Supporting Information

Energetic transition metal salts of 5,5'-dinitramino-3,3'-methylene-1H-1,2,4-bistriazole: syntheses, structures and properties

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Table S1 NBO charges of atoms for H_2DNAMT

Atom	Charge/a.u.	Atom	Charge/a.u.	Atom	Charge/a.u.
N1	-0.27533	N10	0.62867	N19	-0.34222
O2	-0.39896	N11	-0.50742	H20	0.40129
O3	-0.42604	H12	0.39612	C21	0.51724
N4	0.63461	O13	-0.44812	C22	-0.45184
N5	-0.30166	C14	0.48573	H23	0.2175
H6	0.38715	N15	-0.29777	H24	0.23659
O7	-0.39397	C16	0.3933	C25	0.39105
N8	-0.34181	N17	-0.33678		
H9	0.40122	N18	-0.56856		

Table S2 NBO charges of atoms for $BNATO^{2-}$

Atom	Charge/a.u.	Atom	Charge/a.u.	Atom	Charge/a.u.
C1	0.19972	N9	-0.32574	H17	0.37204
N2	-0.39046	N10	-0.36968	N18	0.65370
N3	-0.31958	H11	0.37740	O19	-0.49754
N4	-0.51137	C12	0.48897	O20	-0.54132
C5	0.39960	O13	-0.57460	O21	-0.48708
C6	0.53046	N14	-0.51334	O22	-0.39552
C7	0.26198	N15	0.61351		
N8	-0.53437	N16	-0.43678		

Table S3 Bond Lengths for H_2DNAMT (1).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N7	N8	1.383(8)	N10	N9	1.344(9)
N7	C4	1.318(9)	N6	C5	1.352(9)
O1	N1	1.260(8)	N6	C4	1.375(9)
O2	N1	1.243(8)	C5	N8	1.347(9)
N1	N2	1.327(8)	C5	N9	1.343(9)
N4	N5	1.385(8)	N5	C2	1.301(9)
N4	C1	1.341(9)	C2	N3	1.368(9)
O4	N10	1.245(8)	C2	C3	1.506(10)
N2	C1	1.352(9)	N3	C1	1.351(9)
N10	O3	1.259(8)	C3	C4	1.460(10)

Table S4 Bond Angles for H_2DNAMT (1)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N7	N8	104.6(6)	N5	C2	N3	113.1(6)
O1	N1	N2	115.6(6)	N5	C2	C3	124.8(7)

O2	N1	O1	123.4(6)	N3	C2	C3	121.9(6)
O2	N1	N2	121.1(7)	C5	N8	N7	111.0(6)
C1	N4	N5	111.9(6)	C1	N3	C2	106.3(6)
N1	N2	C1	118.3(7)	C5	N9	N10	117.5(7)
O4	N10	O3	122.8(7)	N4	C1	N2	133.3(7)
O4	N10	N9	115.6(7)	N4	C1	N3	105.9(6)
O3	N10	N9	121.5(7)	N3	C1	N2	120.8(7)
C5	N6	C4	107.4(6)	C4	C3	C2	114.1(6)
N8	C5	N6	106.1(7)	N7	C4	N6	110.9(6)
N9	C5	N6	134.9(7)	N7	C4	C3	124.2(7)
N9	C5	N8	119.0(7)	N6	C4	C3	124.9(7)
C2	N5	N4	102.9(6)				

Table S5 Torsion Angles for H_2DNAMT (1)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N1	N2	C1	177.5(6)	N5	C2	C3	C4	33.5(11)
O2	N1	N2	C1	-1.5(10)	C2	N3	C1	N4	0.0(8)
N1	N2	C1	N4	3.1(12)	C2	N3	C1	N2	179.0(7)
N1	N2	C1	N3	-175.5(6)	C2	C3	C4	N7	-97.1(9)
N4	N5	C2	N3	0.8(8)	C2	C3	C4	N6	83.7(9)
N4	N5	C2	C3	175.8(7)	N8	N7	C4	N6	1.3(8)
O4	N10	N9	C5	-178.8(6)	N8	N7	C4	C3	-178.0(6)
N6	C5	N8	N7	-0.3(8)	N8	C5	N9	N10	175.3(6)
N6	C5	N9	N10	-6.2(12)	N3	C2	C3	C4	-151.9(7)
O3	N10	N9	C5	2.8(10)	N9	C5	N8	N7	178.6(6)
C5	N6	C4	N7	-1.6(8)	C1	N4	N5	C2	-0.8(8)
C5	N6	C4	C3	177.7(7)	C3	C2	N3	C1	-175.7(7)
N5	N4	C1	N2	-178.3(8)	C4	N7	N8	C5	-0.6(8)
N5	N4	C1	N3	0.5(8)	C4	N6	C5	N8	1.1(7)
N5	C2	N3	C1	-0.5(8)	C4	N6	C5	N9	-177.6(8)

