Supporting Inforamtion

Synthesis and Characterization of Thermal Stable Energetic Complexes with 3,5-diaminopyrazolone-4-oxime as Nitrogen-Rich Ligand

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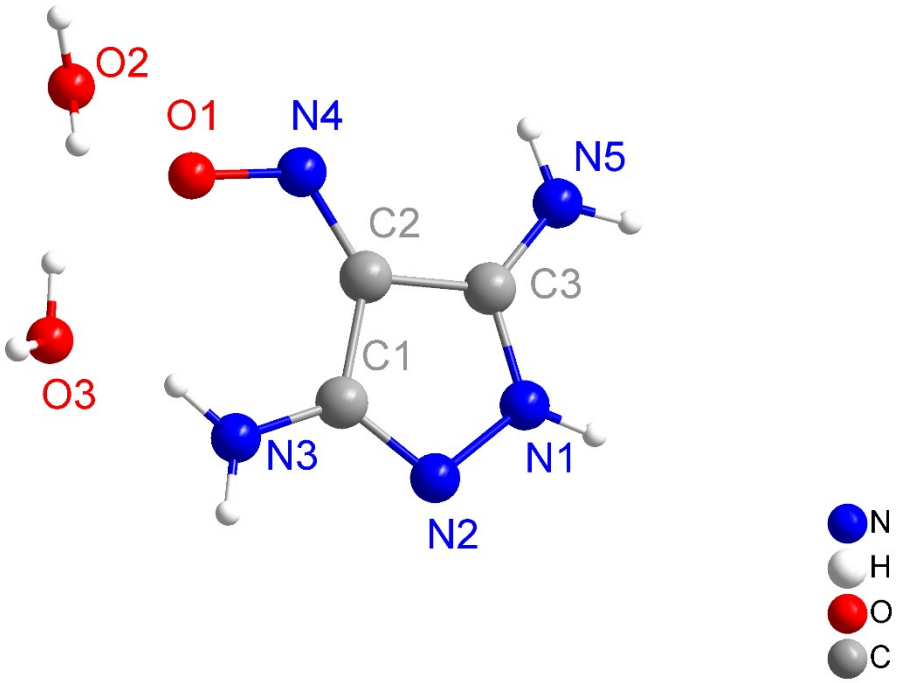


Supplementary Figure 1. Single-crystal X-ray structure of DAPO

Supplementary Table 1. Bond Lengths for DAPO

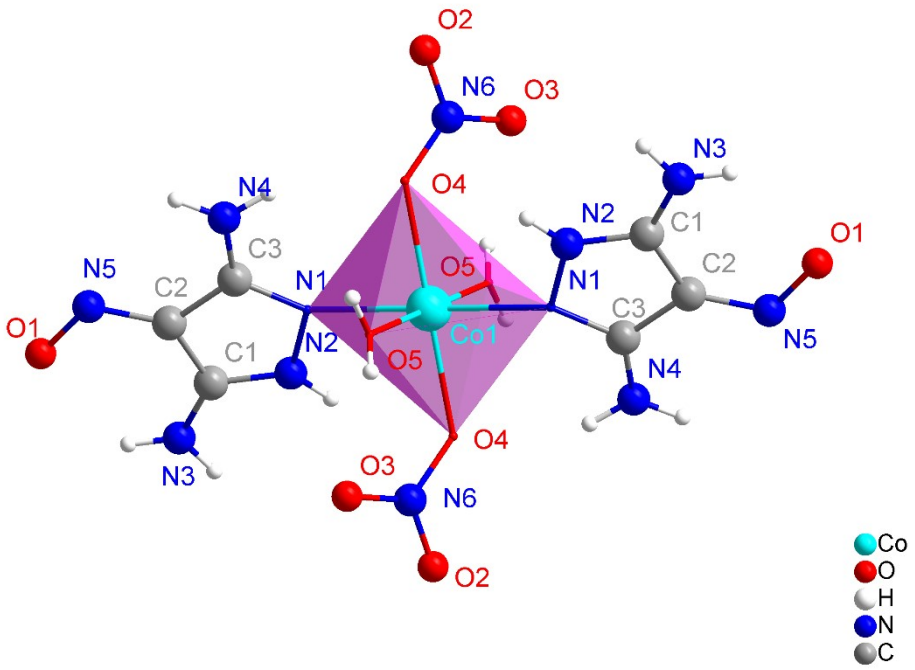
Bond	Length/Å
N1-C3	1.329(4)
N1-N2	1.431(3)
N1-H1	0.86
N2-C1	1.310(4)
N3-C1	1.361(4)
N3-H3A	0.86
N3-H3B	0.86
N4-O1	1.315(3)
N4-C2	1.323(4)
N5-C3	1.330(4)
N5-H5A	0.86
N5-H5B	0.86
O2-H2C	0.85
O2-H2D	0.85
O2-H2A	0.85
O3-H3C	0.85
O3-H3D	0.85
O3-H3E	0.85
C1-C2	1.481(4)
C2-C3	1.463(4)

