Supporting Information

Energetic metal−organic frameworks achieved from furazan and triazole ligand: synthesis, crystal structure, thermal stability and energetic performance

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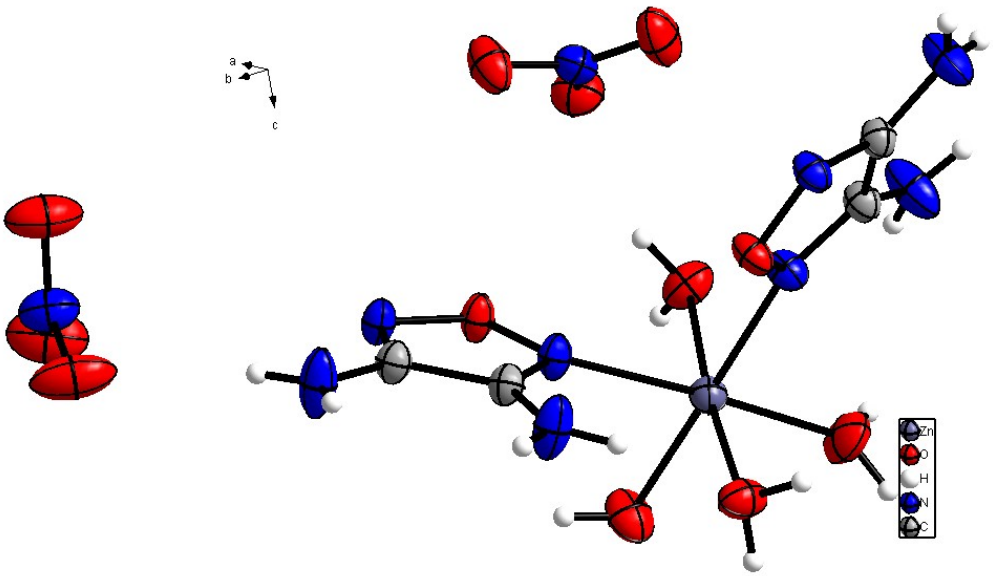


Supplementary Figure 1. Single-crystal X-ray structure of complex **1**.

Supplementary Table 1. Crystal data and structure refinement for complex **1**.

CCDC	2104532
Formula	$C_2H_{13}N_6O_{11}Zn$
Mr	362.55
crystal system	monoclinic
space group	$P2_1/n$
a [Å]	11.5599(2)
b [Å]	8.4029(2)
c [Å]	13.1796(4)
α [Å]	90
β [Å]	98.3160(10)
γ [Å]	90
V [Å^3]	1266.76(5)
Z	4
T [K]	296.15
ρ[g·cm^{-3}]	1.901
μ[mm^{-1}]	2.010
F(000)	740.0
θ [°]	5.066 to 52.198
index range	$-14 \le h \le 14$
	$-10 \le k \le 10$
	$-16 \le l \le 16$
reflections collected	14447
independent reflections	2520 [R_{int} = 0.0227, R_{sigma} = 0.0145]
data/restraints/paraneters	2520/18/222
GOF on F^2	1.086
R_1 [I>2σ(I)]	0.0231
wR_2 [I>2σ(I)]	0.0619
R_1(all data)	0.0256
wR_2(all data)	0.0634
largest diff. peak and hole [e Å^{-3}]	0.29/-0.84

Supplementary Table 2. Bond Lengths for complex **1**.

Bond	Length/Å
Zn01-O003	2.0942(14)
Zn01-O004	2.0618(14)
Zn01-O006	2.0511(14)
Zn01-O008	2.0930(15)
Zn01-N009	2.1424(15)
Zn01-N00A[1]	2.1990(15)
O1-N009	1.3917(19)
O1-N00A	1.3959(19)
O005-N00E	1.252(2)
O007-N00E	1.242(2)
N009-C00H	1.297(2)
N00A-C00J	1.300(2)
O00B-N00E	1.243(2)
O00C-N00F	1.230(11)
O00D-N00F	1.220(3)
N00F-O00K	1.266(7)
N00F-O2	1.243(9)
N00F-O00L	1.243(6)
N00G-C00H	1.335(3)
C00H-C00J	1.451(3)
N00I-C00J	1.331(3)

Supplementary Table 3. Bond angles for complex **1**.

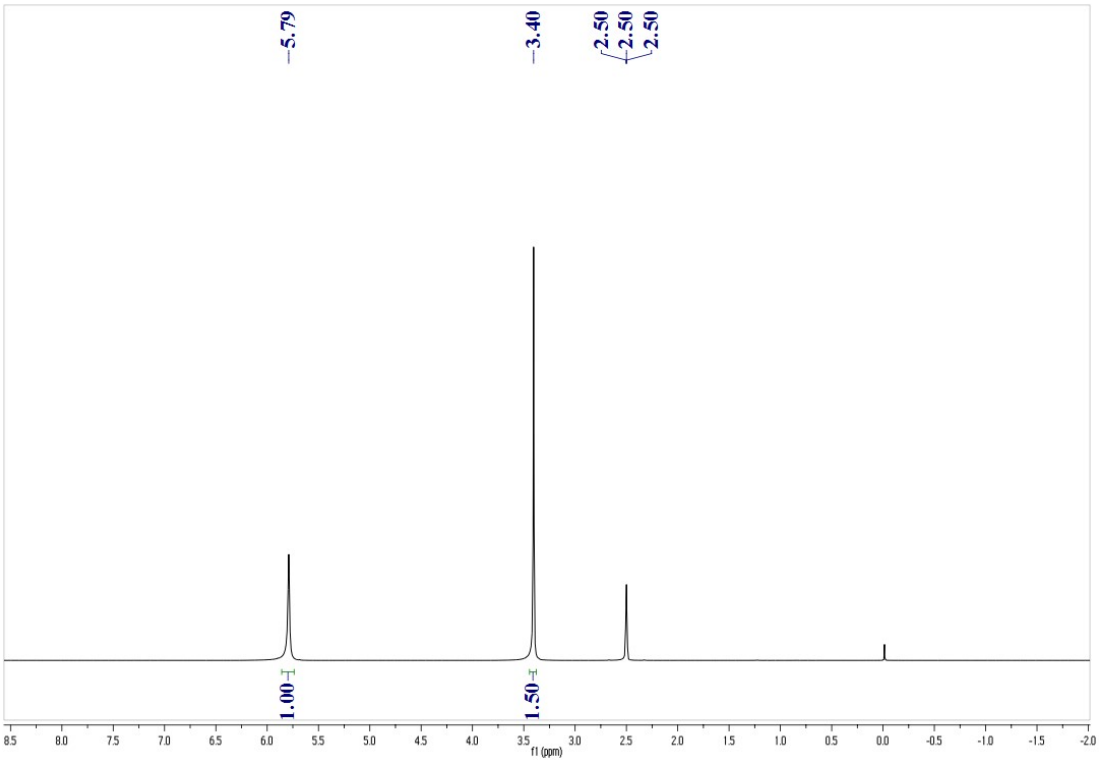
Bond	Angle/°
O003-Zn01-N009	87.17(6)
O003-Zn01-N00A[1]	94.16(6)
O004-Zn01-O003	174.85(6)
O004-Zn01-O008	91.78(7)
O004-Zn01-N009	89.42(6)
O004-Zn01-N00A[1]	89.78(6)
O006-Zn01-O003	94.56(6)
O006-Zn01-O004	88.96(6)
O006-Zn01-O008	88.81(7)
O006-Zn01-N009	177.64(6)
O006-Zn01-N00A[1]	86.82(6)
O008-Zn01-O003	84.55(6)
O008-Zn01-N009	92.96(7)
O008-Zn01-N00A[1]	175.33(7)
N009-Zn01-N00A[1]	91.46(6)
N009-O1-N00A	108.96(12)
O1-N009-Zn01	116.00(10)
C00H-N009-Zn01	136.70(13)
C00H-N009-O1	107.30(14)
C00J-N00A-O1	107.00(14)
O007-N00E-O00B	120.55(18)
O00B-N00E-O005	119.18(18)
O00C-N00F-O00K	117.3(12)
O00D-N00F-O00C	124.1(11)
O00D-N00F-O00K	118.0(6)
O00D-N00F-O2	120.0(9)
O00D-N00F-O00L	119.2(5)
O2-N00F-O00L	119.9(10)
N009-C00H-N00G	125.81(18)
N009-C00H-C00J	108.35(16)
N00G-C00H-C00J	125.79(18)
N00A-C00J-C00H	108.38(16)
N00A-C00J-N00I	125.56(18)
N00I-C00J-C00H	126.06(18)

