Electronic Supplementary Material (ESI) for Dalton Transactions

The aza-heterocyclic ligand assisted assembly of new cobalt MOFs with *pcu* and graphite related structures

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ELECTRONIC SUPPLEMENTARY INFORMATION

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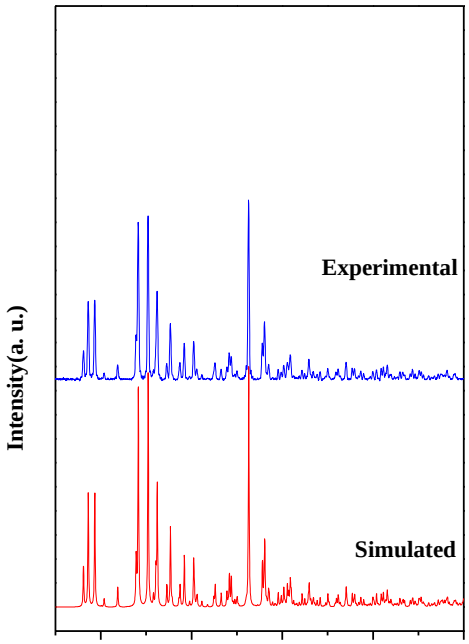

Fig. S1. Powder X-ray diffraction pattern of compound-**I**

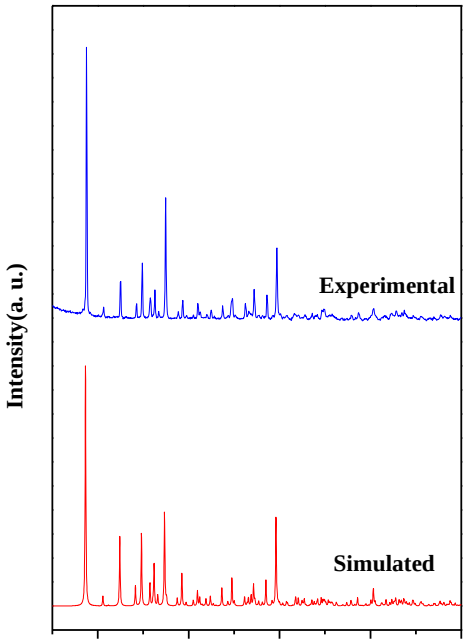

Fig. S2. Powder X-ray diffraction pattern of compound-**II**

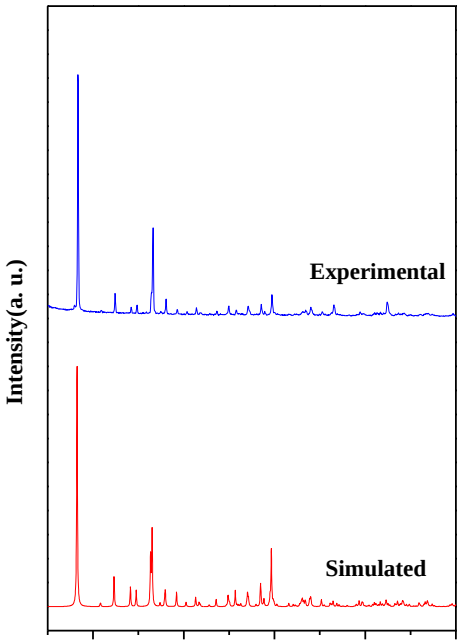

Fig. S3. Powder X-ray diffraction pattern of compound-**III**

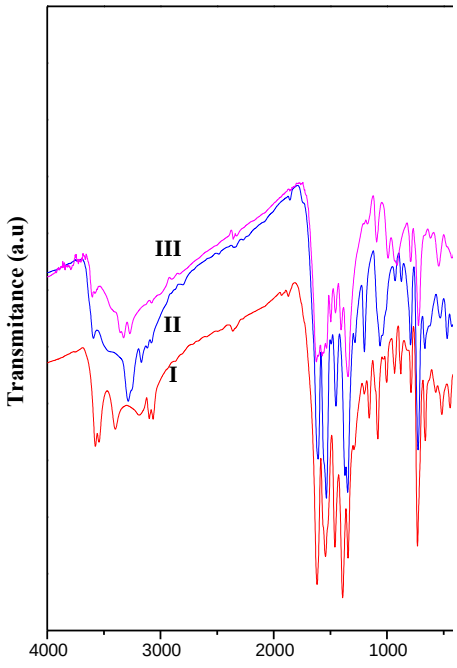

Fig. S4. Room temperature IR spectra of compound-**I**, compound-**II** and compound-**III**