Table S6 Bond Lengths for $[Co(DNAMT)(H_2O)_4]\cdot 2H_2O$ (2)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O1	2.042(2)	N3	N2	1.366(2)
Co1	$O2^1$	2.1054(15)	N3	C3	1.339(3)
Co1	O2	2.1054(15)	N5	N4	1.308(2)
Co1	O3	2.138(2)	N4	C3	1.378(3)
Co1	$N1^1$	2.1423(17)	N1	C2	1.364(3)

Co1	N1	2.1423(17)	N1	C3	1.345(3)
O5	N5	1.254(2)	N2	C2	1.316(3)
O4	N5	1.267(2)	C2	C1	1.493(3)

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

Table S7 Bond Angles for [Co(DNAMT)(H_2O)$_4$]·2H_2O (2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Co1	O2[1]	90.93(7)	O5	N5	O4	120.01(17)
O1	Co1	O2	90.93(7)	O5	N5	N4	123.71(18)
O1	Co1	O3	178.18(11)	O4	N5	N4	116.28(17)
O1	Co1	N1	94.00(7)	N5	N4	C3	116.40(18)
O1	Co1	N1[1]	94.00(7)	C2	N1	Co1	123.17(14)
O2[1]	Co1	O2	88.60(9)	C3	N1	Co1	131.08(14)
O2[1]	Co1	O3	87.77(7)	C3	N1	C2	103.53(17)
O2	Co1	O3	87.77(7)	C2	N2	N3	103.13(17)
O2	Co1	N1	175.07(7)	N1	C2	C1	122.7(2)
O2[1]	Co1	N1[1]	175.07(7)	N2	C2	N1	114.11(18)
O2	Co1	N1[1]	91.50(6)	N2	C2	C1	123.2(2)
O2[1]	Co1	N1	91.50(6)	N3	C3	N4	131.58(19)
O3	Co1	N1[1]	87.31(7)	N3	C3	N1	109.05(18)
O3	Co1	N1	87.31(7)	N1	C3	N4	119.35(18)
N1[1]	Co1	N1	87.98(9)	C2[1]	C1	C2	111.3(2)
C3	N3	N2	110.18(17)				

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

Table S8 Torsion Angles for [Co(DNAMT)(H_2O)$_4$]·2H_2O (2)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Co1	N1	C2	N2	-164.41(14)	N1	C2	C1	C2[1]	-57.0(3)
Co1	N1	C2	C1	14.6(3)	N2	N3	C3	N4	-179.3(2)
Co1	N1	C3	N3	163.35(14)	N2	N3	C3	N1	-0.9(2)
Co1	N1	C3	N4	-18.0(3)	N2	C2	C1	C2[1]	121.9(2)
O5	N5	N4	C3	-1.1(3)	C2	N1	C3	N3	0.4(2)
O4	N5	N4	C3	178.52(19)	C2	N1	C3	N4	179.00(18)
N3	N2	C2	N1	-0.8(2)	C3	N3	N2	C2	1.0(2)
N3	N2	C2	C1	-179.8(2)	C3	N1	C2	N2	0.3(2)
N5	N4	C3	N3	-1.1(3)	C3	N1	C2	C1	179.3(2)
N5	N4	C3	N1	-179.43(18)					

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

Table S9 Bond Lengths for [Ni(DNAMT)(H_2O)$_4$]·2H_2O (3)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O3	2.103(2)	N3	C1	1.351(3)
Ni1	O4	2.032(2)	N3	C2	1.365(3)
Ni1	O5[1]	2.0703(17)	N5	C2	1.317(3)
Ni1	O5	2.0704(17)	N2	N1	1.306(3)
Ni1	N3	2.094(2)	N2	C1	1.380(3)
Ni1	N3[1]	2.0938(19)	O2	N1	1.271(3)
N4	N5	1.372(3)	C3	C2[1]	1.495(3)
N4	C1	1.337(3)	C3	C2	1.495(3)