Supplementary Table 4. Torsion angles for complex **1**.

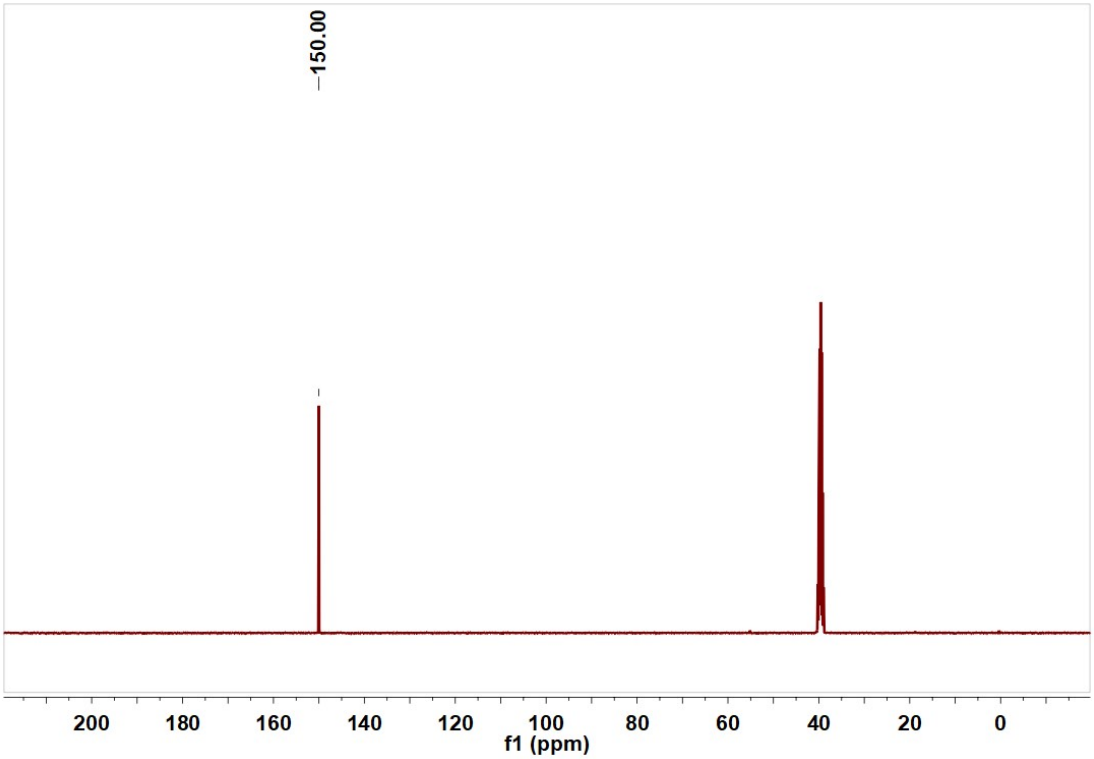
Bond	Torsion angle/°
Zn01-N009-C00H-N00G	2.5(3)
Zn01-N009-C00H-C00J	-179.75(14)
Zn01[1]-N00A-C00J-C00H	-160.20(14)
Zn01[1]-N00A-C00J-N00I	19.6(3)
O1-N009-C00HN00G	-177.3(2)
O1-N009-C00H-C00J	0.4(2)
O1-N00A-C00J-C00H	-0.7(2)
O1-N00A-C00J-N00I	179.1(2)
N009-O1-N00A-Zn01[1]	165.40(11)
N009-O1-N00A-C00J	1.02(19)
N009-C00H-C00J-N00A	0.2(2)
N009-C00H-C00J-N00I	-179.6(2)
N00A-O1-N009-Zn01	179.24(11)
N00A-O1-N009-C00H	-0.90(19)
N00G-C00H-C00J-N00A	177.9(2)
N00G-C00H-C00J-N00I	-1.9(4)

Supplementary Table 5. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å2×10^3) for complex **1**.