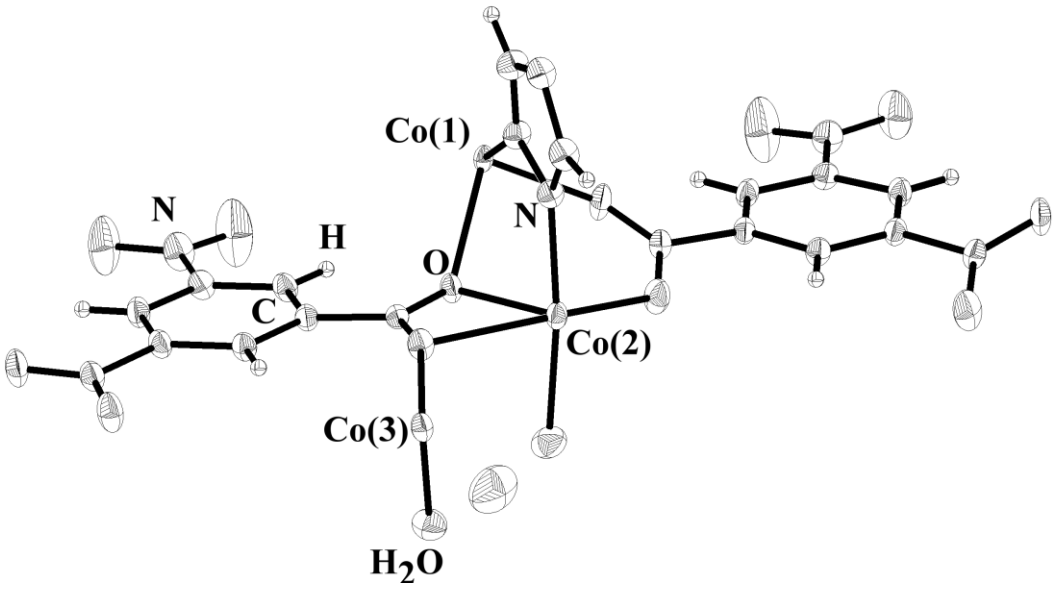

Fig. S5. Figure shows the ORTEP diagram of compound-**I.**

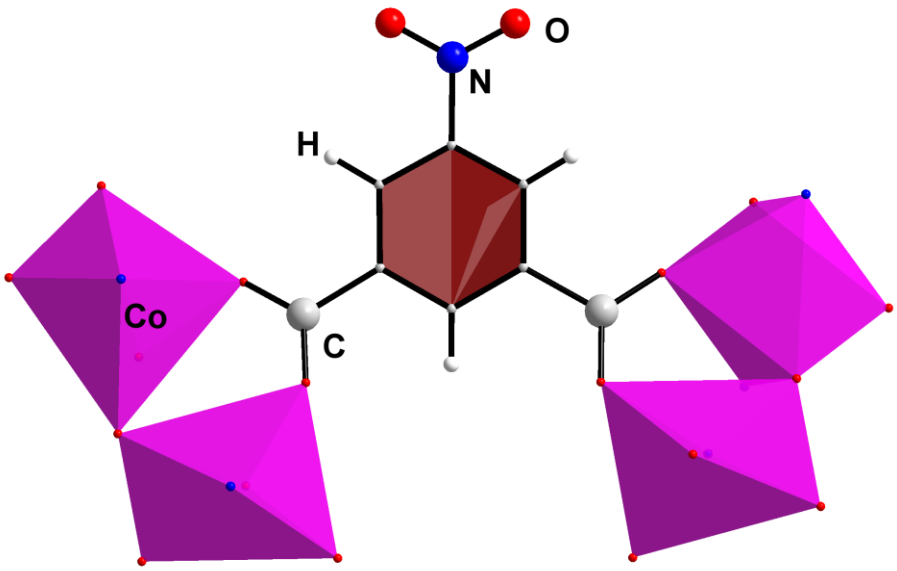

Fig. S6. Figure shows the connectivity of NIPA(1) in compound-**I.**

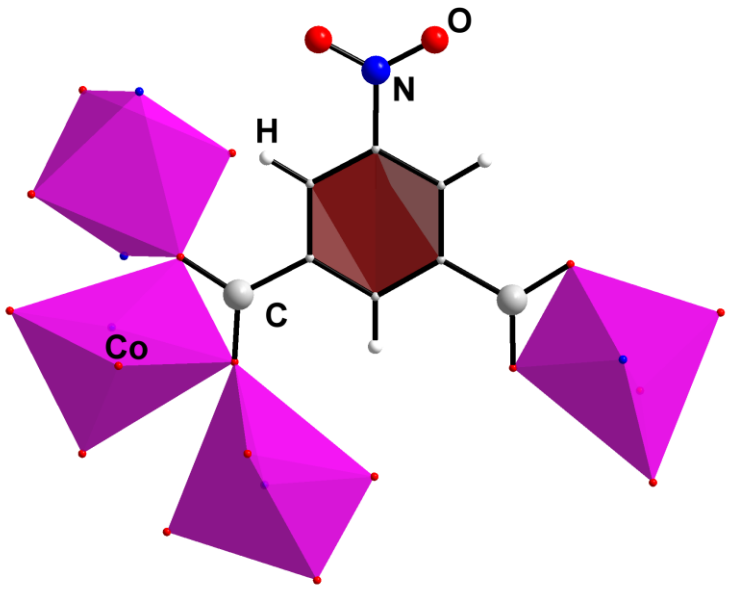

Fig. S7. Figure shows the connectivity of NIPA(2) in compound- **I.**

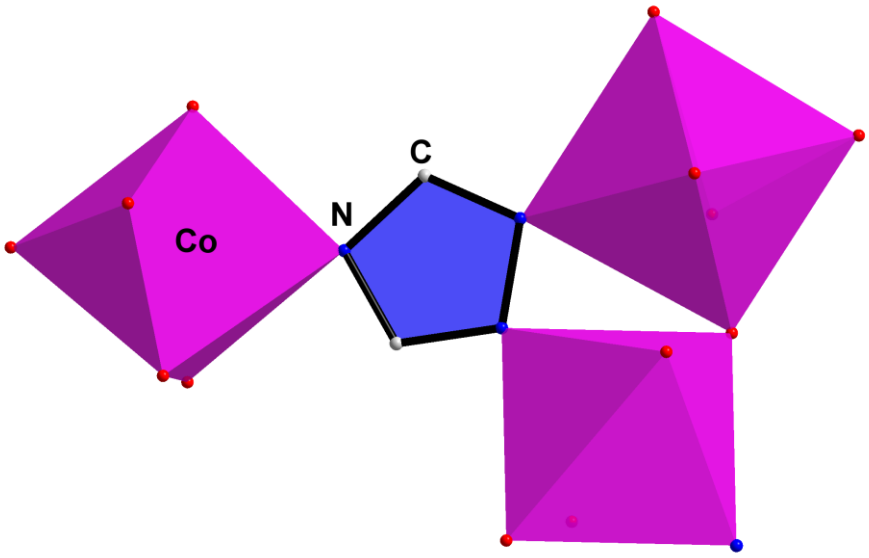

Fig. S8. Figure shows the connectivity of 1,2,4-triazolate in compound-**I.**

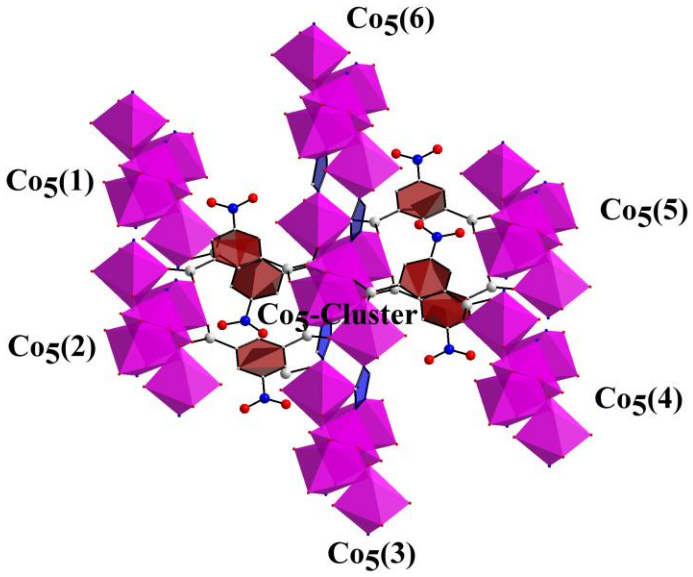

Fig. S9. Figure shows the connectivity of each Co_5 cluster to six other clusters in compound-**I.**

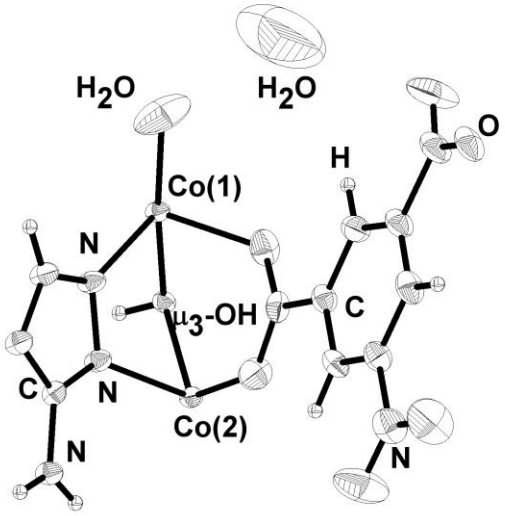

Fig. S10. Figure shows the ORTEP diagram of compound-**II.**

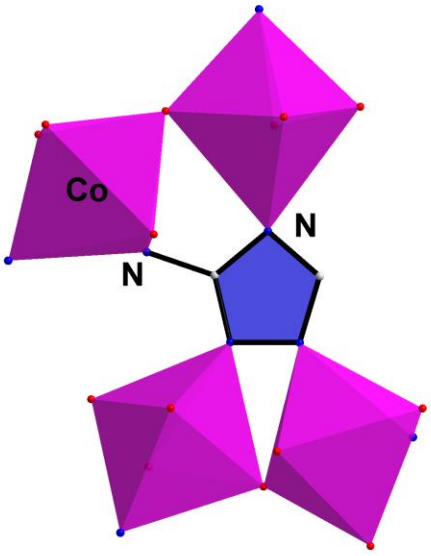

Fig. S11. Figure shows the connectivity of 3-amino-1,2,4-triazolate in compound-**II.**