[1]+X, 3/2-Y, +Z

Table S10 Bond Angles for [Ni(DNAMT)(H_2O)$_4$]·2H_2O (3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	Ni1	O3	177.40(11)	C1	N3	Ni1	130.94(16)
O4	Ni1	O5[1]	90.09(8)	C1	N3	C2	103.21(19)
O4	Ni1	O5	90.09(7)	C2	N3	Ni1	123.44(15)
O4	Ni1	N3	94.16(8)	C2	N5	N4	103.15(19)
O4	Ni1	N3[1]	94.16(8)	N1	N2	C1	116.20(19)
O5[1]	Ni1	O3	88.02(8)	O1	N1	N2	123.9(2)
O5	Ni1	O3	88.01(7)	O1	N1	O2	119.57(19)
O5[1]	Ni1	O5	86.05(10)	O2	N1	N2	116.52(19)
O5[1]	Ni1	N3	175.49(7)	N4	C1	N3	109.3(2)
O5	Ni1	N3	92.42(7)	N4	C1	N2	131.3(2)
O5[1]	Ni1	N3[1]	92.42(7)	N3	C1	N2	119.4(2)
O5	Ni1	N3[1]	175.49(7)	C2[1]	C3	C2	110.0(3)
N3[1]	Ni1	O3	87.69(8)	N3	C2	C3	122.5(2)
N3	Ni1	O3	87.69(8)	N5	C2	N3	114.3(2)
N3[1]	Ni1	N3	88.78(11)	N5	C2	C3	123.2(2)
C1	N4	N5	110.01(19)				

[1]+X, 3/2-Y, +Z

Table S11 Torsion Angles for [Ni(DNAMT)(H_2O)$_4$]·2H_2O (3)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ni1	N3	C1	N4	-161.95(15)	C1	N4	N5	C2	-0.7(2)
Ni1	N3	C1	N2	18.8(3)	C1	N3	C2	N5	-0.9(3)
Ni1	N3	C2	N5	163.15(15)	C1	N3	C2	C3	-179.1(2)
Ni1	N3	C2	C3	-15.0(3)	C1	N2	N1	O1	1.1(3)
N4	N5	C2	N3	1.0(3)	C1	N2	N1	O2	-178.5(2)

N4	N5	C2	C3	179.2(2)	C2	N3	C1	N4	0.4(2)
N5	N4	C1	N3	0.2(3)	C2	N3	C1	N2	-178.9(2)
N5	N4	C1	N2	179.3(2)	C2[1]	C3	C2	N3	56.9(4)
N1	N2	C1	N4	0.8(4)	C2[1]	C3	C2	N5	-121.1(2)
N1	N2	C1	N3	179.9(2)					

[1]+X, 3/2-Y, +Z

Table S12 Bond Lengths for [Zn(DNAMT)(H_2O)$_4$]·2H_2O (4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O4	2.058(3)	N1	N2	1.309(3)
Zn1	O5[1]	2.096(2)	N3	N4	1.372(3)
Zn1	O5	2.096(2)	N3	C1	1.339(3)
Zn1	O6	2.180(3)	N4	C2	1.319(4)
Zn1	N5[1]	2.150(2)	N5	C1	1.349(4)
Zn1	N5	2.150(2)	N5	C2	1.366(4)
O2	N1	1.257(3)	N2	C1	1.377(4)
O1	N1	1.268(3)	C2	C3	1.492(4)

[1]+X, 3/2-Y, +Z

Table S13 Bond Angles for [Zn(DNAMT)(H_2O)$_4$]·2H_2O (4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	Zn1	O5	91.33(9)	O2	N1	N2	123.7(2)
O4	Zn1	O5[1]	91.33(9)	O1	N1	N2	116.5(2)
O4	Zn1	O6	178.29(13)	C1	N3	N4	110.1(2)
O4	Zn1	N5[1]	94.75(10)	C2	N4	N3	103.2(2)
O4	Zn1	N5	94.75(10)	C1	N5	Zn1	130.65(19)
O5	Zn1	O5[1]	87.45(12)	C1	N5	C2	103.6(2)
O5[1]	Zn1	O6	87.44(9)	C2	N5	Zn1	123.05(18)
O5	Zn1	O6	87.44(9)	N1	N2	C1	116.3(2)
O5[1]	Zn1	N5	92.08(8)	N3	C1	N5	109.0(2)
O5	Zn1	N5[1]	92.08(8)	N3	C1	N2	131.6(3)
O5[1]	Zn1	N5[1]	173.91(9)	N5	C1	N2	119.4(2)
O5	Zn1	N5	173.91(9)	N4	C2	N5	114.0(3)
N5	Zn1	O6	86.47(9)	N4	C2	C3	123.0(3)
N5[1]	Zn1	O6	86.47(9)	N5	C2	C3	123.0(3)
N5	Zn1	N5[1]	87.74(12)	C2	C3	C2[1]	110.7(3)
O2	N1	O1	119.8(2)				