Supplementary Table 2. Bond angles for DAPO

Bond	Angle/°
C3-N1-N2	113.9(2)
C3-N1-H1	123.1
N2-N1-H1	123.1
C1-N2-N1	105.0(2)
C1-N3-H3A	120.0
C1-N3-H3B	120.0
H3A-N3-H3B	120.0
O1-N4-C2	116.5(2)
C3-N5-H5A	120.0
C3-N5-H5B	120.0
H5A-N5-H5B	120.0
H2C-O2-H2D	108.2
H2C-O2--H2A	109.7
H2D-O2-H2A	109.7
H3C-O3-H3D	110.3
H3C-O3-H3E	108.5
H3D-O3-H3E	110.3
N2-C1-N3	123.1(3)
N2-C1-C2	111.8(3)
N3-C1-C2	125.2(3)
N4-C2-C3	123.4(3)
N4-C2-C1	133.2(3)
C3-C2-C1	103.4(2)
N1-C3-N5	124.8(3)
N1-C3-C2	105.9(3)
N5-C3-C2	129.2(3)

Supplementary Table 3. Torsion angles for DAPO

Bond	Torsion angle/°
C3-N1-N2-C1	0.7(3)
N1-N2-C1-N3	178.7(3)
N1-N2-C1-C2	-0.4(3)
O1-N4-C2-C3	-179.4(3)
O1-N4-C2-C1	-1.9(5)
N2-C1-C2-N4	-177.9(3)
N3-C1-C2-N4	3.0(6)
N2-C1-C2-C3	0.0(4)
N3-C1-C2-C3	-179.1(3)
N2-N1-C3-N5	179.2(3)
N2-N1-C3-C2	-0.7(3)
N4-C2-C3-N1	178.6(3)
C1-C2-C3-N1	0.4(3)
N4-C2-C3-N5	-1.3(5)
C1-C2-C3-N5	-179.5(3)



Supplementary Figure 2. Single-crystal X-ray structure of $[Co(DAPO)_2(H_2O)_2](NO_3)_2$

Supplementary Table 4. Bond Lengths for $[Co(DAPO)_2(H_2O)_2](NO_3)_2$

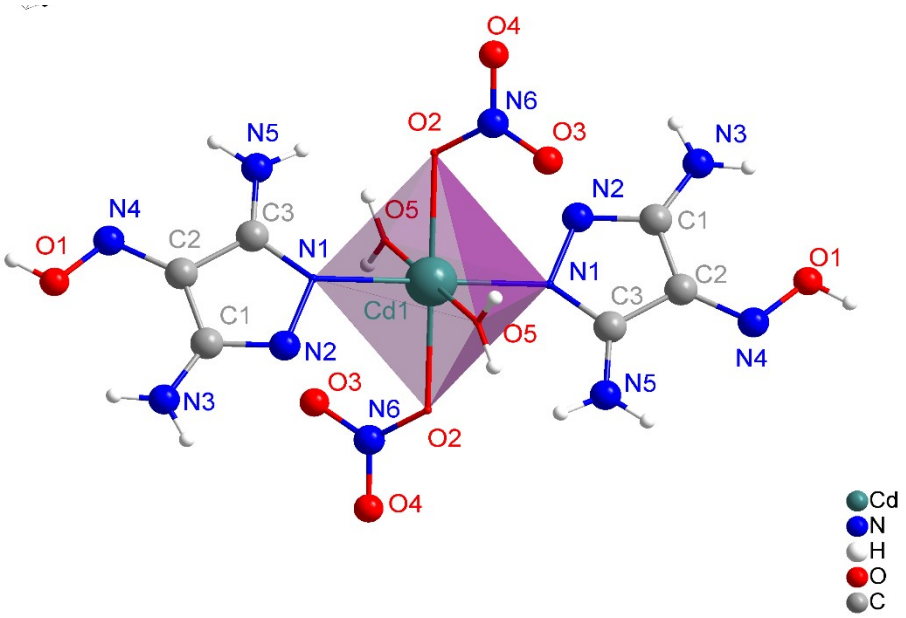
Bond	Length/Å
Co1-O5[1]	2.146(3)
Co1-O5	2.146(3)
Co1-O4[1]	2.200(3)
Co1-O4	2.200(3)
Co1-N1[1]	2.261(3)
Co1-N1	2.261(3)
O2-N6	1.251(4)
N6-O3	1.234(4)
N6-O4	1.267(4)
N2-N1	1.417(4)
N2-C1	1.324(4)
N4-C3	1.353(4)
N5-O1	1.275(4)
N5-C2	1.345(4)
C2-C3	1.449(4)
C2-C1	1.433(4)
N1-C3	1.317(4)
C1-N3	1.325(4)

Supplementary Table 5. Bond angles for $[Co(DAPO)_2(H_2O)_2](NO_3)_2$

Bond	Angle/°
$O5^1$-Co1-O5	180.0
O5-Co1-O4	97.68(11)
$O5^1$-Co1-O4	82.32(11)
O5-Co1-$O4^1$	82.32(11)
$O5^1$-Co1-$O4^1$	97.68(11)
$O5^1$-Co1-$N1^1$	91.38(12)
$O5^1$-Co1-N1	88.62(12)
O5-Co1-$N1^1$	88.62(12)
O5-Co1-N1	91.38(12)
$O4^1$-Co1-O4	180.0
$O4^1$-Co1-$N1^1$	90.83(11)
$O4^1$-Co1-N1	89.17(11)
O4-Co1-$N1^1$	89.17(11)
O4-Co1-N1	90.83(11)
$N1^1$-Co1-N1	180.00(8)
O2-N6-O4	118.9(3)
O3-N6-O2	120.7(3)
O3-N6-O4	120.4(3)
N6-O4-$Co1^1$	129.2(2)
C1-N2-N1	112.7(3)
O1-N5-C2	115.5(4)
N5-C2-C3	125.1(4)
N5-C2-C1	130.3(3)
C1-C2-C3	104.5(3)
N2-N1-$Co1^1$	119.4(2)
C3-N1-$Co1^1$	131.4(3)
C3-N1-N2	105.4(3)
N4-C3-C2	125.6(4)
N1-C3-N4	123.6(3)
N1-C3-C2	110.8(3)
N2-C1-C2	106.5(3)
N2-C1-N3	124.9(4)
N3-C1-C2	128.6(4)