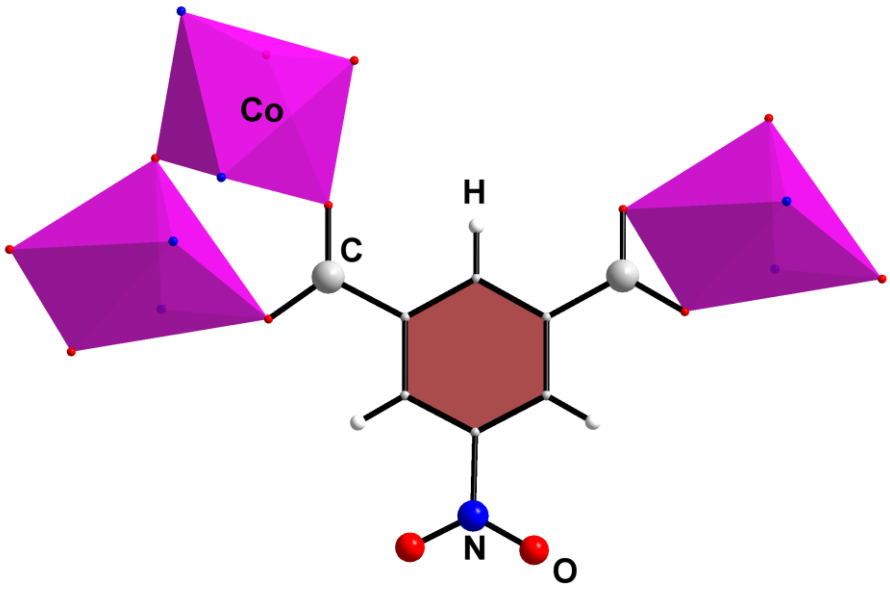

Fig. S12. Figure shows the connectivity of NIPA in compound-**II.**

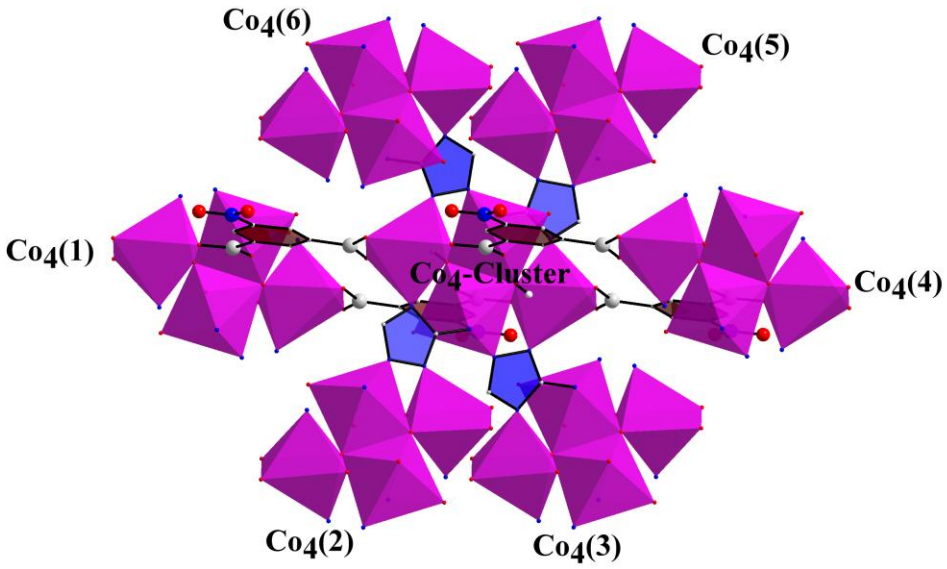

Fig. S13. Figure shows the connectivity of each Co_4 cluster to six other clusters in compound-**II.**

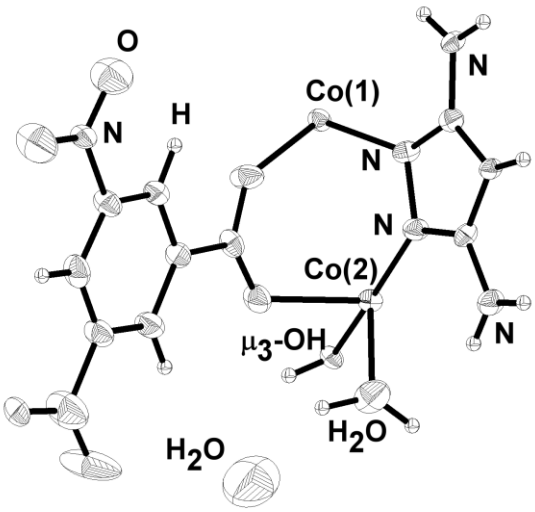

Fig. S14. Figure shows the ORTEP diagram of compound-**III.**

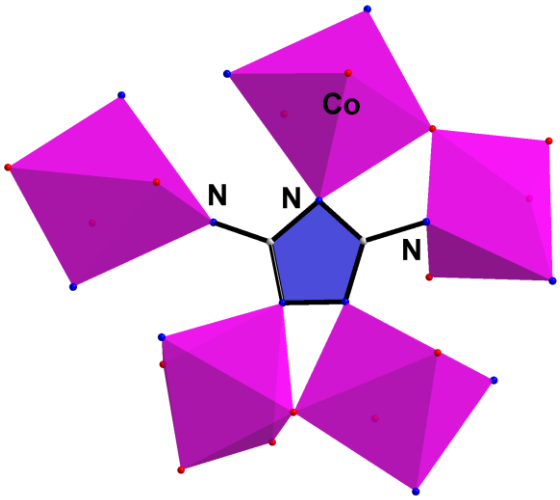

Fig. S15. Figure shows the connectivity of 3,5-diamino-1,2,4-triazolate in compound- **III.**

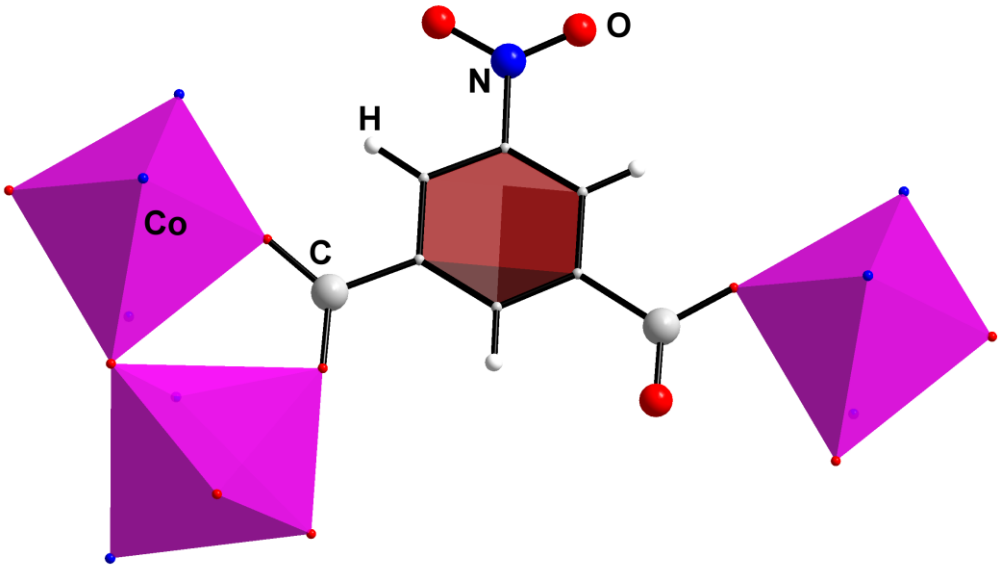

Fig. S16. Figure shows the connectivity of NIPA in compound-**III.**

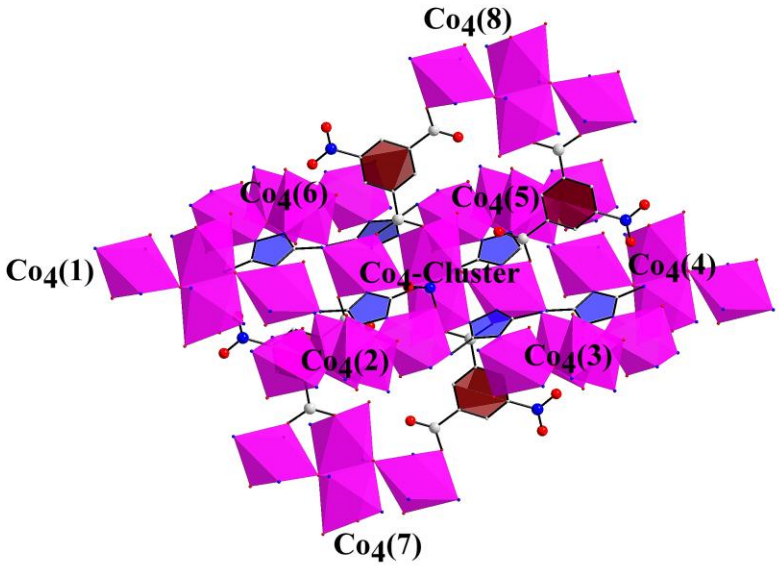

Fig. S17. Figure shows the connectivity of each Co_4 cluster to eight other clusters in compound-**III.**