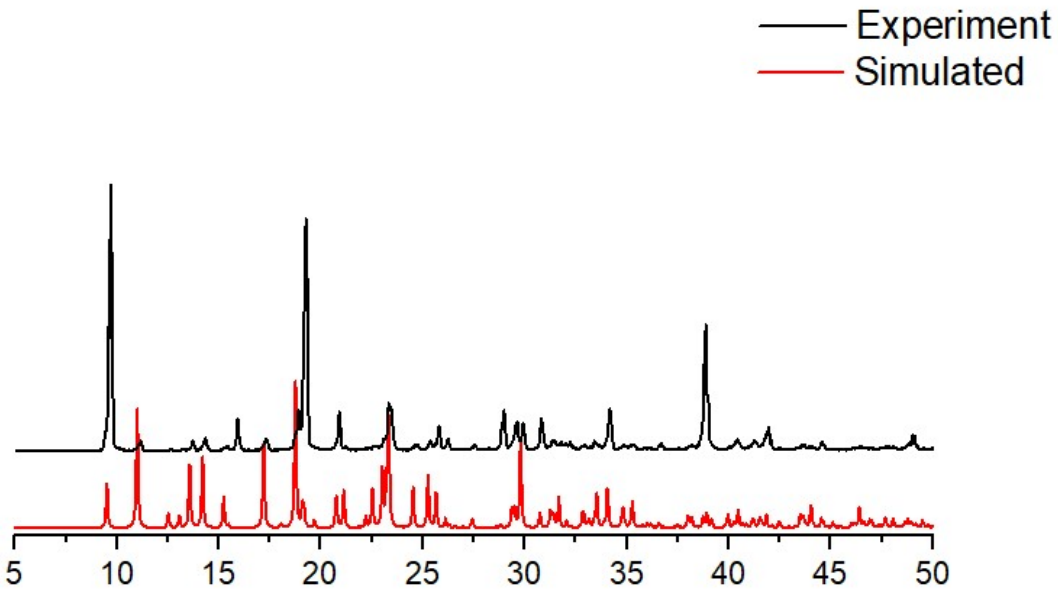
Atom	x	y	z	U(eq)
H00A	5138.01	9985.57	7897.06	51
H00B	4401.18	9240.51	8444.55	51
H00C	3514.89	7247.56	4855.83	51
H00D	3396.26	5930.43	5413.12	51
H00E	4649.47	10689.99	6102.99	60
H00F	3478.64	10646.78	5811.14	60
H00G	6309.69	7663.08	6758.13	66
H00H	5870.53	7061.19	5838.01	66
H00K	3710(20)	1960(30)	9340(20)	37(7)
H00L	4770(20)	2590(30)	9410(20)	36(7)
H00I	5920(20)	6110(40)	8310(20)	50(8)
H00J	6020(30)	4670(40)	8830(20)	54(8)



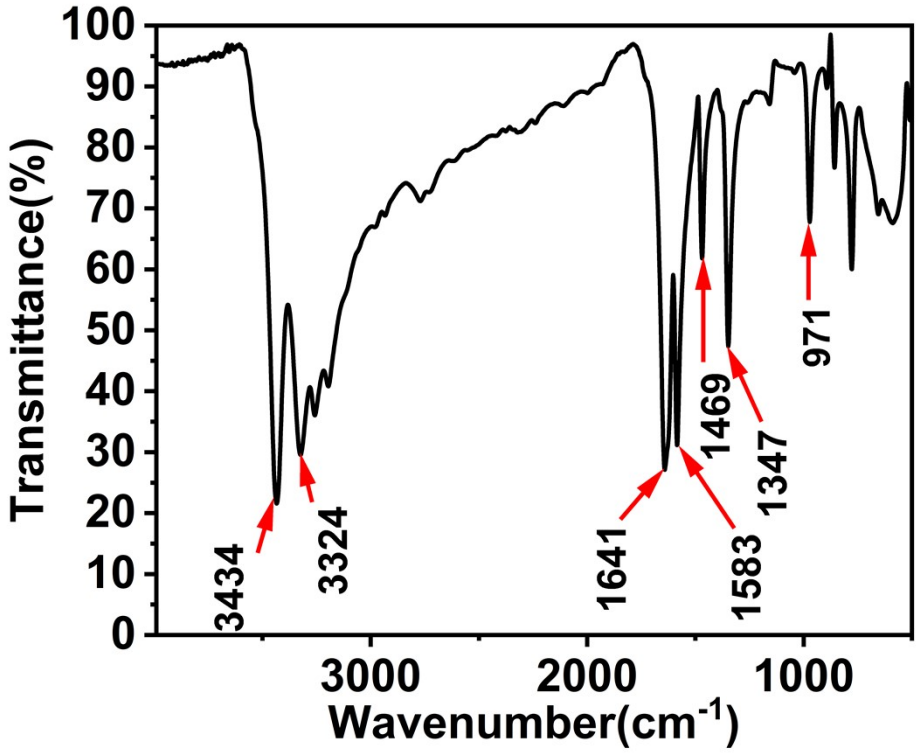
Supplementary Figure 2. ^{1}H NMR spectrum of complex **1**.



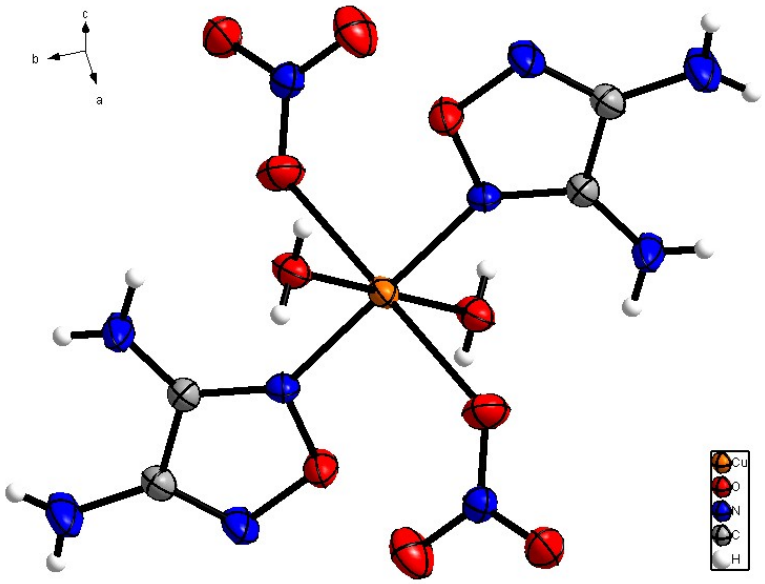
Supplementary Figure 3. ^{13}C NMR spectrum of complex **1**.



Supplementary Figure 4. PXRD patterns of complex **1**.



Supplementary Figure 5. IR spectrum of complex **1**.



Supplementary Figure 6. Single-crystal X-ray structure of complex **2**.

Supplementary Table 6. Crystal data and structure refinement for complex **2**.