[1]+X, 3/2-Y, +Z

Table S14 Torsion Angles for [Zn(DNAMT)(H_2O)$_4$]·2H_2O (4)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zn1	N5	C1	N3	162.32(19)	N4	N3	C1	N5	-1.1(3)
Zn1	N5	C1	N2	-19.3(4)	N4	N3	C1	N2	-179.3(3)
Zn1	N5	C2	N4	-163.64(19)	N4	C2	C3	C2[1]	121.2(3)
Zn1	N5	C2	C3	15.2(4)	N5	C2	C3	C2[1]	-57.6(5)
O2	N1	N2	C1	-0.8(4)	C1	N3	N4	C2	0.8(3)
O1	N1	N2	C1	178.6(3)	C1	N5	C2	N4	-0.4(3)
N1	N2	C1	N3	-0.9(5)	C1	N5	C2	C3	178.5(3)
N1	N2	C1	N5	-178.9(2)	C2	N5	C1	N3	0.9(3)
N3	N4	C2	N5	-0.2(3)	C2	N5	C1	N2	179.3(3)
N3	N4	C2	C3	-179.1(3)					

[1]+X, 3/2-Y, +Z

Table S15 Bond Lengths for [Cd(DNAMT)(H_2O)$_4$]·2H_2O (5)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cd1	O4	2.354(6)	N1	C1	1.341(6)
Cd1	O3	2.256(6)	N1	C2	1.363(7)
Cd1	N1	2.302(4)	N5	O1	1.251(6)
Cd1	N11	2.302(4)	N5	N4	1.308(6)
Cd1	O51	2.268(4)	N2	C2	1.315(6)
Cd1	O5	2.268(4)	N4	C1	1.375(7)
N3	N2	1.362(6)	C3	C21	1.489(6)
N3	C1	1.337(6)	C3	C2	1.489(6)
O2	N5	1.270(6)			

1+X, 3/2-Y, +Z

Table S16 Bond Angles for [Cd(DNAMT)(H_2O)$_4$]·2H_2O (5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Cd1	O4	177.6(2)	C1	N1	Cd1	129.2(4)
O3	Cd1	N1[1]	96.32(17)	C1	N1	C2	104.1(4)
O3	Cd1	N1	96.32(17)	C2	N1	Cd1	124.3(3)
O3	Cd1	O5	90.04(16)	O2	N5	N4	116.4(4)
O3	Cd1	O5[1]	90.04(16)	O1	N5	O2	119.9(4)
N1[1]	Cd1	O4	85.47(16)	O1	N5	N4	123.7(5)
N1	Cd1	O4	85.47(16)	C2	N2	N3	104.0(4)
N1[1]	Cd1	N1	83.1(2)	N5	N4	C1	116.1(4)
O5[1]	Cd1	O4	88.29(15)	N3	C1	N1	108.9(5)

O5	Cd1	O4	88.29(15)	N3	C1	N4	132.5(5)
O5	Cd1	N1[1]	172.33(15)	N1	C1	N4	118.5(5)
O5	Cd1	N1	91.96(15)	C2	C3	C2[1]	112.4(6)
O5[1]	Cd1	N1	172.33(15)	N1	C2	C3	123.6(5)
O5[1]	Cd1	N1[1]	91.96(15)	N2	C2	N1	113.1(5)
O5[1]	Cd1	O5	92.3(2)	N2	C2	C3	123.3(5)
C1	N3	N2	109.8(4)				