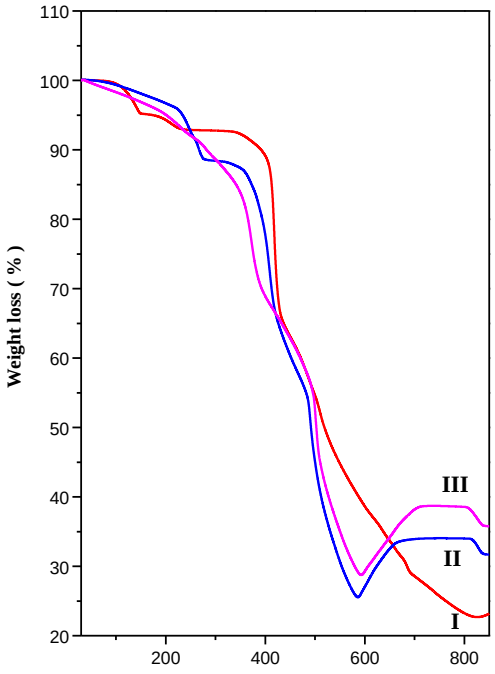

Fig. S18. Thermogravimetric analysis of the compound-**I**, compound-**II**, compound-**III.**

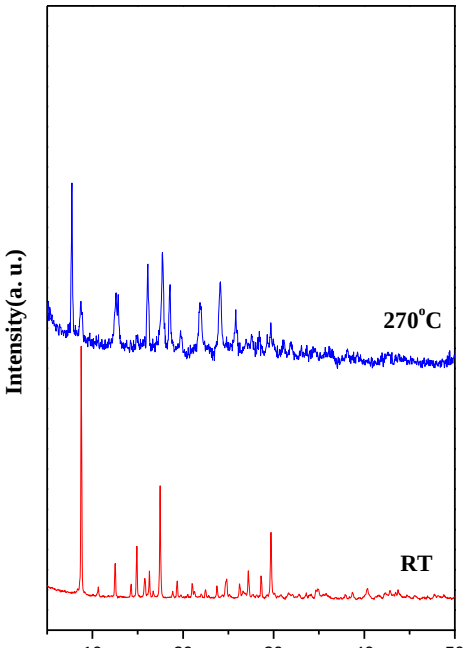

Fig. S19. Figture shows the the PXRD pattern of v compound-**I** after the removal of the water

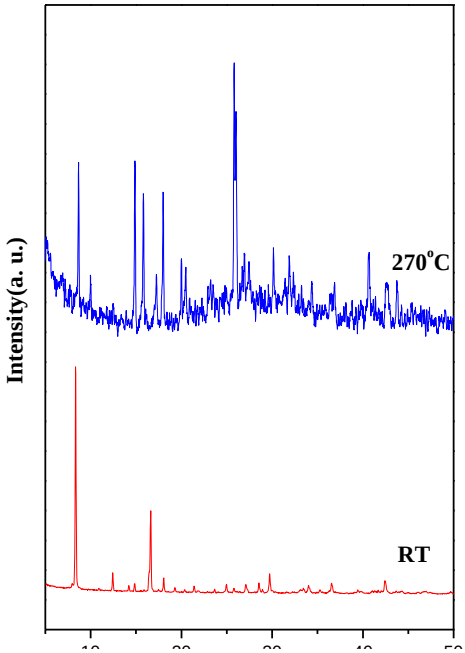

Fig. S20. Figture shows the the PXRD pattern of compound-**III** after the removal of the water

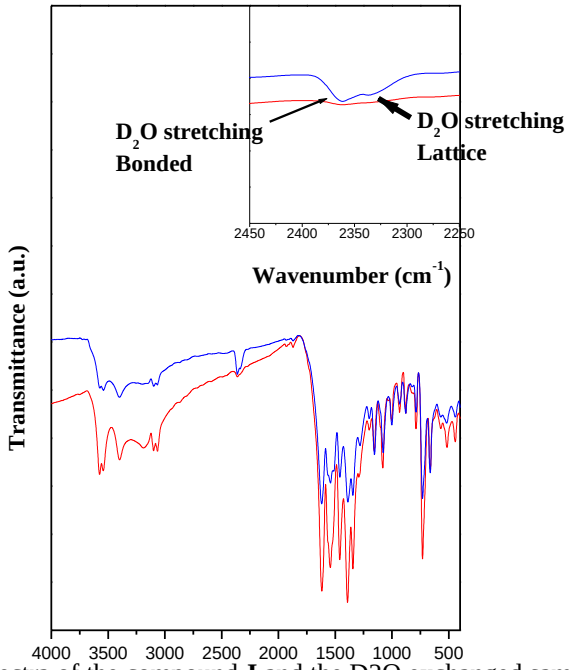

Fig. S21: Room temperature IR spectra of the compound-**I** and the D2O exchanged sample of compound-**I**. The inset shows the enlarged portion of the D_2O stretching region.

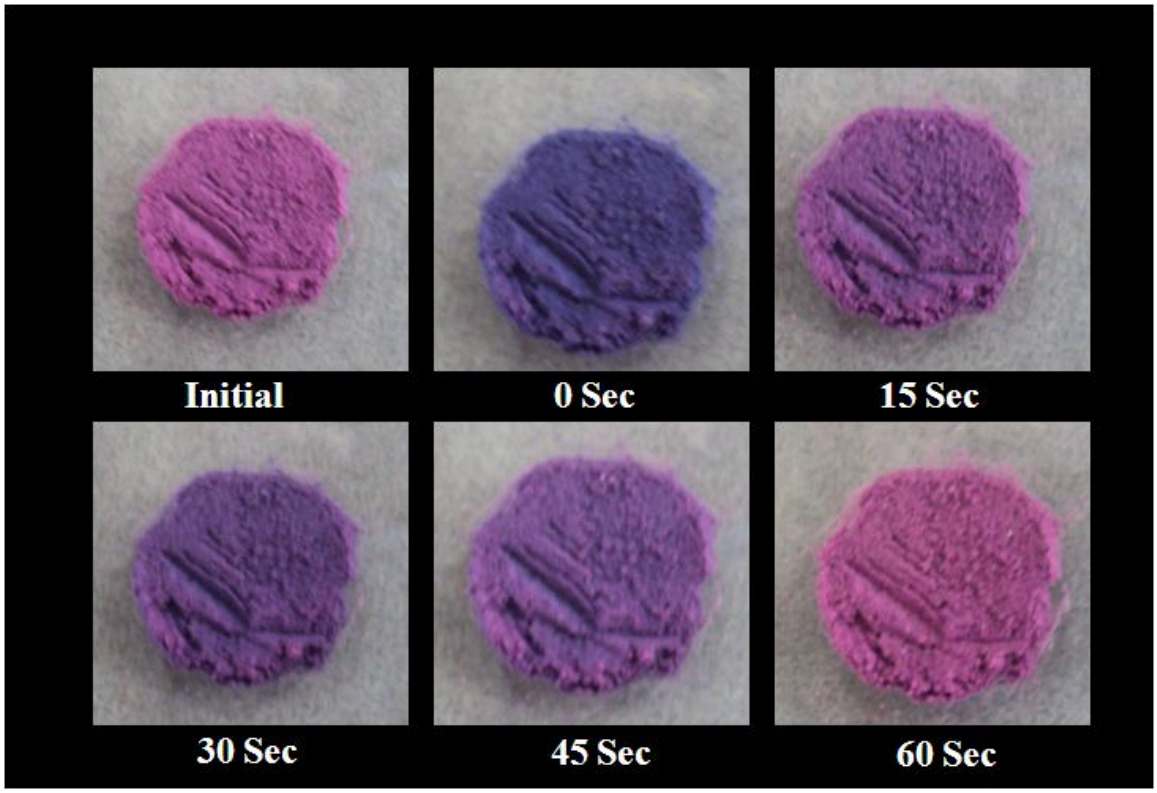

Fig. S22: Figure shows the change in colour during dehydration and rehydration in the bulk sample of compound **I**.

