<Electronic Supplementary Information>

Water-reservoir properties dependent on packing modes of $[Ni(II)_3L_6]$ cages

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Electronic supplementary information (ESI) available: Experimental details and crystal-structure determination. IR spectra and full ^1H NMR spectra of each sample (L^1, L^2, L^3, $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4\cdot 34H_2O$, $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4\cdot 38H_2O$, $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4\cdot 13H_2O$, and $Cl_2@[Ni_3Cl_3L^3{}_6(H_2O)_3]Cl\cdot 5C_4H_8O_2$). TGA curves of $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4\cdot 34H_2O$, $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4\cdot 38H_2O$, and $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4\cdot 13H_2O$.

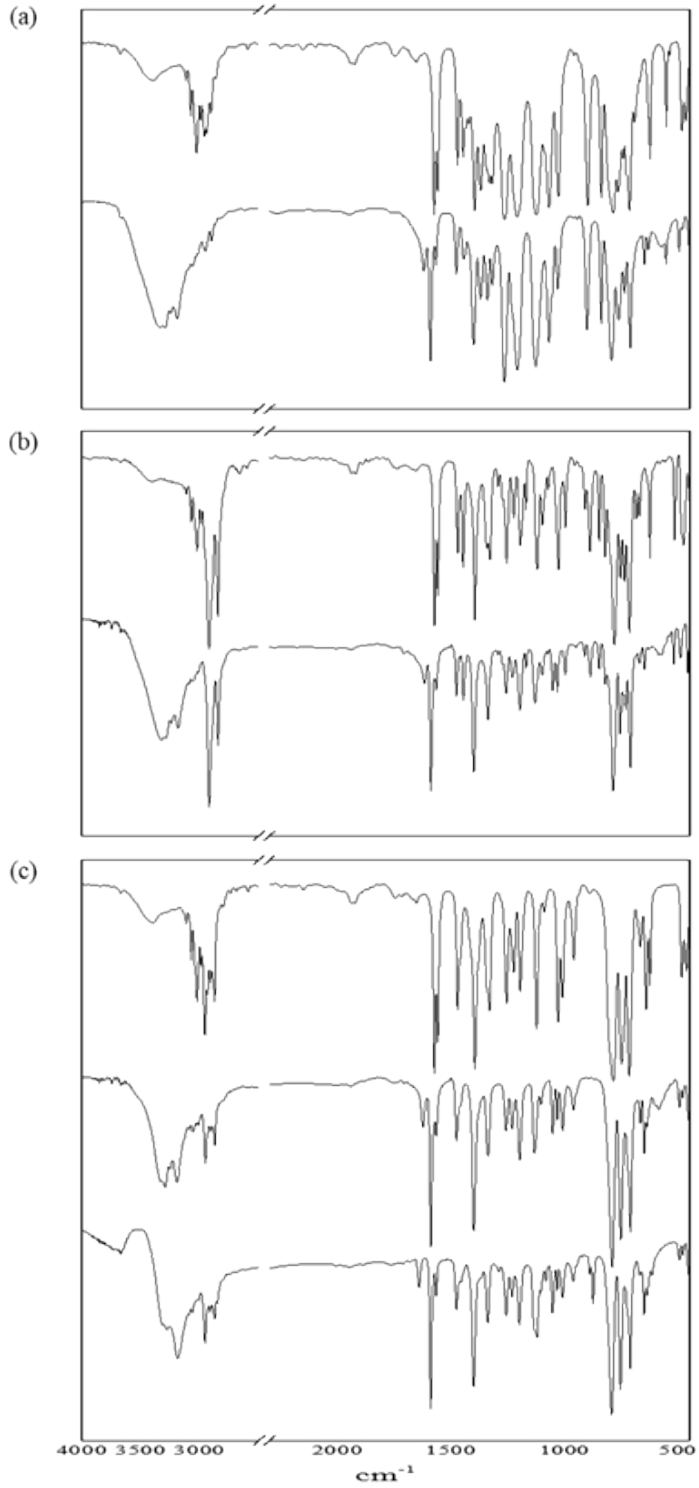

Fig. S1 IR spectra of L^1 and $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4 \cdot 34H_2O$ (a), L^2 and $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4 \cdot 38H_2O$ (b), and L^3, $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4 \cdot 13H_2O$, and $Cl_2@[Ni_3Cl_3L^3{}_6(H_2O)_3]Cl \cdot 5C_4H_8O_2$ (c).

