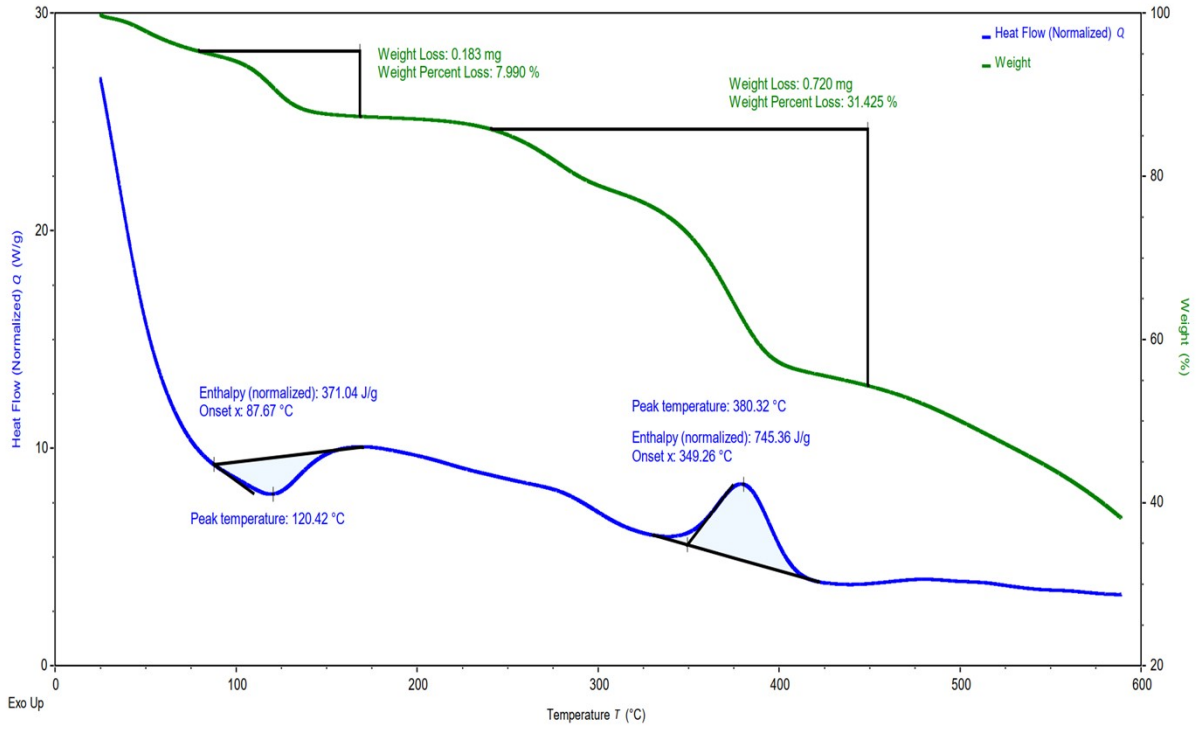


Figure S19. TGA-DSC spectra of compound **5**.