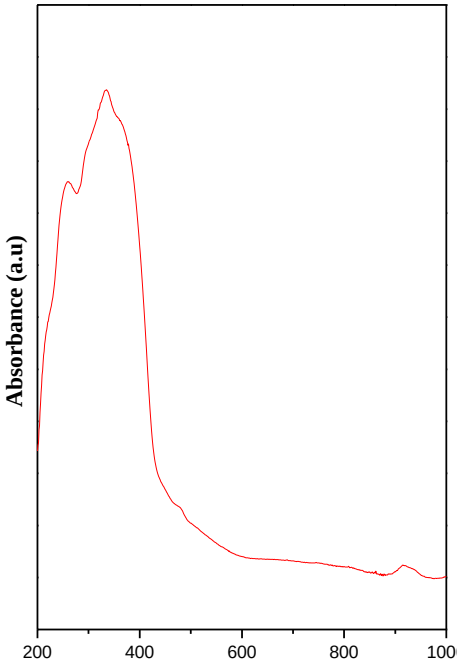

Fig. S23: Figure shows the UV- vis spectra of Na salt of NIPA.

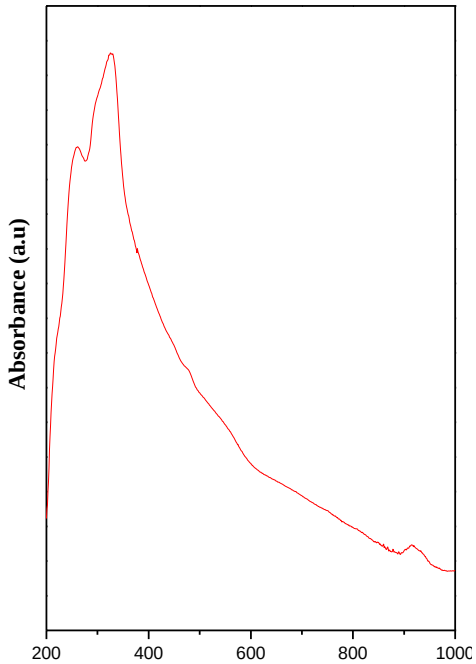

Fig. S24: Figure shows the UV- vis spectra of 1,2,4 – triazole.

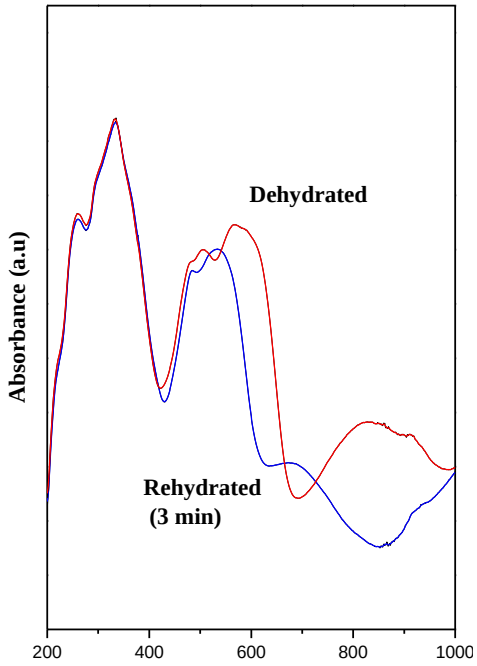

Fig. S25: UV-vis spectra of compound **I** (blue) and the dehydrated phase (red).

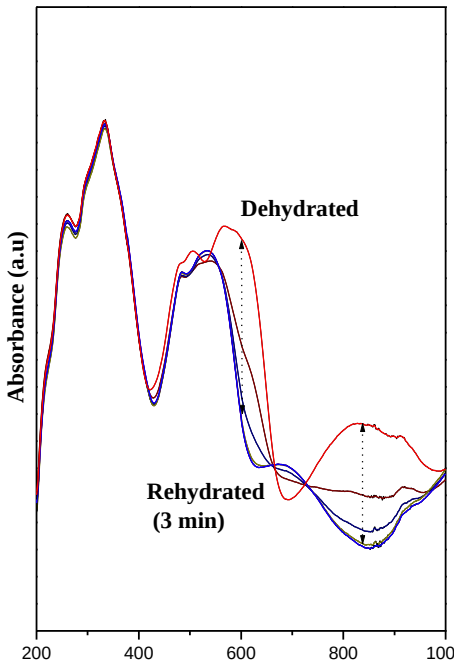

Fig. S26: UV-vis spectra of the dehydrated sample (compound-**Ia**) after exposure to the atmosphere for various times