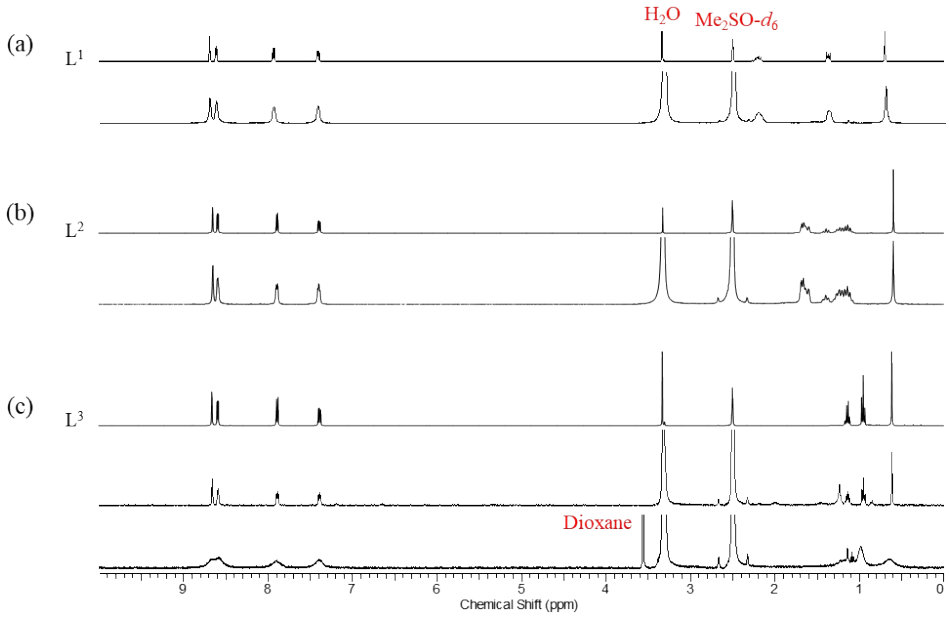

Fig. S2 ^{1}H NMR spectra of L^1 and $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4\cdot 34H_2O$ (a), L^2 and $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4\cdot 38H_2O$ (b), and L^3, $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4\cdot 13H_2O$, and $Cl_2@[Ni_3L^3{}_6\ Cl_3(H_2O)_3]Cl\cdot 5C_4H_8O_2$ (c). The cage complexes were dissociated in Me_2SO.