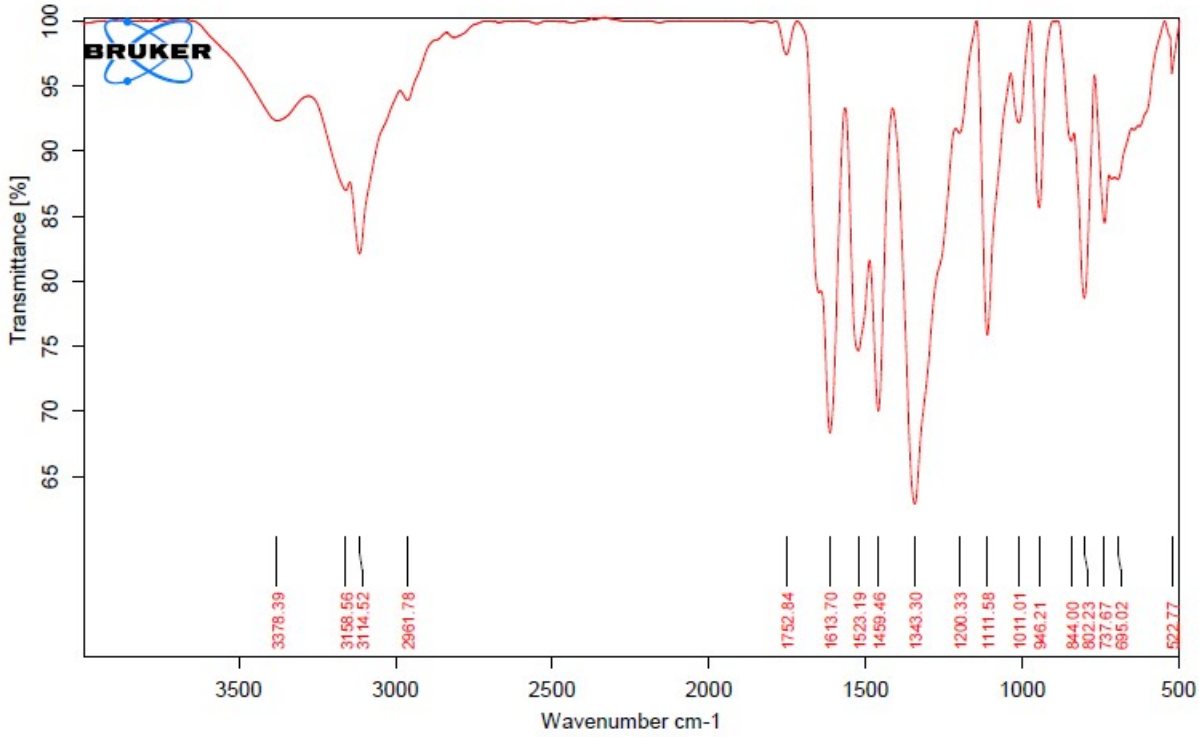


Figure S20. IR spectrum of compound **6.**

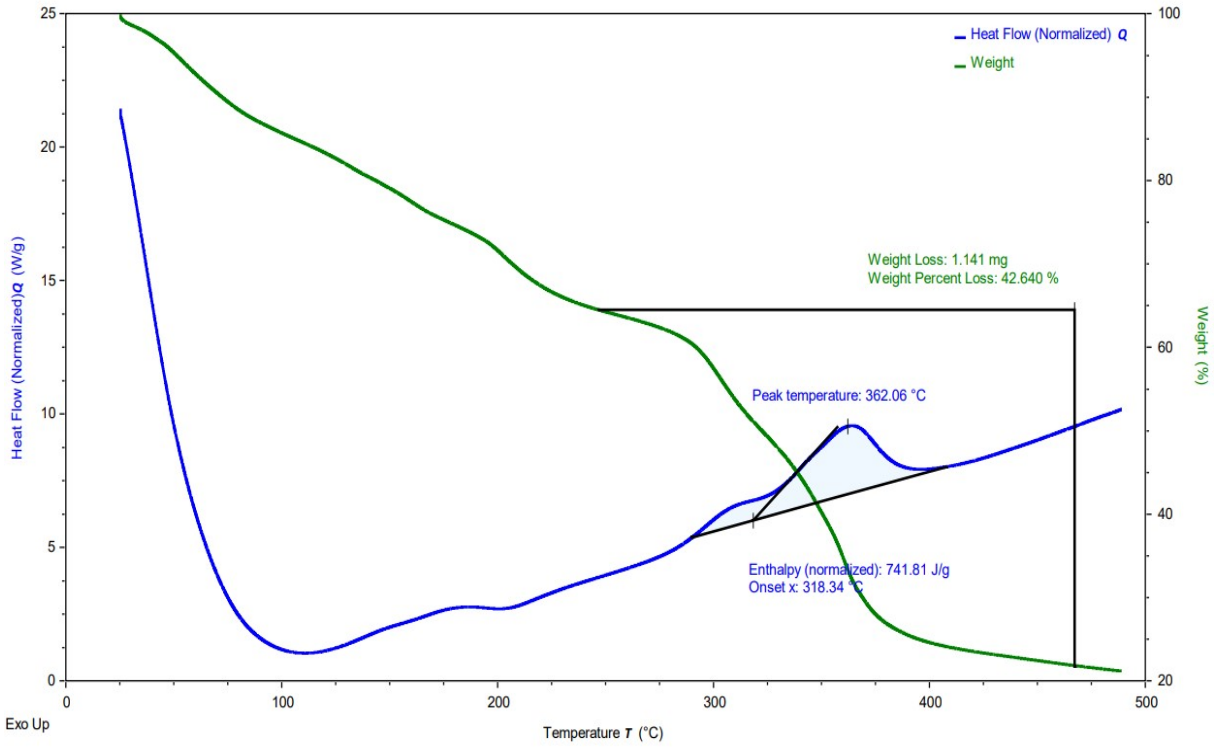


Figure S21. TGA-DSC spectra of compound **6**.