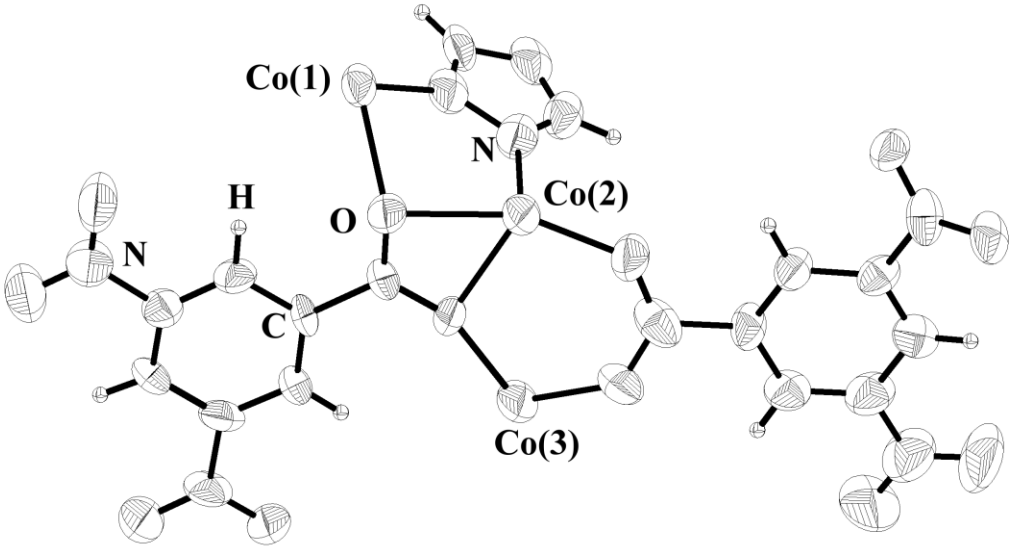

Fig. S27. Figure shows the ORTEP diagram of compound-**Ia.**

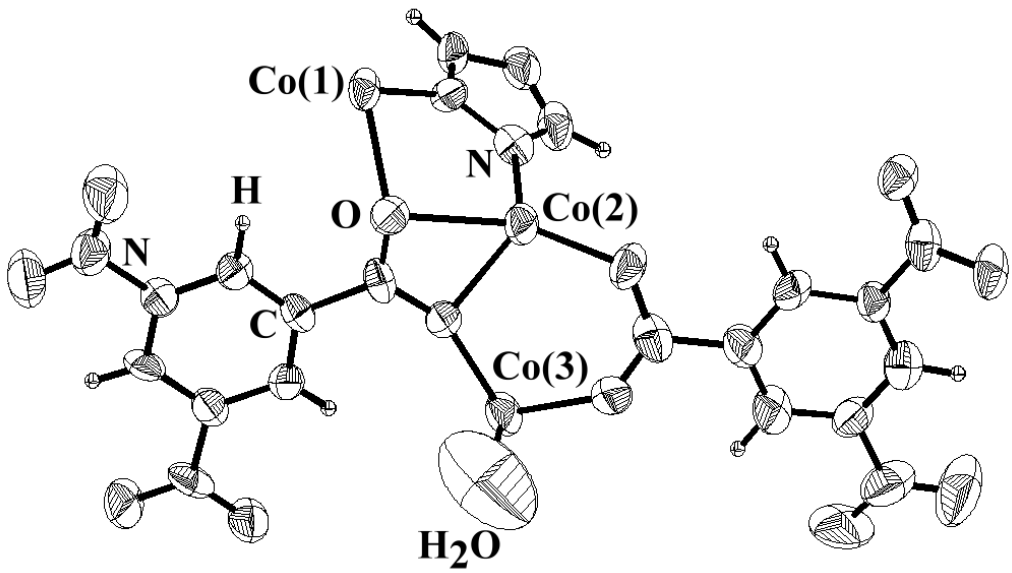

Fig. S28. Figure shows the ORTEP diagram of compound-**Ib.**

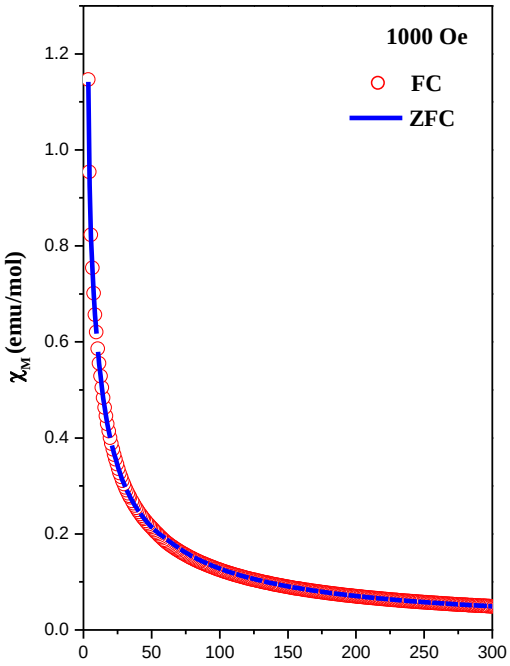

Fig. S29. Figure shows field cooled and zero field cooled (H = 1000 Oe) magnetization of compound-**I**

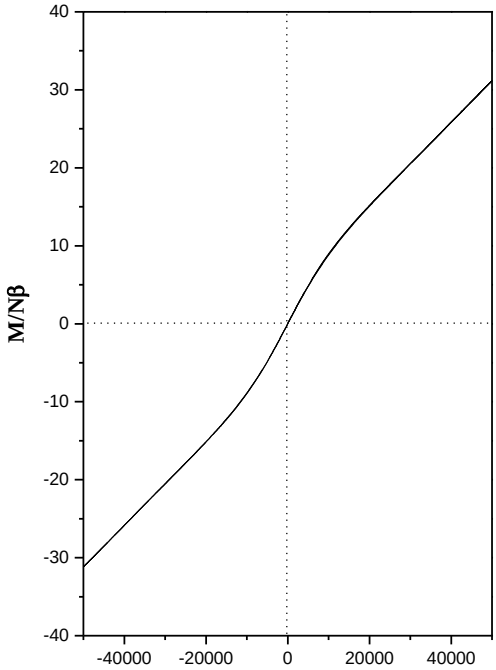

Fig. S30. Figure shows M vs. H plot at 3.5 K for the compound-**I**

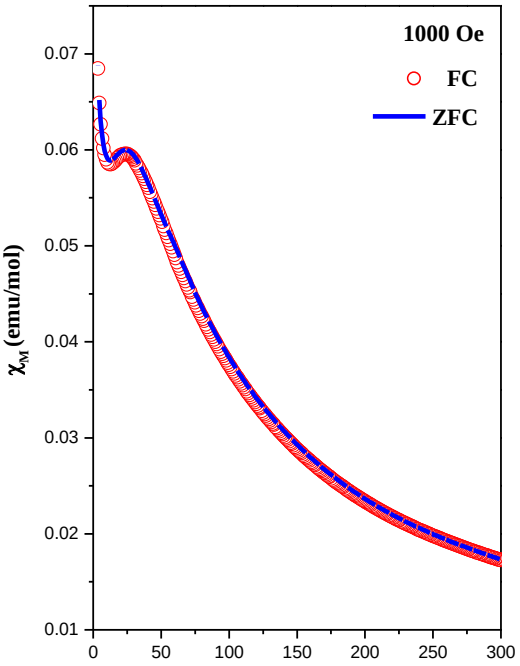

Fig. S31. Figure shows field cooled and zero field cooled (H = 1000 Oe) magnetization of compound-**II**

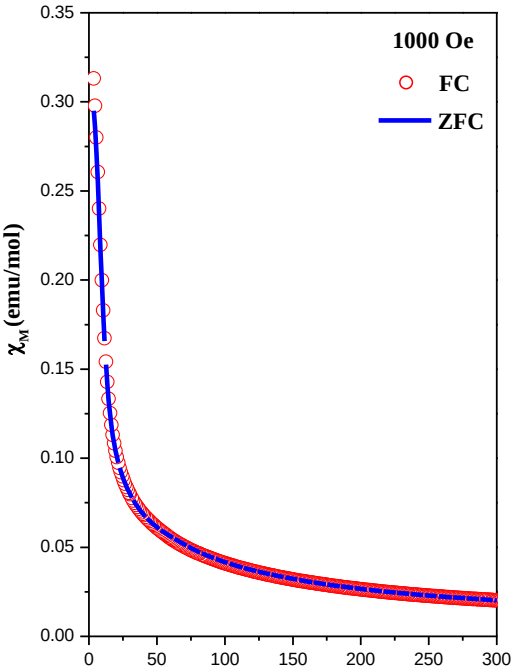

Fig. S32. Figure shows field cooled and zero field cooled (H = 1000 Oe) magnetization of compound-**III**

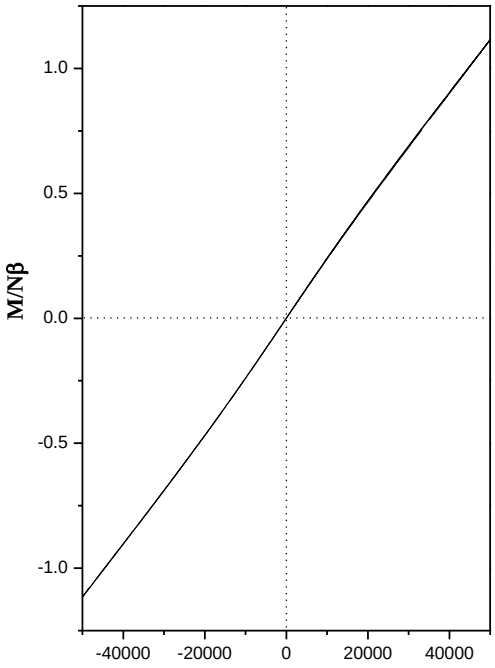

Fig. S33. Figure shows M vs. H plot at 3.5 K for the compound-**II**

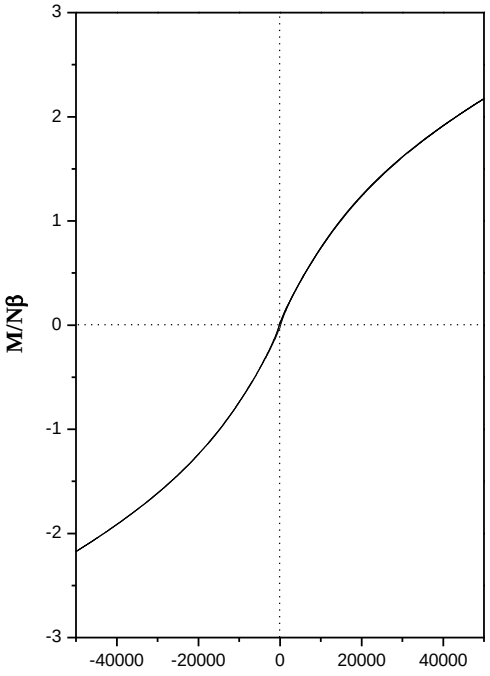

Fig. S34. Figure shows M vs. H plot at 3.5 K for the compound- **III**

Table S1. List of important IR – bands present in the compound-**I**, compound-**II** and compound-**III**.