[1]+X, 3/2-Y, +Z

Table S17 Torsion Angles for [Cd(DNAMT)(H_2O)$_4$]·2H_2O (5)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cd1	N1	C1	N3	-163.4(3)	N2	N3	C1	N1	1.0(6)
Cd1	N1	C1	N4	16.9(7)	N2	N3	C1	N4	-179.4(5)
Cd1	N1	C2	N2	164.1(3)	C1	N3	N2	C2	-0.8(6)
Cd1	N1	C2	C3	-14.8(8)	C1	N1	C2	N2	0.3(6)
N3	N2	C2	N1	0.3(6)	C1	N1	C2	C3	-178.5(5)
N3	N2	C2	C3	179.1(5)	C2	N1	C1	N3	-0.8(6)
O2	N5	N4	C1	-178.9(4)	C2	N1	C1	N4	179.6(5)
N5	N4	C1	N3	-0.8(9)	C2[1]	C3	C2	N1	57.9(9)
N5	N4	C1	N1	178.8(5)	C2[1]	C3	C2	N2	-120.8(6)
O1	N5	N4	C1	1.1(7)					

[1]+X, 3/2-Y, +Z

Table S18 Bond Lengths for [Fe (BNATO)(H_2O)$_4$]·2H_2O (6)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O5	2.1661(14)	N5	C1	1.347(2)
Fe1	O5[1]	2.1661(14)	N5	C2	1.366(2)
Fe1	O4[1]	2.1258(14)	N1	N2	1.322(2)
Fe1	O4	2.1258(14)	N3	N4	1.362(2)
Fe1	N5	2.1705(16)	N3	C1	1.348(2)
Fe1	N5[1]	2.1705(16)	N4	C2	1.320(2)
O2	N1	1.272(2)	N2	C1	1.366(2)
O1	N1	1.237(2)	C2	C3	1.486(2)

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

Table S19 Bond Angles for [Fe(BNATO)(H_2O)$_4$]·2H_2O (6)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5[1]	Fe1	O5	175.67(7)	C2	N5	Fe1	128.98(13)

O5[1]	Fe1	N5	87.06(5)	O2	N1	N2	122.04(16)
O5	Fe1	N5[1]	87.06(5)	O1	N1	O2	120.80(17)
O5	Fe1	N5	89.77(6)	O1	N1	N2	117.16(16)
O5[1]	Fe1	N5[1]	89.77(6)	C1	N3	N4	110.60(15)
O4	Fe1	O5	94.08(5)	C2	N4	N3	102.79(16)
O4[1]	Fe1	O5	89.19(5)	N1	N2	C1	118.41(16)
O4	Fe1	O5[1]	89.19(5)	N5	C1	N3	108.71(16)
O4[1]	Fe1	O5[1]	94.08(5)	N5	C1	N2	119.28(17)
O4[1]	Fe1	O4	82.13(8)	N3	C1	N2	132.01(17)
O4[1]	Fe1	N5	95.96(6)	N5	C2	C3	127.24(18)
O4[1]	Fe1	N5[1]	175.67(6)	N4	C2	N5	114.52(17)
O4	Fe1	N5	175.67(6)	N4	C2	C3	118.19(18)
O4	Fe1	N5[1]	95.96(6)	O3	C3	C2[1]	119.34(12)
N5	Fe1	N5[1]	86.20(8)	O3	C3	C2	119.34(12)
C1	N5	Fe1	127.48(13)	C2[1]	C3	C2	121.3(2)

1/2-X, 1/2-Y, +Z

Table S20 Torsion Angles for [Fe(BNATO)(H_2O)$_4$]·2H_2O (6)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	N5	C1	N3	175.74(12)	N3	N4	C2	C3	-177.81(14)
Fe1	N5	C1	N2	-4.6(3)	N4	N3	C1	N5	-0.2(2)
Fe1	N5	C2	N4	-175.58(12)	N4	N3	C1	N2	-179.80(19)
Fe1	N5	C2	C3	2.0(3)	N4	C2	C3	O3	-3.57(19)
O2	N1	N2	C1	-0.4(3)	N4	C2	C3	C2[1]	176.43(19)
O1	N1	N2	C1	179.39(17)	C1	N5	C2	N4	-0.1(2)
N5	C2	C3	O3	178.96(14)	C1	N5	C2	C3	177.47(15)
N5	C2	C3	C2[1]	-1.04(14)	C1	N3	N4	C2	0.1(2)
N1	N2	C1	N5	178.12(16)	C2	N5	C1	N3	0.1(2)
N1	N2	C1	N3	-2.3(3)	C2	N5	C1	N2	179.84(17)