Formula	$C_4H_{12}CuN_{10}O_{10}$
Mr	423.78
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	6.3745(3)
b [Å]	16.2753(9)
c [Å]	7.2274(4)
α [Å]	90
β [Å]	109.429(2)
γ [Å]	90
V [Å^3]	707.12(7)
Z	2
T [K]	296.15
ρ[g·cm^{-3}]	1.990
μ[mm^{-1}]	1.628
F(000)	430.0
θ [°]	6.48 to 55.18
index range	$-8 \le h \le 7$
	$-16 \le k \le 21$
	$-9 \le l \le 6$
reflections collected	3928
independent reflections	1632 [R_{int} = 0.0519, R_{sigma} = 0.0343]
data/restraints/paraneters	1632/0/139
GOF on F_2	1.023
R_1 [I>2σ(I)]	0.0263
wR_2 [I>2σ(I)]	0.0670
R_1(all data)	0.0317
wR_2(all data)	0.0690
largest diff. peak and hole [e Å^{-3}]	0.42/-0.33

Supplementary Table 7. Bond Lengths for complex **2**.

Bond	Length/Å
Cu01-O1	1.9564(13)
Cu01-O1[1]	1.9564(13)
Cu01-N006[1]	1.9863(14)
Cu01-N006	1.9862(14)
O003-N006	1.4065(17)
O003-N009	1.3944(19)
O004-N008	1.2639(19)
Cu01-N006[1]	1.9858(13)
O005-N008	1.2384(18)
N006-C00C	1.311(2)
O007-N008	1.2254(19)
N009-C00D	1.286(2)
N00A-C00C	1.330(2)
N00B-C00D	1.352(2)
C00C-C00D	1.449(2)

Supplementary Table 8. Bond angles for complex **2**.

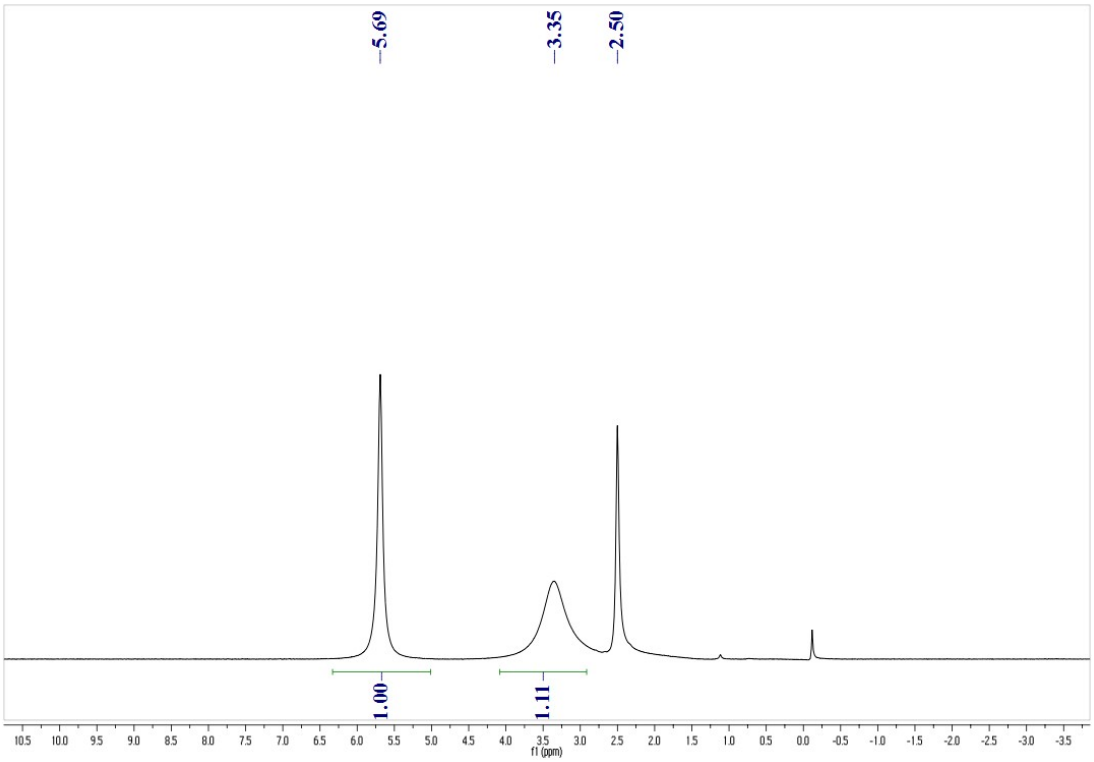
Bond	Angle/°
O1-Cu01-O1[1]	180.0
O1[1]-Cu01-N006	88.15(6)
O1-Cu01-N006	91.85(6)
O1[1]-Cu01-N006[1]	91.85(6)
O1-Cu01-N006[1]	88.15(6)
N006-Cu01-N006[1]	180.0
N009-O003-N006	109.11(12)
O003-N006-Cu01	116.56(10)
C00C-N006-Cu01	136.65(11)
C00C-N006-O003	106.66(12)
O005-N008-O004	118.47(15)
O007-N00-O004	120.12(15)
O007-N008-O005	121.39(15)
C00D-N009-O003	106.81(13)
N006-C00C-N00A	126.37(15)
N00A-C00C-C00D	126.01(16)
N006-C00C-C00D	107.62(14)
N009-C00D-N00B	125.09(17)
N009-C00D-C00C	109.77(15)
N00B-C00D-C00C	125.12(17)

Supplementary Table 9. Torsion angles for complex **2**.

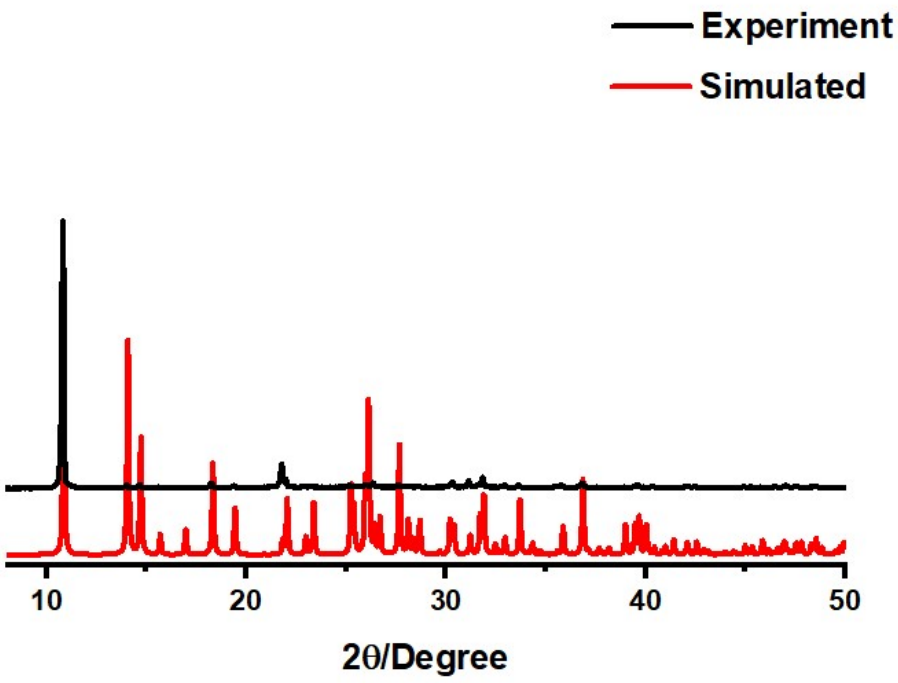
Bond	Torsion angle/°
Cu01-N006-C00C-N00A	3.4(3)
Cu01-N006-C00C-C00D	-177.15(13)
O003-N006-C00C-N00A	178.92(18)
O003-N006-C00C-C00D	-1.65(19)
O003-N009 C00D-N00B	-178.33(18)
O003-N009-C00D-C00C	0.2(2)
N006-O003-N009-C00D	-1.26(19)
N006-C00C-C00D-N009	0.9(2)
N006-C00C-C00D-N00B	179.50(19)
N009-O003-N006-Cu01	178.39(10)
N009-O003-N006-C00C	1.85(19)
N00A-C00C-C00D-N009	-179.63(19)
N00A-C00C-C00D-N00B	-1.1(3)