Heat of combustion

The heat of combustion is a vital indicator for evaluating the energetic properties of the explosives. The constant-volume combustion energies of the compounds were determined by

a precise oxygen bomb calorimetry (Parr 6200 calorimeter). Approximately, 120 mg of compound and benzoic acid were mixed with a mass ratio of 1:3. The sample was sealed in a bomb, which subsequently burned in the pure oxygen atmosphere.

The $\Delta_c U$ values for **1-6** are determined to be –7.54, –6.33, –6.10, –9.98, –9.71 and –8.76 kJ·g^{-1} respectively. The enthalpies of combustion ($\Delta_c H^o$) of **1-6** are calculated to be –7.50, –6.3, –6.07, –9.94, –9.67 and –8.73 kJ·g^{-1}, respectively, on the basis of $\Delta_c H = \Delta_c U + \Delta nRT$, where $\Delta n = n_g$ (products) – n_g (reactants), R = 8.314 J·mol^{-1}·K^{-1}, T = 298.15 K (n_g is the total molar amount of gases in the products or reactants). The combustion equations of the complexes are as follows-

$$Ni_2C_{10}H_{20}N_{16}O_{16}(s) + 8O_2(g) = 2NiO(s) + 10CO_2(g) + 10H_2O(l) + 8N_2(g) \quad (1)$$

$$Co_2C_{10}H_{20}N_{16}O_{16}(s) + 8O_2(g) = 2CoO(s) + 10CO_2(g) + 10H_2O(l) + 8N_2(g) \quad (2)$$

$$Zn_2C_{10}H_{20}N_{16}O_{16}(s) + 8O_2(g) = 2ZnO(s) + 10CO_2(g) + 10H_2O(l) + 8N_2(g) \quad (3)$$

$$Ni_2C_{10}H_{16}N_{16}O_{14}(s) + 8O_2(g) = 2NiO(s) + 10CO_2(g) + 8H_2O(l) + 8N_2(g) \quad (4)$$

$$Co_2C_{10}H_{16}N_{16}O_{14}(s) + 8O_2(g) = 2CoO(s) + 10CO_2(g) + 8H_2O(l) + 8N_2(g) \quad (5)$$

$$Zn_2C_{10}H_{16}N_{16}O_{14}(s) + 8O_2(g) = 2ZnO(s) + 10CO_2(g) + 8H_2O(l) + 8N_2(g) \quad (6)$$

The $\Delta_f H°$ values of compounds **1**, **2**, **3, 4, 5** and **6** were calculated to be –2.35, –3.17, –3.90, 0.39, 0.14 and –0.94 kJ·g^{-1}, respectively, according to Hess's Law as shown in equations (7)-(12) with the known enthalpies of NiO (s, –240.0 kJ·mol^{-1}), CoO (s, –237.74 kJ·mol^{-1}), ZnO (s, –350.5 kJ·mol^{-1}), H_2O (l, –285.83 kJ·mol^{-1}), and CO_2 (g, –393.51 kJ·mol^{-1}).

$$\Delta_f H^o[\mathbf{1},s] = 2\Delta_f H^o[NiO,s] + 10\Delta_f H^o[CO_2,g] + 10\Delta_f H^o[H_2O,l] - \Delta_c H^o[\mathbf{1},s] \quad (7)$$

$$\Delta_f H^o[\mathbf{2},s] = 2\Delta_f H^o[CoO,s] + 10\Delta_f H^o[CO_2,g] + 10\Delta_f H^o[H_2O,l] - \Delta_c H^o[\mathbf{2},s] \quad (8)$$

$$\Delta_f H^o[\mathbf{3},s] = 2\Delta_f H^o[ZnO,s] + 10\Delta_f H^o[CO_2,g] + 10\Delta_f H^o[H_2O,l] - \Delta_c H^o[\mathbf{3},s] \quad (9)$$

$$\Delta_f H^o[\mathbf{4},s] = 2\Delta_f H^o[NiO,s] + 10\Delta_f H^o[CO_2,g] + 8\Delta_f H^o[H_2O,l] - \Delta_c H^o[\mathbf{4},s] \quad (10)$$

$$\Delta_f H^o[\mathbf{5},s] = 2\Delta_f H^o[CoO,s] + 10\Delta_f H^o[CO_2,g] + 8\Delta_f H^o[H_2O,l] - \Delta_c H^o[\mathbf{5},s] \quad (11)$$

$$\Delta_f H^o[\mathbf{6},s] = 2\Delta_f H^o[ZnO,s] + 10\Delta_f H^o[CO_2,g] + 8\Delta_f H^o[H_2O,l] - \Delta_c H^o[\mathbf{6},s] \quad (12)$$

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