Supplementary Table 6. Torsion angles for $[Co(DAPO)_2(H_2O)_2](NO_3)_2$

Bond	Torsion angle/°
Co1-N1-C3-N4	-21.6(6)
Co1-N1-C3-C2	155.9(3)
O2-N6-O4-Co1	-176.0(2)
O3-N6-O4-Co1	4.5(5)
N2-N1-C3-N4	-179.0(4)
N2-N1-C3-C2	-1.5(4)
N5-C2-C3-N4	-2.4(7)
N5-C2-C3-N1	-179.9(4)
N5-C2-C1-N2	-179.1(4)
N5-C2-C1-N3	0.5(7)
O1-N5-C2-C3	178.0(4)
O1-N5-C2-C1	-3.3(6)
N1-N2-C1-C2	-0.7(5)
N1-N2-C1-N3	179.6(4)
C3-C2-C1-N2	-0.2(4)
C3-C2-C1-N3	179.5(4)
C1-N2-N1-Co1	-159.2(3)
C1-N2-N1-C3	1.4(4)
C1-C2-C3-N4	178.6(4)
C1-C2-C3-N1	1.1(4)



Supplementary Figure 3. Single-crystal X-ray structure of $[Cd(DAPO)_2(H_2O)_2](NO_3)_2$

Supplementary Table 7. Bond Lengths for $[Cd(DAPO)_2(H_2O)_2](NO_3)_2$

Bond	Length/Å
Cd(1)-O(5)	2.260(4)
Cd(1)-O(5)#1	2.260(4)
Cd(1)-N(1)	2.291(4)
Cd(1)-N(1)#1	2.291(4)
Cd(1)-O(2)#1	2.329(4)
Cd(1)-O(2)	2.329(4)
N(1)-C(3)	1.301(7)
N(1)-N(2)	1.419(7)
N(2)-C(1)	1.331(8)
N(3)-C(1)	1.332(8)
N(3)-H(3A)	0.86
N(3)-H(3B)	0.86
N(4)-O(1)	1.248(7)
N(4)-C(2)	1.374(9)
N(5)-C(3)	1.330(8)
N(5)-H(5A)	0.86
N(5)-H(5B)	0.86
N(6)-O(3)	1.210(6)
N(6)-O(4)	1.236(6)
N(6)-O(2)	1.253(6)
O(1)-H(1)	0.82
O(5)-H(5E)	0.85
O(5)-H(5F)	0.85
C(1)-C(2)	1.411(10)
C(2)-C(3)	1.437(8)

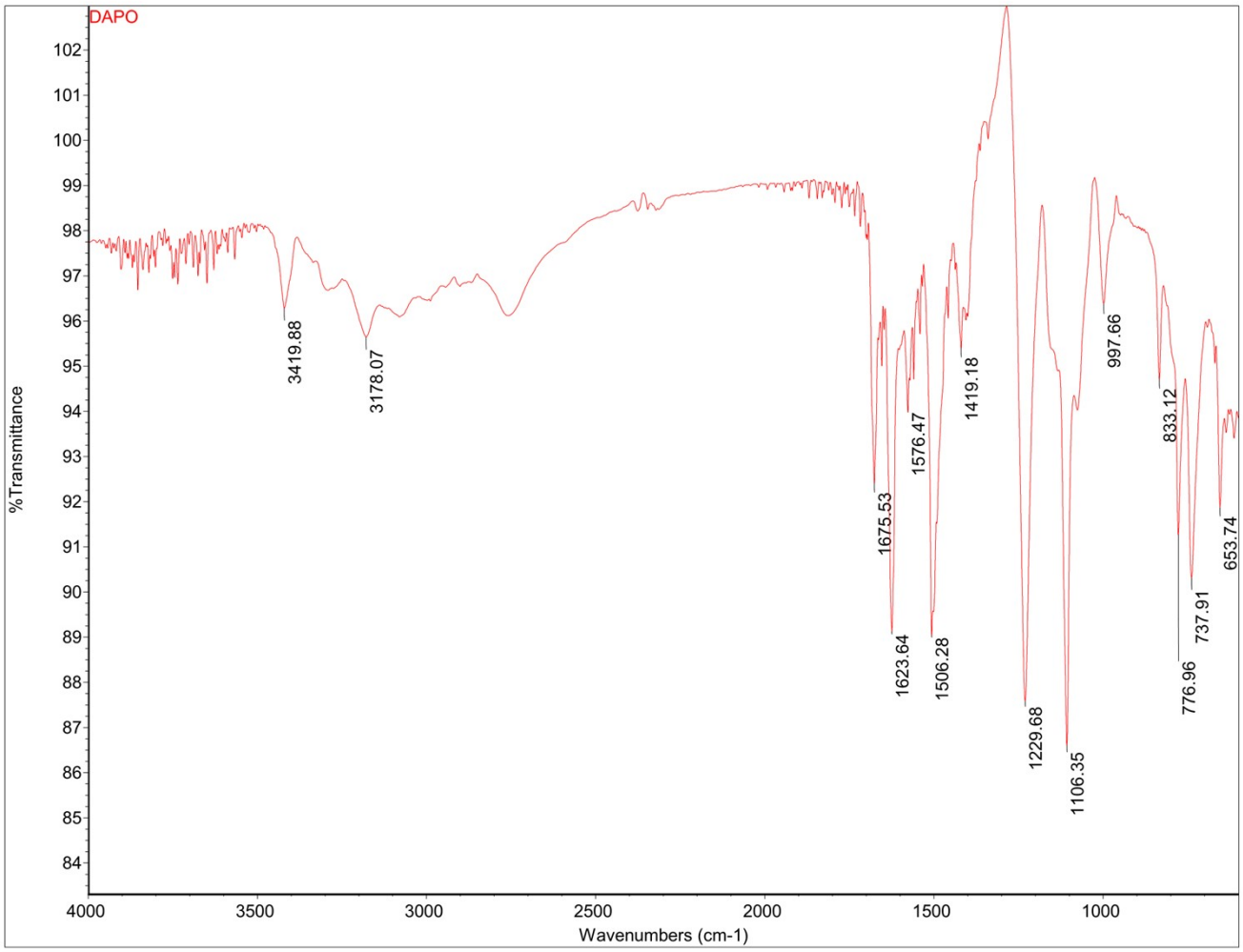
Supplementary Table 8. Bond angles for $[Cd(DAPO)_2(H_2O)_2](NO_3)_2$