Supplementary Table 10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for complex **2**.

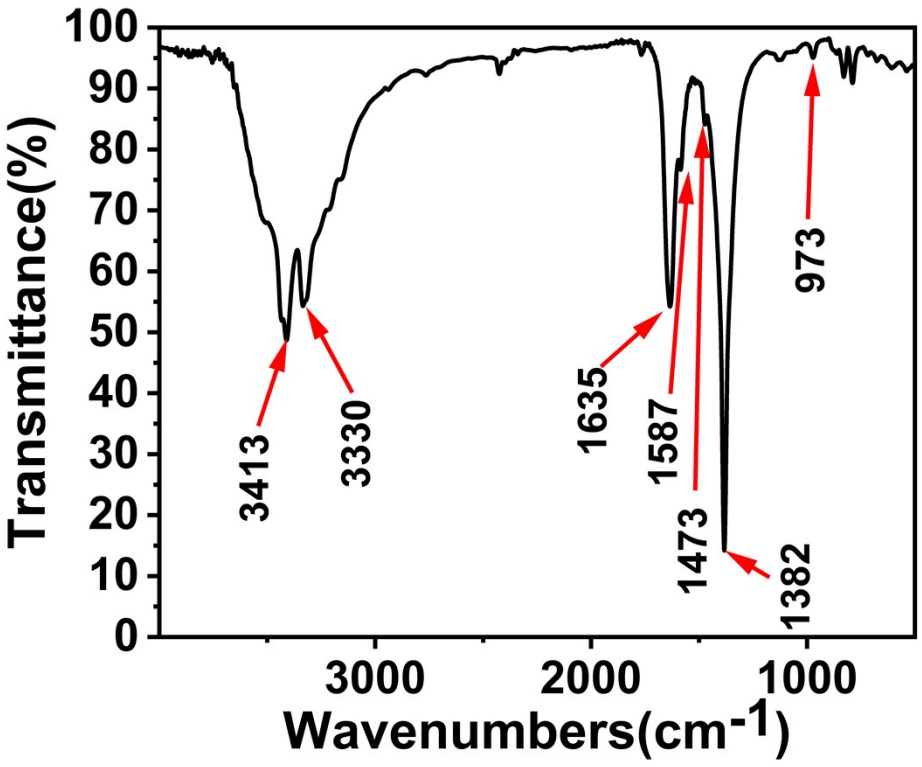
Atom	x	y	z	U(eq)
H00A	7070(40)	3121(14)	56O0(30)	31(6)
H00C	2820(40)	1595(15)	5660(40)	40(7)
H00B	6130(40)	2390(17)	5640(30)	37(7)
H00D	710(50)	1693(15)	5300(30)	36(6)
H1A	1230(50)	5234(17)	2890(40)	47(8)
H1B	2440(50)	5565(18)	2180(40)	55(9)



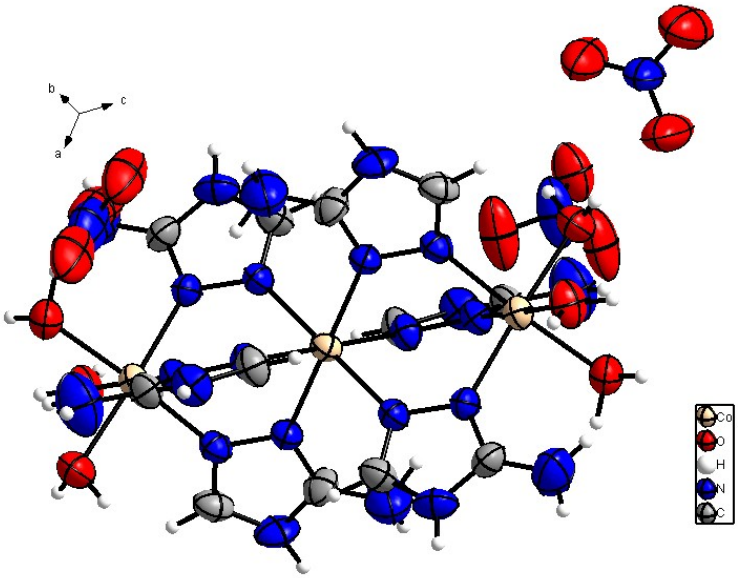
Supplementary Figure 7. ^{1}H NMR spectrum of complex **2**.



Supplementary Figure 8. PXRD patterns of complex **2**.



Supplementary Figure 9. IR spectrum of complex **2**.



Supplementary Figure 10. Single-crystal X-ray structure of complex **3**.

Supplementary Table 11. Crystal data and structure refinement for complex **3**.

Formula	$C_{12}H_{40}Co_3N_{30}O_{26}$
Mr	1197.53
crystal system	monoclinic
space group	$P2_1/n$
a [Å]	13.2909(18)
b [Å]	12.1643(16)
c [Å]	14.587(2)
α [Å]	90
β [Å]	113.269(7)
γ [Å]	90
V [Å^3]	2166.5(6)
Z	2
T [K]	296(2)
ρ[g·cm^{-3}]	1.836
μ[mm^{-1}]	1.258
F(000)	1222.0
θ [°]	8.684 to 55.258
index range	$-17 \le h \le 17$
	$-15 \le k \le 11$
	$-17 \le l \le 19$
reflections collected	10807
independent reflections	4938 [Rint = 0.0376, Rsigma = 0.0608]
data/restraints/paraneters	4938/275/391
GOF on F^2	1.030
R_1 [I>2σ(I)]	0.0716
wR_2 [I>2σ(I)]	0.2025
R_1(all data)	0.1206
wR_2(all data)	0.2349
largest diff. peak and hole [e Å^{-3}]	1.94/-0.54

Supplementary Table 12. Bond Lengths for complex **3**.