Compound	**I**	**II**	**III**
γ_{as}(O – H)	~ 3580 & 3539	~ 3600	~ 3606 & 3573
γ_{s}(N – H)	–	~ 3285 & 3252	~ 3359, 3325 & 3272
γ_{s}(C – H)$_{aromatic}$	~ 3104 & 3064	~ 3117 & 3078	~ 3131 & 3078
γ_{s}(C =O)	~ 1619	~ 1613	~ 1626
δ_{s}(H_2O)	~ 1540	~ 1535	~ 1532
δ_{s}(COO)	~ 1458	~ 1445	~ 1452
γ_{s}(N – O)	~ 1338	~ 1345	~ 1345
γ_{s}(C – C)$_{skeletal}$	~ 1004	~ 1037	~ 997
δ (C – N)$_{skeletal}$	~ 938	~ 930	~ 910
δ (C–H$_{aromatic}$)$_{out\ of\ plane}$	~ 730	~ 727	~ 717

Table S2. Important H-bonding interactions observed in compound-**II** and compound- **III.**

D – H⋯ A	D – H, (Å)	H … A, (Å)	D … A, (Å)	D – H … A, (°)
II				
O(1)-H(1a) ⋯O(8)#a	0.85(2)	2.54(2)	2.944(3)	110
N(2)-H(2a) ⋯O(5)#b	0.86	2.28	3.011(2)	143
III				
O(3)-H(3A) ⋯ O(8)	0.84(5)	2.24(6)	2.914(7)	137
N(4)-H(4A) ⋯ O(1)#a	0.86	2.56	3.186(5)	131
N(4)-H(4A) ⋯ N(3)#b	0.86	2.56	3.085(6)	121
N(4)-H(4B) ⋯ O(4)#c	0.86	2.45	3.249(5)	155
N(4)-H(4B) ⋯ O(3)#b	0.86	2.55	3.125(5)	125
N(5)-H(5A) ⋯ O(5)#d	0.86	2.40	3.125(6)	143
N(5)-H(5B) ⋯ N(1)	0.86	2.55	3.228(6)	136
N(5)-H(5B) ⋯ O(1)#e	0.86	2.48	3.067(6)	126
N(5)-H(5B) ⋯ N(5)#e	0.86	2.62	3.261(6)	132
O(5)-H(51) ⋯ O(100)#f	0.95(6)	1.89(5)	2.745(11)	149
O(5)-H(52) ⋯ N(2)#g	0.95(4)	2.29(8)	3.138(6)	149

Symmetry transformations used to generate equivalent atoms:

For **II**: #a -1+x,y,z; #a -1+x, ½-y, -1/2+z

For **III**: #a 2-x,1/2+y,1/2-z; #b 2-x,1-y,-z; #c 1+x,y,z; #d 1+x,1/2-y,1/2+z; #e 2-x,1-y,1-z; #f x,1/2-y,-1/2+z;

#g -1+x,1/2-y,-1/2+z

Table S3. Selected bond angles for compound- **I** compound-**II**, compound-- **III.**

Angle	Amplitude (º)	Angle	Amplitude (º)	Angle	Amplitude (º)
$[Co_5(H_2O)_4\{(NO_2)\text{-}C_6H_3\text{-}(COO)_2\}_4(C_2N_3H_2)_2]. 2H_2O$, compound- **I**					
N(2)#2-Co(1)-N(1)	180.000(1)	O(1)#2-Co(1)-O(1)	180.0	N(1)#2-Co(1)-O(2)#2	85.95(6)
N(2)#2-Co(1)-O(1)#2	94.13(7)	N(1)#2-Co(1)-O(2)	94.05(6)	N(1)-Co(1)-O(2)#2	94.05(6)
N(1)-Co(1)-O(1)#2	85.87(7)	N(1)-Co(1)-O(2)	85.95(6)	O(1)#2-Co(1)-O(2)#2	89.16(6)
N(1)#2-Co(1)-O(1)	85.87(7)	O(1)#2-Co(1)-O(2)	90.84(6)	O(1)-Co(1)-O(2)#2	90.84(6)
N(1)-Co(1)-O(1)	94.13(7)	O(1)-Co(1)-O(2)	89.16(6)	O(2)-Co(1)-O(2)#2	180.0
O(3)#1-Co(2)-O(4)	97.38(7)	N(2)-Co(2)-O(2)	89.53(6)	O(3)#1-Co(2)-O(6)	99.62(6)
O(3)#1-Co(2)-N(2)	96.21(7)	O(3)#1-Co(2)-O(5)	89.03(7)	O(4)-Co(2)-O(6)	159.96(6)
O(4)-Co(2)-N(2)	96.19(7)	O(4)-Co(2)-O(5)	87.05(7)	N(2)-Co(2)-O(6)	92.45(6)
O(3)#1-Co(2)-O(2)	157.26(6)	N(2)-Co(2)-O(5)	173.42(7)	O(2)-Co(2)-O(6)	58.05(5)
O(4)-Co(2)-O(2)	103.87(6)	O(1)-Co(2)-O(5)	84.12(6)	O(5)-Co(2)-O(6)	82.72(6)
O(7)#1-Co(3)-N(3)#3	92.64(7)	O(8)#4-Co(3)-O(6)	106.15(6)	O(7)#1-Co(3)-O(10)#4	85.50(6)
O(7)#1-Co(3)-O(8)#4	143.68(6)	O(7)#1-Co(3)-O(9)	84.88(7)	N(3)#3-Co(3)-O(10)#4	88.49(7)
N(3)#3-Co(3)-O(8)#4	98.19(7)	N(3)#3-Co(3)-O(9)	173.50(7)	O(8)#4-Co(3)-O(10)#4	60.42(6)
O(7)#1-Co(3)-O(6)	108.45(6)	O(8)#4-Co(3)-O(9)	87.29(7)	O(6)-Co(3)-O(10)#4	166.01(6)
N(3)#3-Co(3)-O(6)	89.83(6)	O(6)-Co(3)-O(9)	85.28(6)	O(9)-Co(3)-O(10)#4	97.29(6)
$[Co_5\{(NO_2)\text{-}C_6H_3\text{-}(COO)_2\}_4(C_2N_3H_2)_2]$, compound-**Ia**					
O(2)-Co(1)-O(1)#1	99.7(4)	O(2)-Co(1)-N(1)	99.3(4)	O(1)#1-Co(1)-N(1)	102.3(5)
O(2)-Co(1)-O(5)	144.0(4)	O(1)#1-Co(1)-O(5)	101.8(3)	N(1)-Co(1)-O(5)	103.8(4)
O(2)-Co(1)-O(3)	94.7(3)	O(1)#1-Co(1)-O(3)	159.1(4)	N(1)-Co(1)-O(3)	90.1(4)
O(5)-Co(1)-O(3)	58.5(3)	N(2)#2-Co(2)-N(2)	180.000(2)	N(2)#2-Co(2)-O(6)#2	93.4(4)