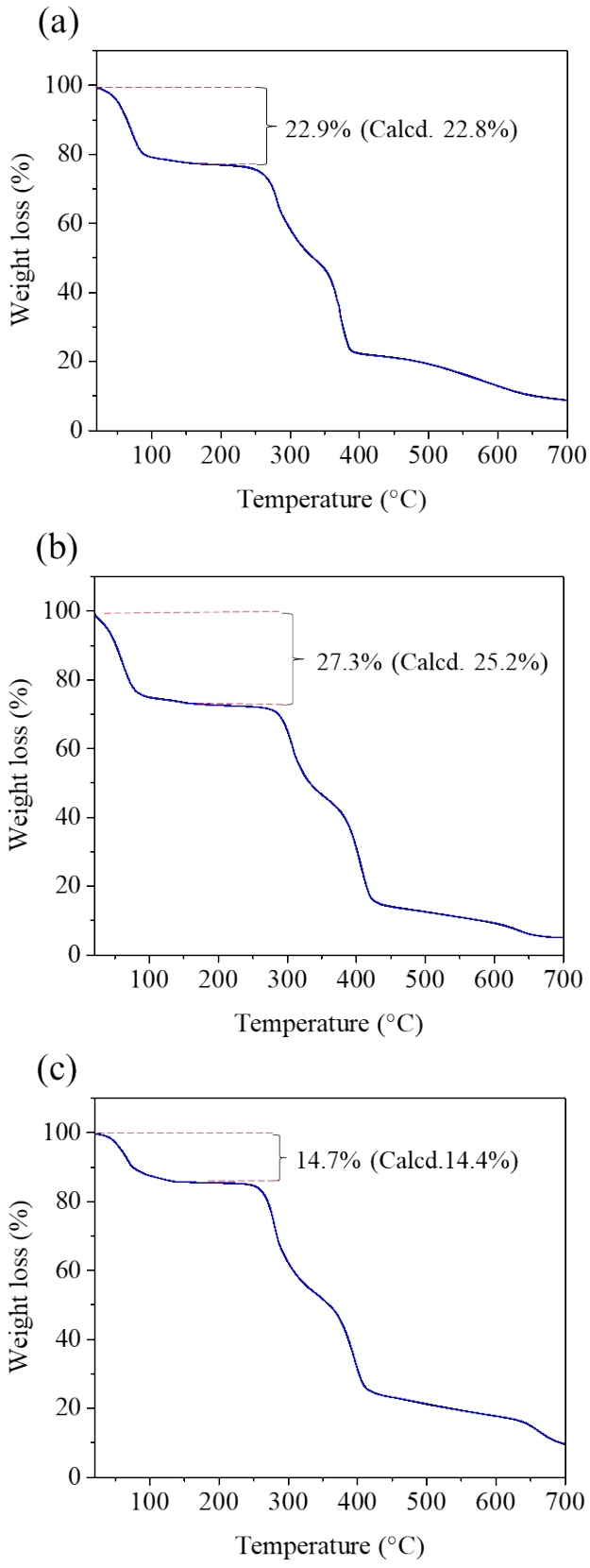

Fig. S3 TGA results of original product for $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4{\cdot}34H_2O$ (a), $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4{\cdot}38H_2O$ (b), and $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4{\cdot}13H_2O$ (c).

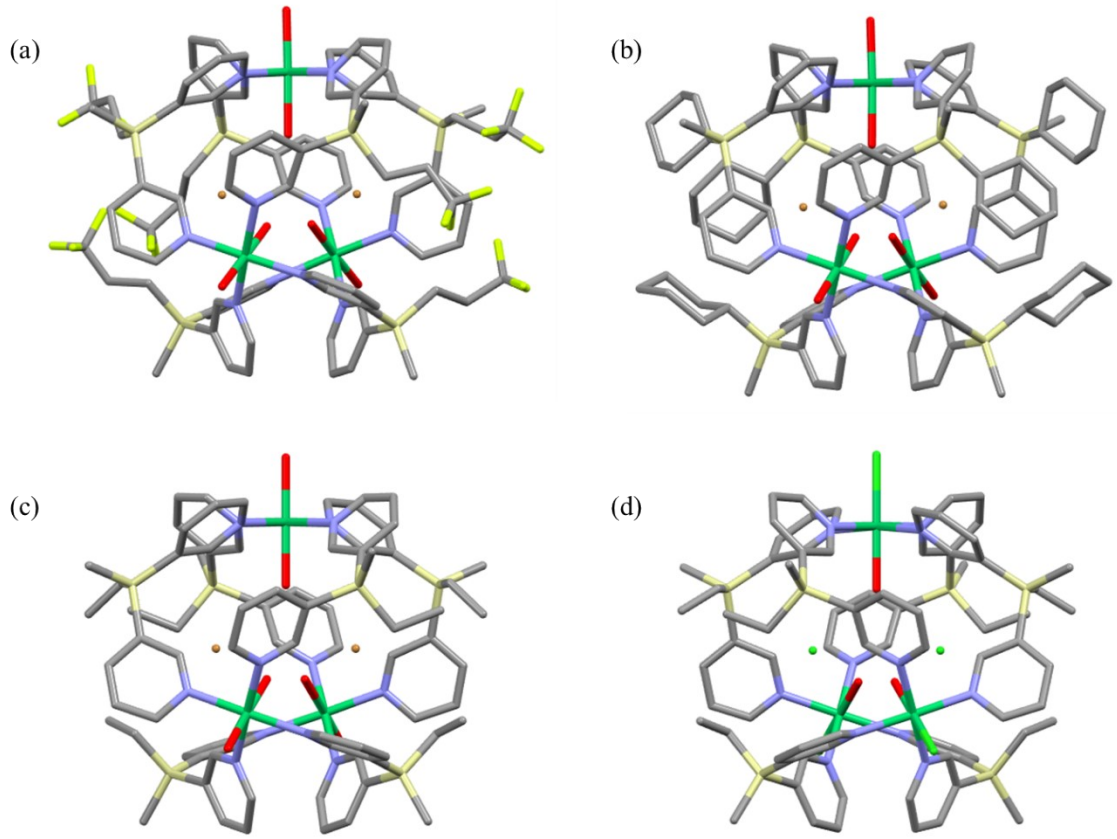

Fig. S4 Molecular structures for $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4 \cdot 34H_2O$ (a), $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4 \cdot 38H_2O$ (b), $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4 \cdot 13H_2O$ (c), and $Cl_2@[Ni_3L^3{}_6Cl_3(H_2O)_3]Cl \cdot 5C_4H_8O_2$ (d).