Bond	Length/Å
Co01-N008[1]	2.132(4)
Co01-N008	2.132(4)
Co01-N007[1]	2.124(4)
Co01-N007	2.124(4)
Co01-N009	2.170(5)
Co01-N0091	2.170(5)
Co02-N006	2.095(4)
Co02-O4	2.093(4)
Co02-N00B	2.095(4)
Co02-N00A	2.106(4)
Co02-O3	2.121(4)
Co02-O	2.133(4)
N006-C00H	1.326(7)
N006-N008	1.393(6)
N007-C00G	1.306(7)
N007-N00A	1.402(6)
N008-C00J	1.307(7)
N009-C00K	1.310(7)
N009-N00B	1.363(6)
N00A-C00I	1.306(7)
N00B-C00P	1.297(7)
N00C-C00J	1.344(8)
N00C-C00H	1.342(8)
N00D-C00P	1.334(8)
N00D-C00K	1.354(8)
N00E-C00G	1.327(8)
N00E-C00I	1.323(8)
C00G-N00V	1.316(9)
C00H-N00T	1.322(9)
N00L-O00O	1.208(7)
N00L-O00S	1.239(8)
N00L-O00M	1.222(8)
C00P-N00Y	1.330(10)
N00U-O00Z	1.130(12)
N00U-O00W	1.173(10)
N00U-O00X	1.478(16)
N00U-O00Y	1.471(19)
N00U-O7	1.197(18)
N3-O5	1.235(10)
N3-O2	1.239(10)
N3-O1	1.257(11)

N3-O1A	1.234(18)
N3-O2A	1.202(17)
N3-O5A	1.230(19)

Supplementary Table 13. Bond angles for complex **3**.

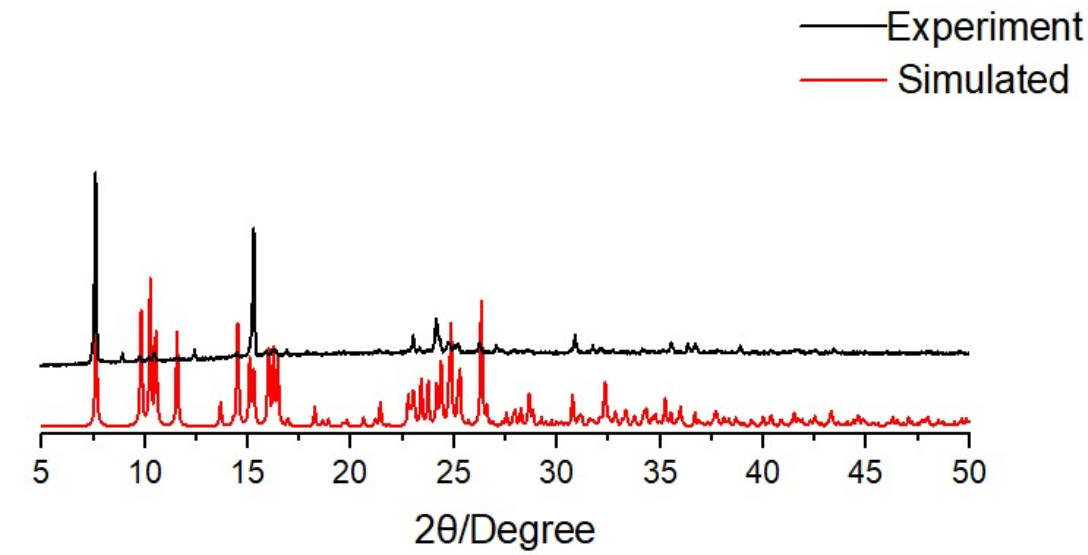
Bond	Angle/°	Bond	Angle/°
N007[1]-Co01-N007	180	N00B-N009-Co01	124.8(3)
N007-Co01-N008	90.04(17)	C00K-N009-Co01	128.4(4)
N007-Co01-N008[1]	89.97(17)	C00K-N009-N00B	106.4(4)
N007[1]-Co01-N008	89.97(17)	N007-N00A-Co02	124.2(3)
N007[1]-Co01-N008[1]	90.03(17)	C00I-N00A-Co02	130.2(4)
N007-Co01-N009	90.38(17)	C00I-N00A-N007	105.6(5)
N007-Co01-N009[1]	89.62(17)	N009-N00B-Co02	123.4(3)
N007[1]-Co01-N009[1]	90.38(17)	C00P-N00B-Co02	129.3(4)
N007[1]-Co01-N009	89.62(17)	C00P-N00B-N009	107.2(4)
N008-Co01-N008[1]	180	C00H-N00C-C00J	106.6(5)
N008[1]-Co01-N009	89.50(17)	C00P-N00D-C00K	105.9(5)
N008-Co01-N009	90.50(17)	C00I-N00E-C00G	105.9(5)
N008-Co01-N009[1]	89.50(17)	N007-C00G-N00E	111.0(5)
N008[1]-Co01-N009[1]	90.50(17)	N007-C00G-N00V	128.6(6)
N009-Co01-N009[1]	180	N00V-C00G-N00E	120.4(6)
O4-Co02-O	86.65(19)	N006-C00H-N00C	110.0(5)
O4-Co02-O3	88.40(19)	N00T-C00H-N006	127.2(6)
O4-Co02-N006	91.70(18)	N00T-C00H-N00C	122.7(6)
O4-Co02-N00A	90.80(18)	N00A-C00I-N00E	111.4(5)
O4-Co02-N00B	174.89(18)	N008-C00J-N00C	109.8(5)
O3-Co02-O	87.15(17)	N009-C00K-N00D	109.9(5)
N006-Co02-O	90.18(17)	O00M-N00L-O00S	119.9(6)
N006-Co02-O3	177.31(17)	O00O-N00L-O00M	122.1(6)
N006-Co02-N00A	92.72(17)	O00O-N00L-O00S	117.6(7)
N006-Co02-N00B	92.86(17)	N00B-C00P-N00D	110.7(5)
N00A-Co02-O	176.19(17)	N00B-C00P-N00Y	129.8(6)
N00A-Co02-O3	89.96(17)	N00Y-C00P-N00D	119.3(6)
N00B-Co02-O	91.03(18)	O00W-N00U-O00X	110.9(11)
N00B-Co02-O3	86.94(18)	O00Z-N00U-O00W	136.8(13)
N00B-Co02-N00A	91.29(17)	O00Z-N00U-O00X	110.9(11)
N008-N006-Co02	123.9(3)	O00{-N00U-O7	112(2)
C00H-N006-Co02	130.2(4)	O00{-N00U-O00Y	161(2)
C00H-N006-N008	105.9(4)	O7-N00U-O00Y	86.2(17)
N00A-N007-Co01	124.5(3)	O5-N3-O2	125.1(10)
C00G-N007-Co01	129.4(4)	O5-N3-O1	114.0(12)
C00G-N007-N00A	106.0(4)	O2-N3-O1	119.2(9)
N006-N008-Co01	125.0(3)	O2A-N3-O5A	128(4)
C00J-N008-Co01	127.2(4)	O2A-N3-O1A	110(2)
C00J-N008-N006	107.7(4)	O5A-N3-O1A	112(4)