Bond	Angle/°
O(5)-Cd(1)-O(5)#1	180.00(17)
O(5)-Cd(1)-N(1)	96.01(17)
O(5)#1-Cd(1)-N(1)	83.99(18)
O(5)-Cd(1)-N(1)#1	83.99(18)
O(5)#1-Cd(1)-N(1)#1	96.01(17)
N(1)-Cd(1)-N(1)#1	180
O(5)-Cd(1)-O(2)#1	78.56(16)
O(5)#1-Cd(1)-O(2)#1	101.44(16)
N(1)-Cd(1)-O(2)#1	86.46(16)
N(1)#1-Cd(1)-O(2)#1	93.54(16)
O(5)-Cd(1)-O(2)	101.44(16)
O(5)#1-Cd(1)-O(2)	78.56(16)
N(1)-Cd(1)-O(2)	93.54(16)
N(1)#1-Cd(1)-O(2)	86.46(16)
O(2)#1-Cd(1)-O(2)	180.000(1)
C(3)-N(1)-N(2)	106.7(5)
C(3)-N(1)-Cd(1)	129.8(4)
N(2)-N(1)-Cd(1)	118.3(4)
C(1)-N(2)-N(1)	110.2(5)
C(1)-N(3)-H(3A)	120
C(1)-N(3)-H(3B)	120
H(3A)-N(3)-H(3B)	120
O(1)-N(4)-C(2)	112.7(6)
C(3)-N(5)-H(5A)	120
C(3)-N(5)-H(5B)	120
H(5A)-N(5)-H(5B)	120
O(3)-N(6)-O(4)	120.9(6)
O(3)-N(6)-O(2)	120.5(6)
O(4)-N(6)-O(2)	118.6(5)
N(4)-O(1)-H(1)	109.5
N(6)-O(2)-Cd(1)	120.0(4)
Cd(1)-O(5)-H(5E)	130.6
Cd(1)-O(5)-H(5F)	118.4
H(5E)-O(5)-H(5F)	108.3
N(2)-C(1)-N(3)	123.2(7)
N(2)-C(1)-C(2)	107.9(5)