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

Table S21 Hydrogen bond lengths / Å and angles / ° of H_2DNAMT (1)

D-H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
N2-H2···N3	0.88	1.95	2.819(9)	173
N4-H4···O2	0.88	2.11	2.594(8)	114
N4-H4···O4	0.88	1.97	2.771(9)	150
N6-H6···O3	0.88	2.19	2.628(8)	110
N6-H6···N5	0.88	2.4	3.186(9)	149
N9-H9···N8	y0.88	2.18	2.871(9)	135

Table S22 Hydrogen bond lengths /Å and angles /° of $[Co(DNAMT)(H_2O)_4]\cdot 2H_2O$ (2)

D-H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O1-H1···O4	0.84	1.89	2.720(2)	170
O2-H2A···O6	0.84	1.81	2.648(3)	177
O2-H2B···N4	0.84	2.07	2.839(2)	153
O3-H3···N2	0.84	2.48	3.303(3)	166
N3-H3A···O5	0.85	2.12	2.555(2)	111
N3-H3A···O4	0.85	1.99	2.797(2)	159
O6-H6A···N2	0.84	2.02	2.849(3)	167
O6-H6B···O5	0.84	2.05	2.865(3)	162

Table S23 Hydrogen bond lengths /Å and angles /° of $[Ni(DNAMT)(H_2O)_4]\cdot 2H_2O$ (3)

D-H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
N3-H3···O2	0.8500	2.1700	2.600(2)	111.00
N3-H3···O5	0.8500	2.0700	2.854(2)	154.00
O4-H4A···O6	0.8400	1.9700	2.803(2)	174.00
O4-H4B···N2	0.8400	1.9200	2.684(2)	150.00
O5-H5A···O1	0.8400	2.5500	3.070(2)	121.00
O5-H5A···O2	0.8400	1.9900	2.8258(19)	176.00
O5-H5A···N1	0.8400	2.5800	3.320(2)	148.00
O5-H5B···O7	0.8400	1.8400	2.678(2)	172.00
O6-H6A···O7	0.8400	2.0300	2.867(2)	172.00
O6-H6B···O3	0.8400	2.4300	3.008(2)	126.00
O6-H6B···N4	0.8400	2.3400	3.052(2)	143.00
O7-H7A···O6	0.8400	2.2400	3.065(2)	168.00
O7-H7B···O6	0.8400	2.1500	2.947(2)	158.00

Table S24 Hydrogen bond lengths /Å and angles /° of $[Zn(DNAMT)(H_2O)_4]\cdot 2H_2O$ (4)

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠DHA**
N3–H3···O2	0.8500	2.0800	2.552(3)	114.00
N3–H3···O1	0.8500	2.0000	2.796(3)	155.00
O3–H3C···N4	0.8400	2.0300	2.855(4)	166.00
O3–H3D···O2	0.8400	2.0400	2.871(4)	173.00

O4–H4···O1	0.8400	1.9000	2.741(3)	174.00
O5–H5A···O3	0.8400	1.8000	2.633(4)	171.00
O5–H5B···N2	0.8400	2.0800	2.858(3)	154.00
O6–H6···N4	0.8400	2.6000	3.335(4)	147.00

Table S25 Hydrogen bond lengths /Å and angles /º of [Cd(DNAMT)(H_2O)$_4$]·2H_2O (5)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O6A-H6A···O1	0.8400	2.0800	2.844(11)	151.00
O6A-H6A···N2	0.8400	2.0700	2.903(10)	171.00
N3- H3···O1	0.8600	2.0800	2.560(6)	114.00
N3- H3···O2	0.8600	2.0400	2.837(6)	154.00
O3- H3A···O2	0.8400	1.9200	2.740(4)	166.00
O5- H5A···O6A	0.8400	1.8400	2.671(11)	168.00
O5- H5B···N4	0.8400	2.1200	2.911(6)	158.00

Table S26 Hydrogen bond lengths / Å and angles / º of [Fe(BNATO)(H_2O)$_4$]·2H_2O (6)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O3-H3···N5	0.84	2.58	3.358(3)	155
O4-H4···O2	0.84	1.91	2.741(2)	169
N4-H4A···O1	0.88	2.04	2.544(3)	115
N4-H4A···O2	0.88	1.97	2.773(3)	152
O5-H5A···N2	0.84	2.05	2.846(3)	157
O5-H5B···O6	0.84	1.84	2.648(7)	162
O6-H6A···N5	0.84	2.16	2.927(6)	151
O6-H6B···O1	0.84	2.32	2.867(6)	123