Supplementary Table 14. Torsion angles for complex **3**.

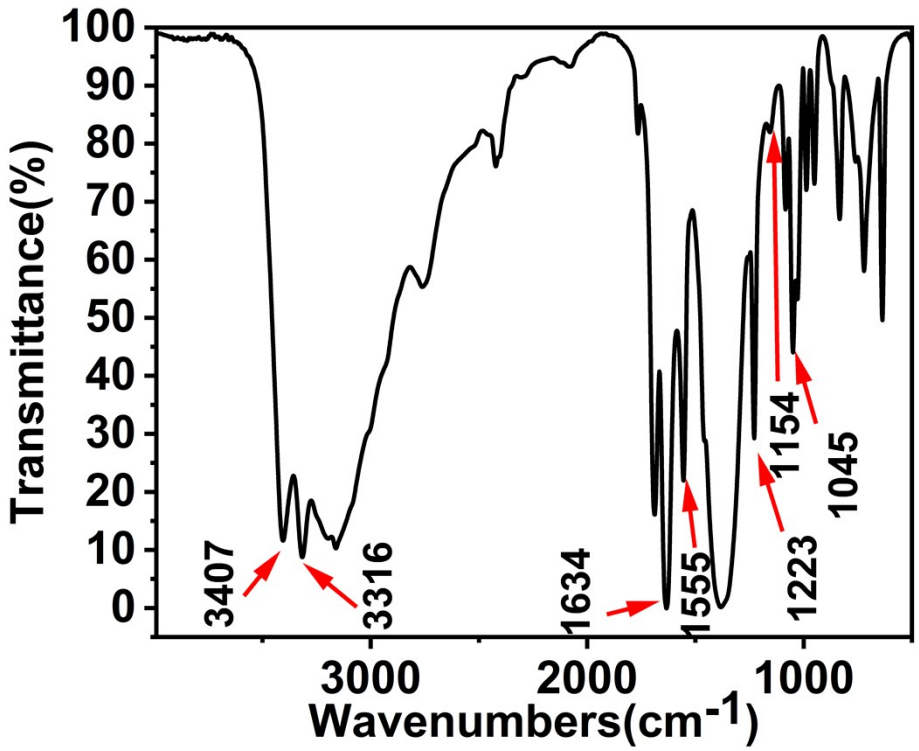
Bond	Torsion angle/°
Co01-N007-N00A-Co02	-0.7(6)
Co01-N007-N00A-C00I	179.2(4)
Co01-N007-C00G-N00E	-179.5(4)
Co01-N007-C00G-N00V	-2.5(11)
Co01-N008-C00J-N00C	176.6(4)
Co01-N009-N00B-Co02	4.4(6)
Co01-N009-N00B-C00P	-171.4(4)
Co01-N009-C00K-N00D	171.2(4)
Co02-N006-N008-Co01	5.6(6)
Co02-N006-N008-C00J	-177.9(4)
Co02-N006-C00H-N00C	177.1(4)
Co02-N006-C00H-N00T	-0.6(10)
Co02-N00A-C00I-N00E	179.6(4)
Co02-N00B-C00P-N00D	-176.6(4)
Co02-N00B-C00P-N00Y	9.1(11)
N006-N008-C00J-N00C	0.3(6)
N007-N00A-C00I-N00E	-0.3(7)
N008-N006-C00H-N00C	-1.4(6)
N008-N006-C00H-N00T	-179.1(7)
N009-N00B-C00P-N00D	-1.1(6)
N009-N00B-C00P-N00Y	-175.4(8)
N00A-N007-C00G-N00E	-1.4(7)
N00A-N007-C00G-N00V	175.6(7)
N00B-N009-C00K-N00D	-1.3(6)
C00G-N007-N00A-Co02	-178.9(4)
C00G-N007-N00A-C00I	1.1(6)
C00G-N00E-C00I-N00A	-0.5(7)
C00H-N006-N008-Co01	-175.8(4)
C00H-N006-N008-C00J	0.7(6)
C00H-N00C-C00J-N008	-1.1(7)
C00I-N00E-C00G-N007	1.2(7)
C00I-N00E-C00G-N00V	-176.0(7)
C00J-N00C-C00H-N006	1.6(7)
C00J-N00C-C00H-N00T	179.4(7)
C00K-N009-N00B-Co02	177.3(4)
C00K-N009-N00B-C00P	1.5(6)
C00K-N00D-C00P-N00B	0.3(7)
C00K-N00D-C00P-N00Y	175.3(7)
C00P-N00D-C00K-N009	0.7(7)

Supplementary Table 15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for complex **3**.