N(2)-Co(2)-O(6)#2	86.6(4)	N(2)#2-Co(2)-O(6)	86.6(4)	N(2)-Co(2)-O(6)	93.4(4)
O(6)#2-Co(2)-O(6)	180.000(1)	N(2)#2-Co(2)-O(3)	94.2(4)	N(2)-Co(2)-O(3)	85.8(4)
O(6)#2-Co(2)-O(3)	90.4(3)	O(6)-Co(2)-O(3)	89.6(3)	N(2)#2-Co(2)-O(3)#2	85.8(4)
N(2)-Co(2)-O(3)#2	94.2(4)	O(6)#2-Co(2)-O(3)#2	89.6(3)	O(6)-Co(2)-O(3)#2	90.4(3)
O(3)-Co(2)-O(3)#2	180.000(2)	O(7)#1-Co(3)-O(8)#3	134.8(4)	O(7)#1-Co(3)-O(5)	99.5(4)
O(8)#3-Co(3)-O(5)	113.1(3)	O(7)#1-Co(3)-N(3)#4	97.1(4)	O(8)#3-Co(3)-N(3)#4	109.7(4)
O(5)-Co(3)-N(3)#4	95.1(4)	O(7)#1-Co(3)-O(10)#3	85.0(4)	O(8)#3-Co(3)-O(10)#3	61.4(3)
O(5)-Co(3)-O(10)#3	174.5(4)	N(3)#4-Co(3)-O(10)#3	87.5(5)		
$[Co_5(H_2O)_2\{(NO_2)\text{-}C_6H_3\text{-}(COO)_2\}_4(C_2N_3H_2)_2]$, compound-**Ib**					
O(2)-Co(1)-O(1)#1	100.0(4)	O(2)-Co(1)-N(1)	101.0(4)	O(1)#1-Co(1)-N(1)	100.1(4)
O(5)-Co(1)-O(3)	58.3(3)	O(2)-Co(1)-O(5)	140.5(4)	O(1)#1-Co(1)-O(5)	104.7(3)
N(1)-Co(1)-O(5)	104.4(4)	O(2)-Co(1)-O(3)	92.5(3)	O(1)#1-Co(1)-O(3)	162.3(4)
N(1)-Co(1)-O(3)	89.6(4)	N(2)#2-Co(2)-N(2)	180.000(2)	N(2)#2-Co(2)-O(6)	87.4(4)
N(2)-Co(2)-O(6)	92.6(4)	N(2)#2-Co(2)-O(6)#2	92.6(4)	N(2)-Co(2)-O(6)#2	87.4(4)
O(6)-Co(2)-O(6)#2	180.00(10)	N(2)#2-Co(2)-O(3)	93.6(4)	N(2)-Co(2)-O(3)	86.4(4)
O(6)-Co(2)-O(3)	89.8(4)	O(6)#2-Co(2)-O(3)	90.2(4)	N(2)#2-Co(2)-O(3)#2	86.4(4)
N(2)-Co(2)-O(3)#2	93.6(4)	O(6)-Co(2)-O(3)#2	90.2(4)	O(6)#2-Co(2)-O(3)#2	89.8(4)
O(3)-Co(2)-O(3)#2	180.000(1)	O(7)#1-Co(3)-N(3)#3	93.9(4)	O(7)#1-Co(3)-O(8)#4	142.8(4)
N(3)#3-Co(3)-O(8)#4	104.2(4)	O(7)#1-Co(3)-O(5)	99.0(4)	N(3)#3-Co(3)-O(5)	91.9(4)
O(8)#4-Co(3)-O(5)	112.4(3)	O(7)#1-Co(3)-O(10)#4	87.9(4)	N(3)#3-Co(3)-O(10)#4	87.8(5)
O(8)#4-Co(3)-O(10)#4	61.1(3)	O(5)-Co(3)-O(10)#4	173.1(3)	O(7)#1-Co(3)-O(9)	80.1(7)
N(3)#3-Co(3)-O(9)	173.4(6)	O(8)#4-Co(3)-O(9)	82.4(6)	O(5)-Co(3)-O(9)	86.3(8)
O(10)#4-Co(3)-O(9)	94.7(8)				

$[Co_2(\mu_3\text{-}OH)(H_2O)\{(NO_2)\text{-}C_6H_3\text{-}(COO)_2\}(C_2N_4H_3)].\ H_2O$, compound-**II**					
O(1)#1-Co(1)-N(1)	170.49(6)	O(1)-Co(1)-O(2)	173.00(9)	O(1)#1-Co(1)-N(2)#2	87.55(5)
O(1)#1-Co(1)-O(1)	81.60(5)	O(1)#1-Co(1)-O(3)	88.69(6)	N(1)-Co(1)-N(2)#2	92.23(6)
N(1)-Co(1)-O(1)	88.90(6)	N(1)-Co(1)-O(3)	91.93(6)	O(1)-Co(1)-N(2)#2	90.26(5)
O(1)#1-Co(1)-O(2)	91.61(9)	O(1)-Co(1)-O(3)	91.92(6)	O(2)-Co(1)-N(2)#2	91.16(7)
N(1)-Co(1)-O(2)	97.90(9)	O(2)-Co(1)-O(3)	86.20(8)	O(3)-Co(1)-N(2)#2	175.34(6)
O(1)-Co(2)-O(4)	113.85(6)	O(5)#3-Co(2)-N(3)#4	95.44(6)	O(1)-Co(2)-O(5)#3	130.58(6)
O(1)-Co(2)-N(4)	84.81(6)	O(4)-Co(2)-O(5)#3	114.16(7)	O(4)-Co(2)-N(4)	82.35(7)
O(1)-Co(2)-N(3)#4	95.22(6)	O(5)#3-Co(2)-N(4)	90.47(6)	O(4)-Co(2)-N(3)#4	90.46(7)
N(3)#4-Co(2)-N(4)	172.12(7)				
$[Co_2(\mu_3\text{-}OH)(H_2O)\{(NO_2)\text{-}C_6H_3\text{-}(COO)_2\}(C_2N_5H_5)].\ H_2O$, compound-**III**					
O(1)#1-Co(1)-O(2)	151.67(17)	O(2)-Co(1)-N(1)#3	89.84(17)	O(2)-Co(1)-N(2)	86.90(17)
O(1)#1-Co(1)-O(3)#2	106.37(16)	O(3)#2-Co(1)-N(1)#3	91.28(15)	O(3)#2-Co(1)-N(2)	83.07(15)
O(2)-Co(1)-O(3)#2	101.30(15)	O(1)#1-Co(1)-N(2)	90.51(16)	N(1)#3-Co(1)-N(2)	172.79(17)
O(1)#1-Co(1)-N(1)#3	95.40(16)	O(3)#2-Co(2)-O(4)	98.40(15)	O(3)-Co(2)-N(4)#4	84.92(15)
O(3)-Co(2)-N(3)	170.17(17)	O(3)-Co(2)-O(5)	96.13(17)	N(3)-Co(2)-N(4)#4	91.67(17)
O(3)-Co(2)-O(3)#2	83.69(15)	N(3)-Co(2)-O(5)	93.10(18)	O(3)#2-Co(2)-N(4)#4	92.33(15)
N(3)-Co(2)-O(3)#2	87.25(15)	O(3)#2-Co(2)-O(5)	177.39(16)	O(4)-Co(2)-N(4)#4	166.89(16)
O(3)-Co(2)-O(4)	88.78(15)	O(4)-Co(2)-O(5)	78.99(17)	O(5)-Co(2)-N(4)#4	90.24(16)
N(3)-Co(2)-O(4)	96.33(16)				

Symmetry transformations used to generate equivalent atoms:

For compound-**I**: #1 -x,-y+1,-z+1; #2 –x+1,-y+1,-z+2; #3 -x+1,-y+1,-z+1; #4 -x+1,-y+2,-z+1

For compound-**Ia**: #1 -x,-y,-z+1; #2 -x+1,-y+1,-z+1; #3 -x,-y+1,-z; #4 -x,-y+1,-z+1

For compound-**Ib**: #1 -x,-y,-z+1; #2 -x+1,-y+1,-z+1; #3 -x,-y+1,-z+1; #4 -x,-y+1,-z

For compound-**II**: #1 -x+1,-y,-z; #2 x,-y+1/2,z-1/2; #3 x-1,y,z; #4 -x+1,y-1/2,-z+1/2

For compound-**III**: #1 x-1,y,z; #2 -x,-y,-z+1; #3 -x,y-1/2,-z+3/2; #4 x,-y+1/2,z-1/2