Table S27 The first exothermic decomposition peak temperatures tested at different heating rates of compounds 1- 6

compound	The first exothermic decomposition peak temperatures (°C)			
	5°C·min^{-1}	10°C·min^{-1}	15°C·min^{-1}	20°C·min^{-1}
1	223.8	230.4	233.7	234.6
2	203.7	211.8	215.8	217.2
3	211.7	221.1	227.3	231.3
4	205.7	215.9	222.9	227.4
5	230.7	245.6	251.5	256.0
6	207.0	223.6	228.4	235.7

Figure S1 The packing diagram, hydrogn bonds and π-π interactions of [Ni(DNAMT)

$(H_2O)_4]\cdot 2H_2O$ (3)

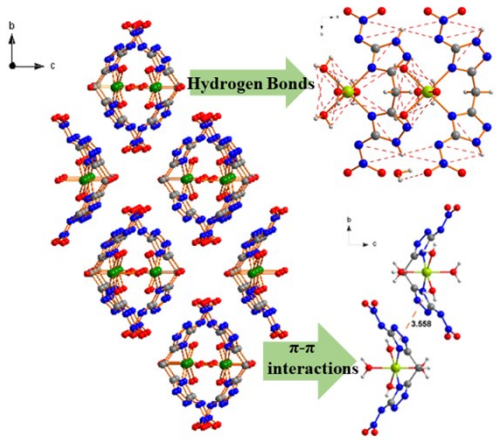

Figure S2 The packing diagram, hydrogn bonds and π-π interactions of [Zn(DNAMT)$(H_2O)_4]\cdot 2H_2O$ (4)

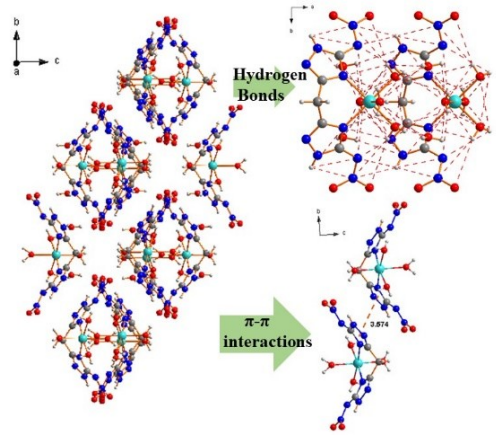

Figure S3 The packing diagram, hydrogn bonds and π-π interactions of [Cd(DNAMT)$(H_2O)_4]\cdot 2H_2O$ (5)

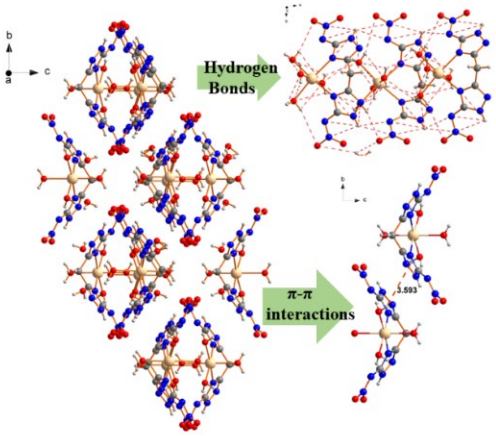

Figure S4 The hydrogen bonds of compound 6 viewed along c axis

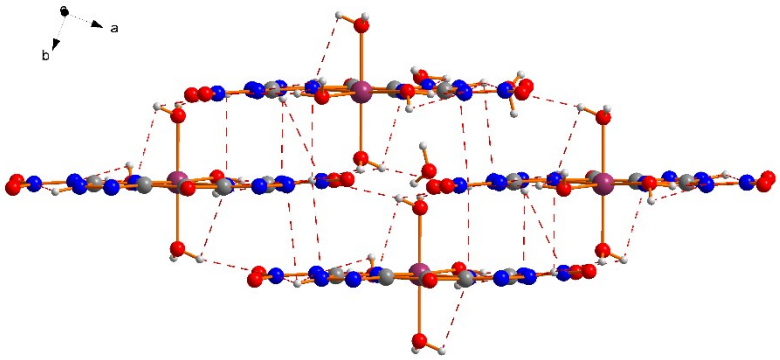

Figure S5 TG-DTG curves of $[Co(DNAMT)(H_2O)_4]\cdot 2H_2O$ (2)