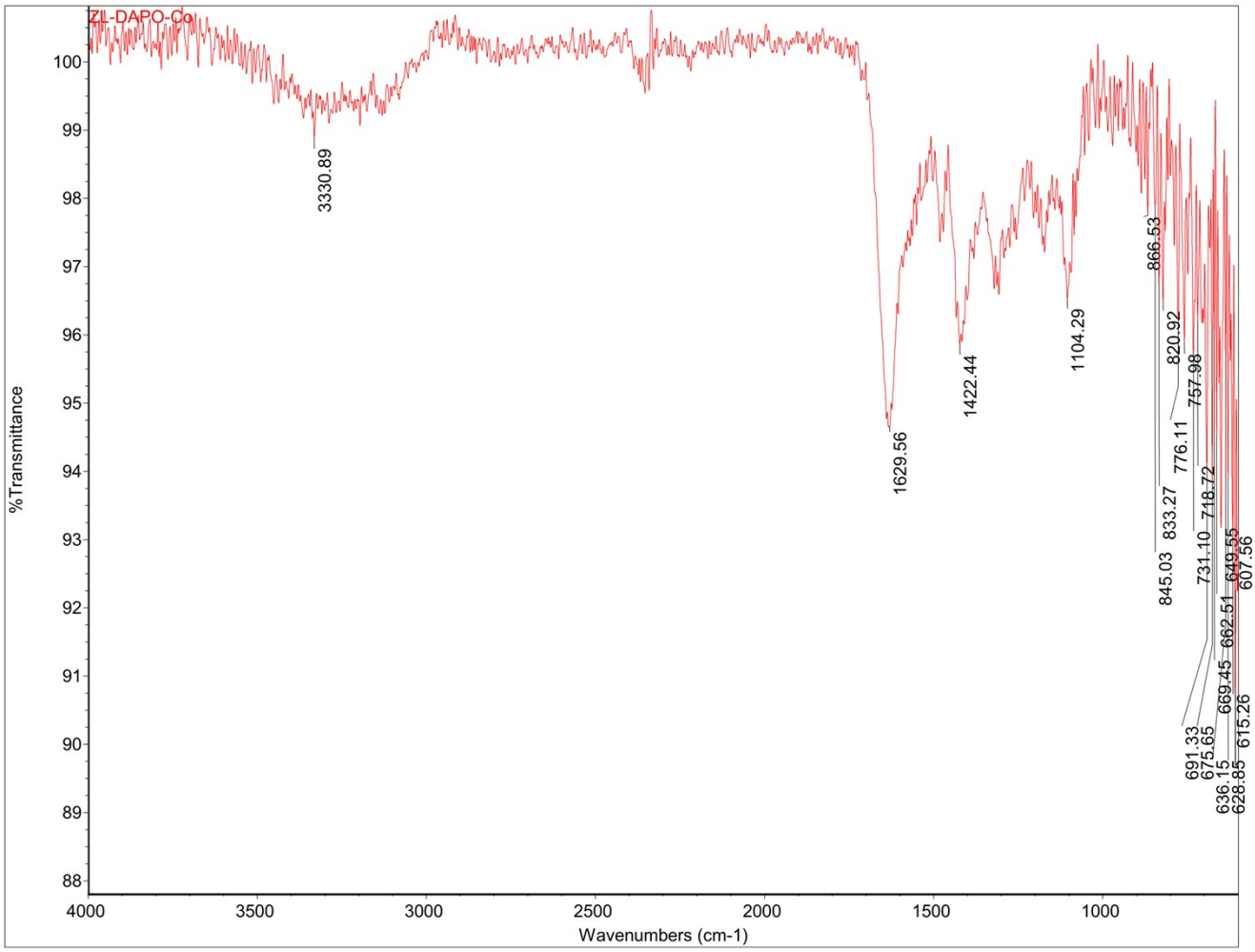
N(3)-C(1)-C(2)	128.9(6)
N(4)-C(2)-C(1)	133.4(6)
N(4)-C(2)-C(3)	122.2(6)
C(1)-C(2)-C(3)	104.4(5)
N(1)-C(3)-N(5)	123.5(6)