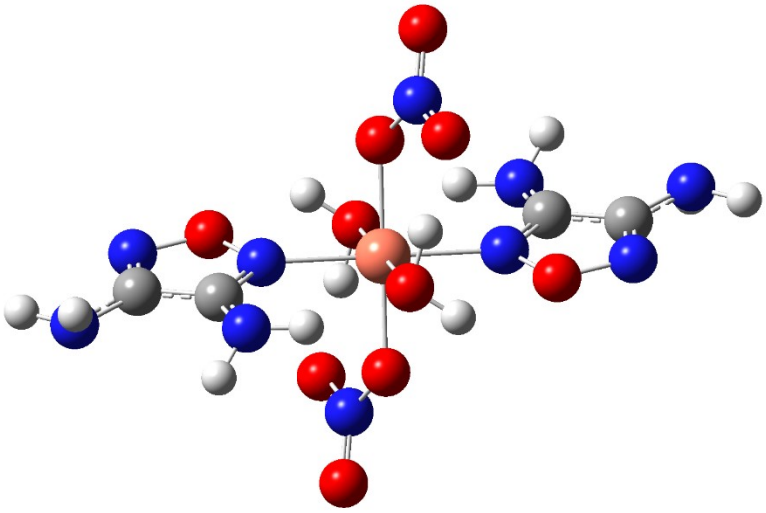
Atom	x	y	z	U(eq)
H4A	3018.8	1583.47	6896.72	96
H4B	3075.65	1509.67	5999.24	96
HA	5838.43	2291.85	8105.16	90
HB	4887.35	1876.65	8215.3	90
H3A	3036.69	4656.36	7419.84	94
H3B	2654.97	3617.32	7469.31	94
H00C	6291.85	1076.24	5304.26	68
H00D	6279.37	6698.23	8462.46	64
H00I	1541.81	3858.76	5418.96	61
H00J	6162.92	2830.41	4522.38	62
H00K	6341.87	6749.95	6835.52	62
H00A	5074.97	943.71	6997.95	112
H00B	5721.64	258.01	6580.48	112
H00F	2838.68	5703.13	3131.93	121
H00G	1682.76	5691.94	2864.21	121
H00H	5051.01	4453.65	8949.94	133
H00L	5601.32	5504.95	9397.01	133
H00E	1000(40)	5080(50)	3820(40)	70(20)
H6A	7777.5	8356.43	11810.34	134
H6B	8023.56	8556.46	12781.25	134



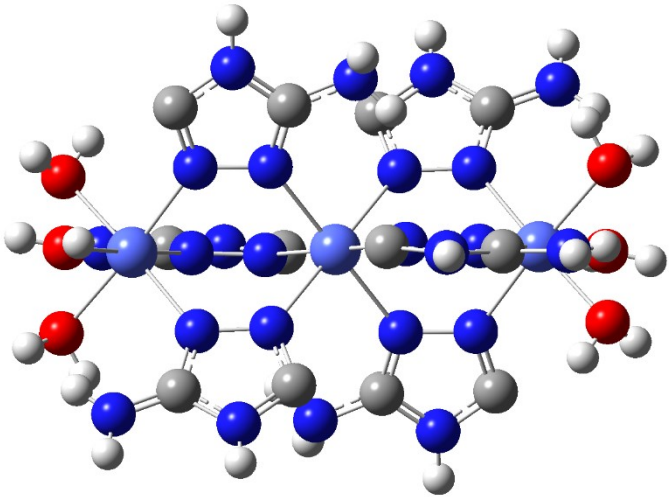
Supplementary Figure 11. PXRD patterns of complex **3**.



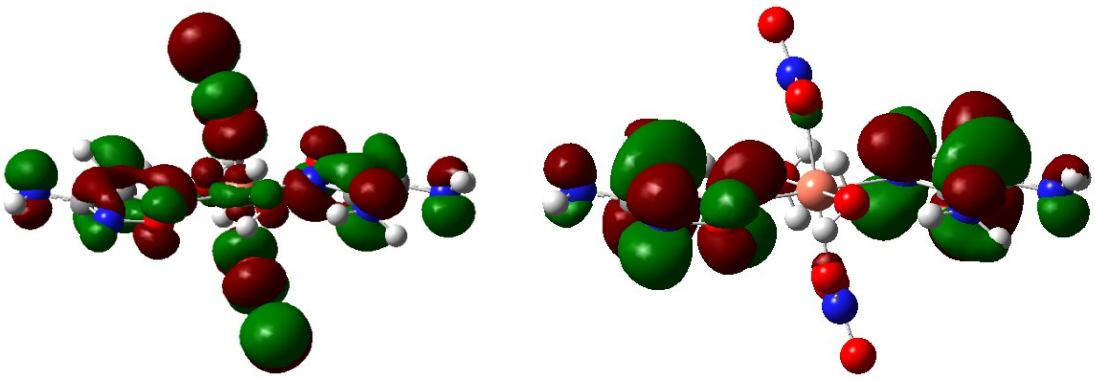
Supplementary Figure 12. IR spectrum of complex **3**.



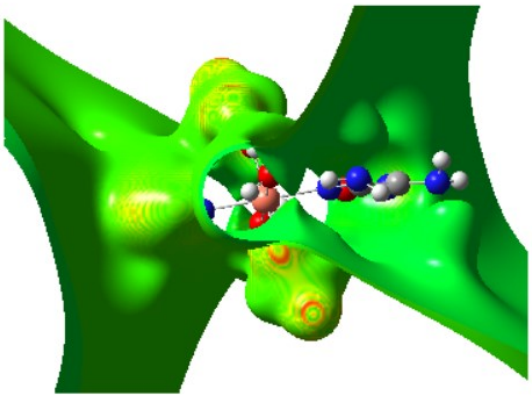
Supplementary Figure 13. Optimized structures of complex **2**.



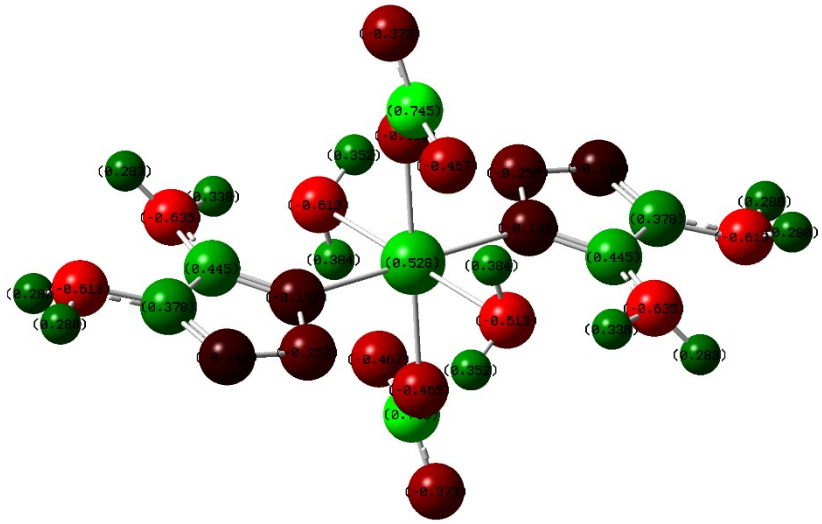
Supplementary Figure 14. Optimized structures of complex **3**.



Supplementary Figure 15. HOMO (left) and LUMO (right) orbitals of complex **2**.



Supplementary Figure 16. Electrostatic potential (ESP) of complex **2**.



Supplementary Figure 17. Mulliken charge of complex **2**.