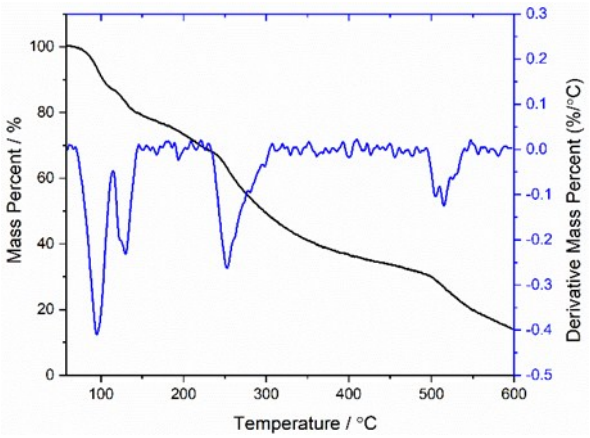

Figure S6 TG-DTG curves of $[Ni(DNAMT)(H_2O)_4]\cdot 2H_2O$ (3)

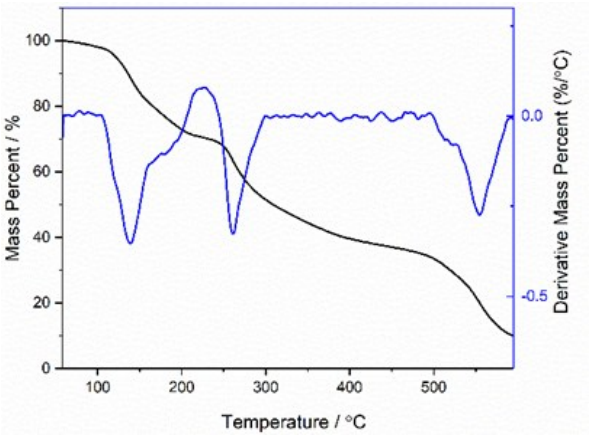

Figure S7 TG-DTG curves of $[Zn(DNAMT)(H_2O)_4]\cdot 2H_2O$ (4)

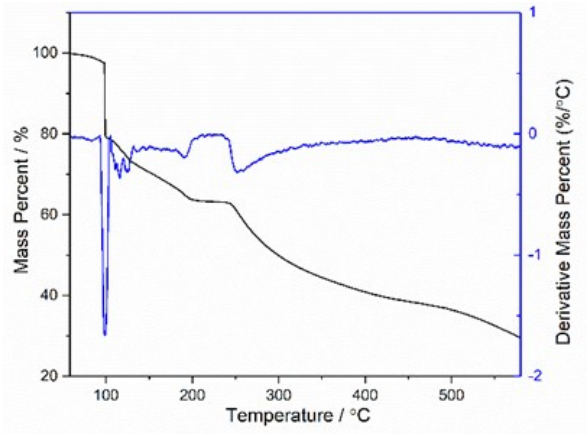

Figure S8 TG-DTG curves of $[Cd(DNAMT)(H_2O)_4]\cdot 2H_2O$ (5)

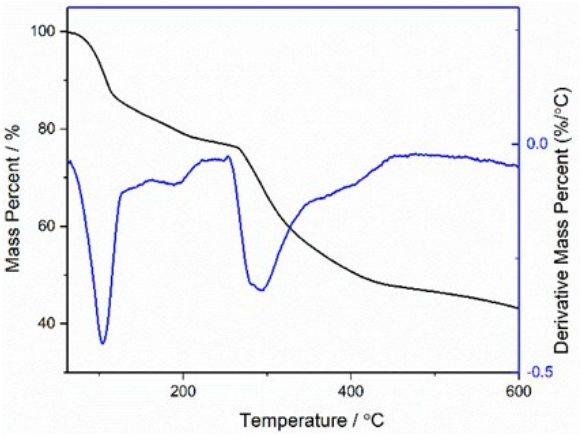

Figure S9 TG-DTG curves of $[Fe(BNATO)(H_2O)_4]\cdot 2H_2O$ (6)