Supplementary Table 9. Torsion angles for $[Cd(DAPO)_2(H_2O)_2](NO_3)_2$

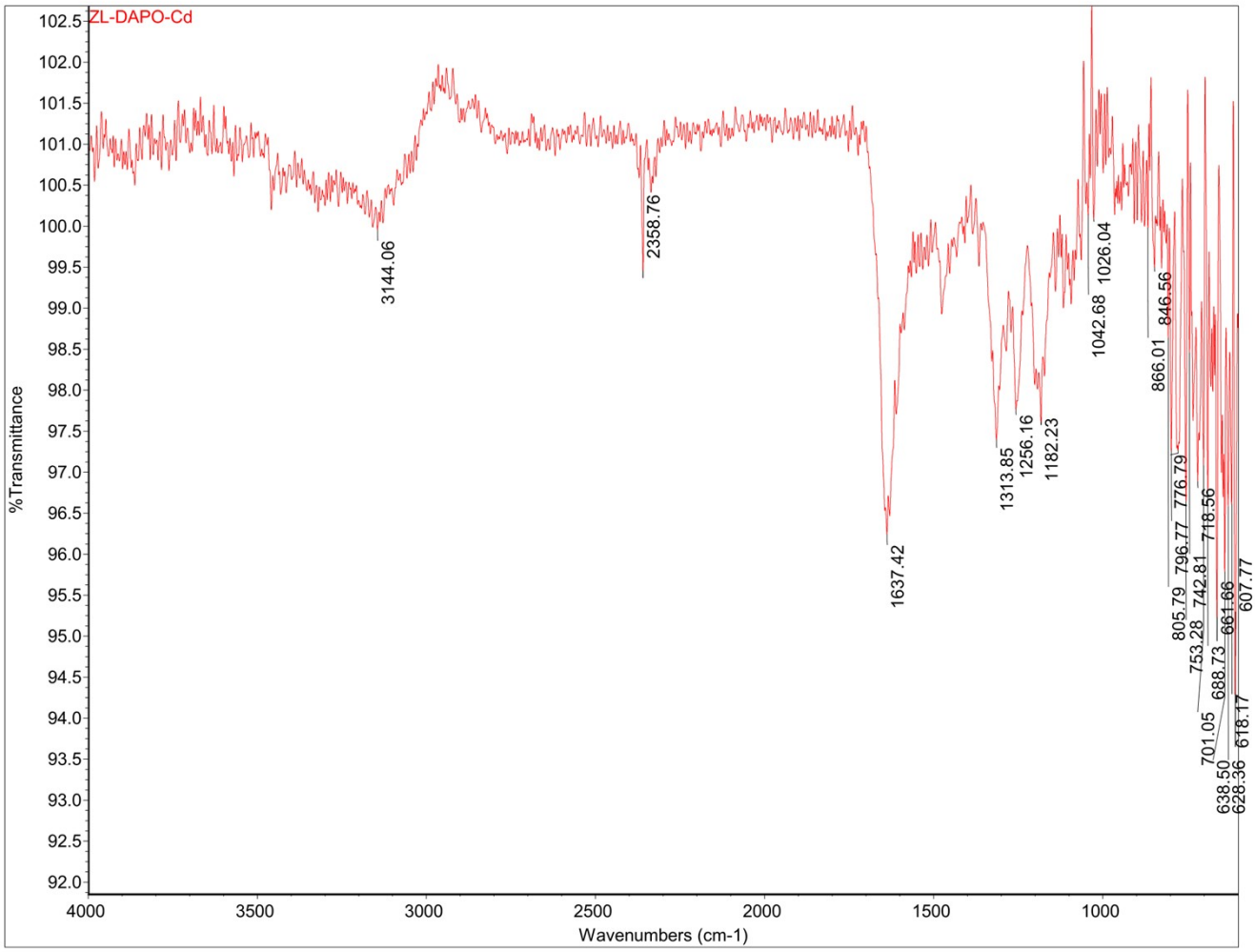
Bond	Torsion angle/°
O(5)-Cd(1)-N(1)-C(3)	28.9(6)
O(5)#1-Cd(1)-N(1)-C(3)	-151.1(6)
N(1)#1-Cd(1)-N(1)-C(3)	-40(100)
O(2)#1-Cd(1)-N(1)-C(3)	-49.2(6)
O(2)-Cd(1)-N(1)-C(3)	130.8(6)
O(5)-Cd(1)-N(1)-N(2)	-122.0(5)
O(5)#1-Cd(1)-N(1)-N(2)	58.0(5)
N(1)#1-Cd(1)-N(1)-N(2)	169(100)
O(2)#1-Cd(1)-N(1)-N(2)	159.9(5)
O(2)-Cd(1)-N(1)-N(2)	-20.1(5)
C(3)-N(1)-N(2)-C(1)	-2.3(7)
Cd(1)-N(1)-N(2)-C(1)	154.7(5)
O(3)-N(6)-O(2)-Cd(1)	0.4(9)
O(4)-N(6)-O(2)-Cd(1)	179.1(4)
O(5)-Cd(1)-O(2)-N(6)	43.1(4)
O(5)#1-Cd(1)-O(2)-N(6)	-136.9(4)
N(1)-Cd(1)-O(2)-N(6)	-53.8(4)
N(1)#1-Cd(1)-O(2)-N(6)	126.2(4)
O(2)#1-Cd(1)-O(2)-N(6)	-44(100)
N(1)-N(2)-C(1)-N(3)	-178.5(6)
N(1)-N(2)-C(1)-C(2)	1.6(8)
O(1)-N(4)-C(2)-C(1)	1.2(10)
O(1)-N(4)-C(2)-C(3)	-179.7(7)
N(2)-C(1)-C(2)-N(4)	178.8(7)
N(3)-C(1)-C(2)-N(4)	-1.1(12)
N(2)-C(1)-C(2)-C(3)	-0.4(7)
N(3)-C(1)-C(2)-C(3)	179.7(6)
N(2)-N(1)-C(3)-N(5)	-179.3(6)
Cd(1)-N(1)-C(3)-N(5)	27.2(9)
N(2)-N(1)-C(3)-C(2)	2.1(7)
Cd(1)-N(1)-C(3)-C(2)	-151.4(4)
N(4)-C(2)-C(3)-N(1)	179.6(6)
C(1)-C(2)-C(3)-N(1)	-1.1(7)
N(4)-C(2)-C(3)-N(5)	1.0(10)
C(1)-C(2)-C(3)-N(5)	-179.7(6)



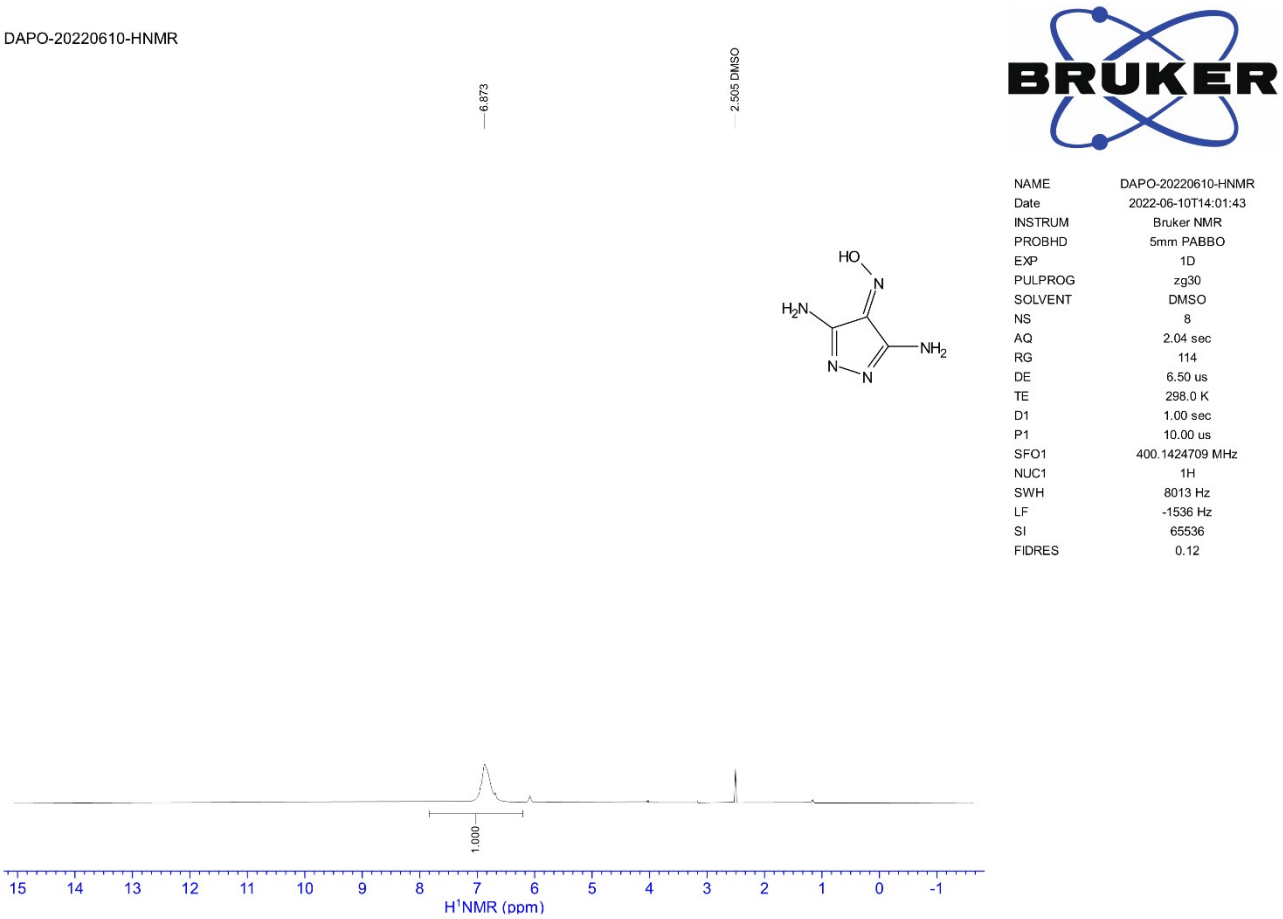
Supplementary Figure 4. IR Spectrum of DAPO



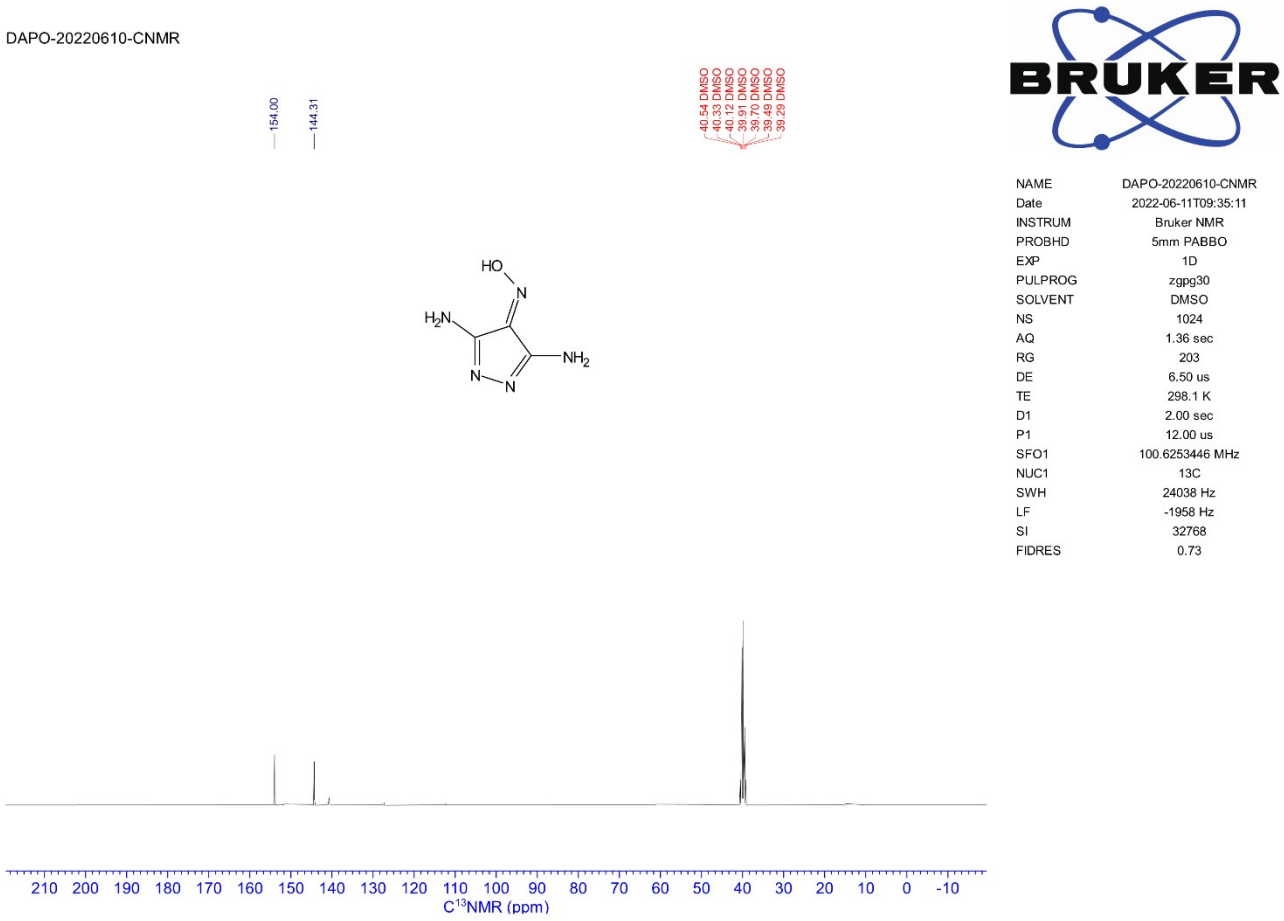
Supplementary Figure 5. IR Spectrum of $[Co(DAPO)_2(H_2O)_2](NO_3)_2$



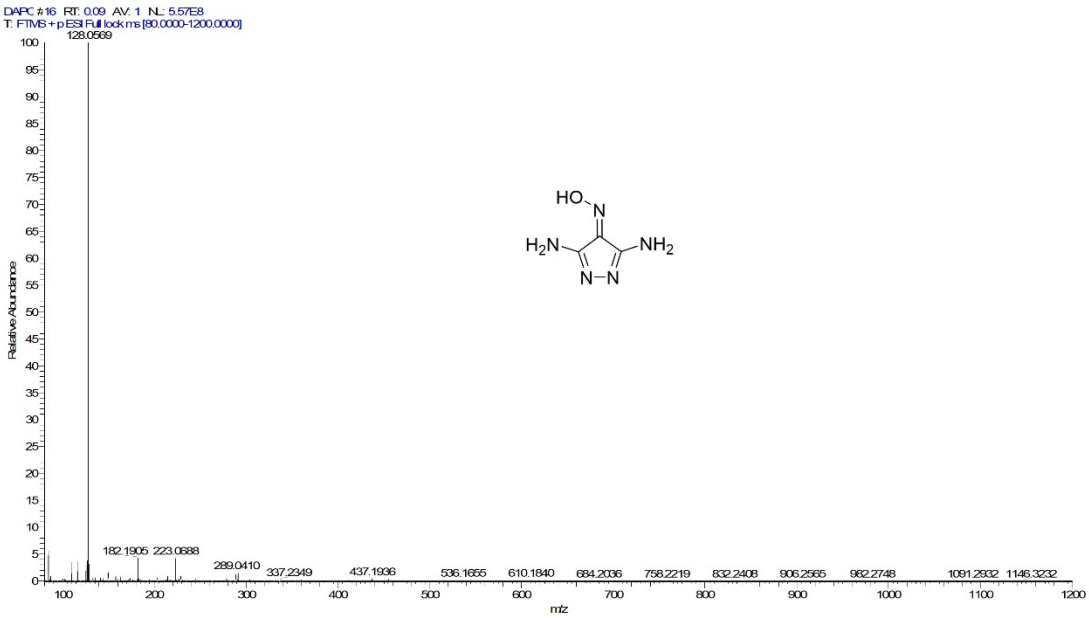
Supplementary Figure 6. IR Spectrum of $[Cd(DAPO)_2(H_2O)_2](NO_3)_2$



Supplementary Figure 7. ^{1}H NMR Spectrum (400MHz) of DAPO in [D_6] DMSO at 25 °C



Supplementary Figure 8. ^{13}C NMR Spectrum (100MHz) of DAPO in [D_6] DMSO at 25 °C



Supplementary Figure 9. Mass Spectrum of DAPO

Energetic properties

The enthalpy change from the most stable element in the standard state to 1 mol of the compound in the standard state is called the standard enthalpy of formation of the compound. Taking the CHNO system as an example, the corresponding generation reaction formula is as follows:

$$aC+\frac{b}{2}H_2+\frac{c}{2}N_2+\frac{d}{2}O_2\rightarrow C_aH_bO_cN_d \text{ \\* MERGEFORMAT (S1)}$$

By definition, the enthalpy of formation is the reaction enthalpy of the above formula. The enthalpy of each species in the reaction formula can be calculated by Gaussian09, and the difference between the enthalpy of the product and the enthalpy of the reactant is the reaction enthalpy. Calculated as follows:

$$\Delta_f H_m^\theta=\Delta_r H_m^\theta=H\left(C_aH_bN_cO_d\right)-aH\left(C\right)-\frac{b}{2}H\left(H_2\right)-\frac{c}{2}H\left(N_2\right)-\frac{d}{2}H\left(O_2\right) \quad \text{\\* MERGEFORMAT (S2)}$$

All the above enthalpy values are the enthalpy values of the stable phase at 298 K, so the calculated enthalpy of formation is also the enthalpy of formation at 298 K. It should be noted that C is a solid at room temperature, and the enthalpy calculated by Gaussian09 is the enthalpy of formation in the gaseous state, so *H(C)* needs to subtract the sublimation enthalpy of C from the calculation result of Gaussian09, while the other two compounds The same is true for Co and Cd in .

The enthalpy of formation definition reaction formula of the three compounds synthesized is as follows:

$$3C+5/2\,H_2+5/2\,N_2+1/2\,O_2\rightarrow C_3H_5N_5O \text{ \\* MERGEFORMAT (S3)}$$

$$6C+8H_2+6N_2+5O_2+Co\rightarrow C_6H_{16}N_{12}O_{10}Co \text{ \\* MERGEFORMAT (S4)}$$

$$6C+8H_2+6N_2+5O_2+Cd\rightarrow C_6H_{16}N_{12}O_{10}Cd \text{ \\* MERGEFORMAT (S5)}$$