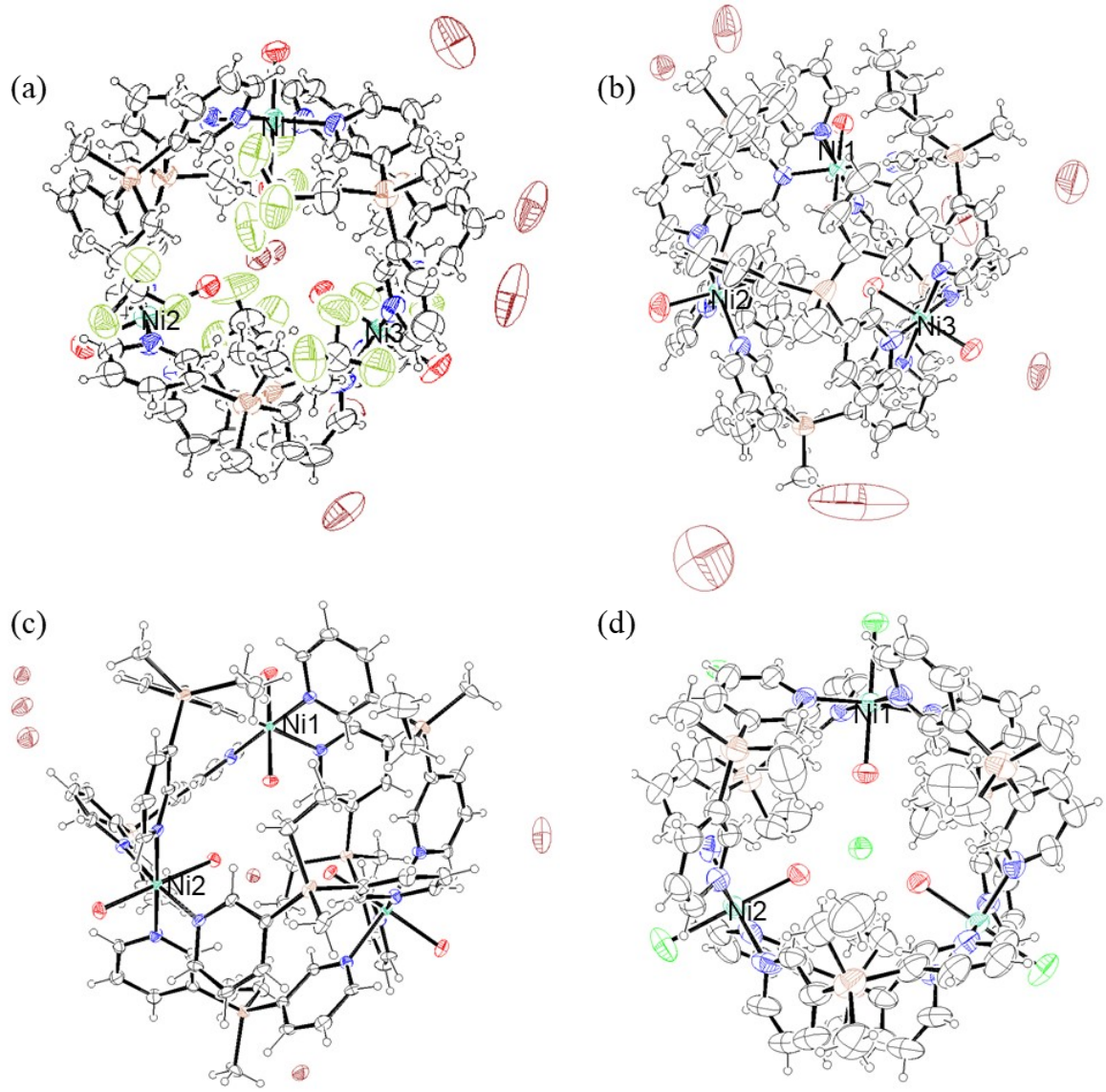

Fig. S5 ORTEP structures of $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4 \cdot 34H_2O$ (a), $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4 \cdot 38H_2O$ (b), $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4 \cdot 13H_2O$ (c), and $Cl_2@[Ni_3L^3{}_6Cl_3(H_2O)_3]Cl \cdot 5C_4H_8O_2$ (d) with thermal ellipsoids drawn at 30% probability

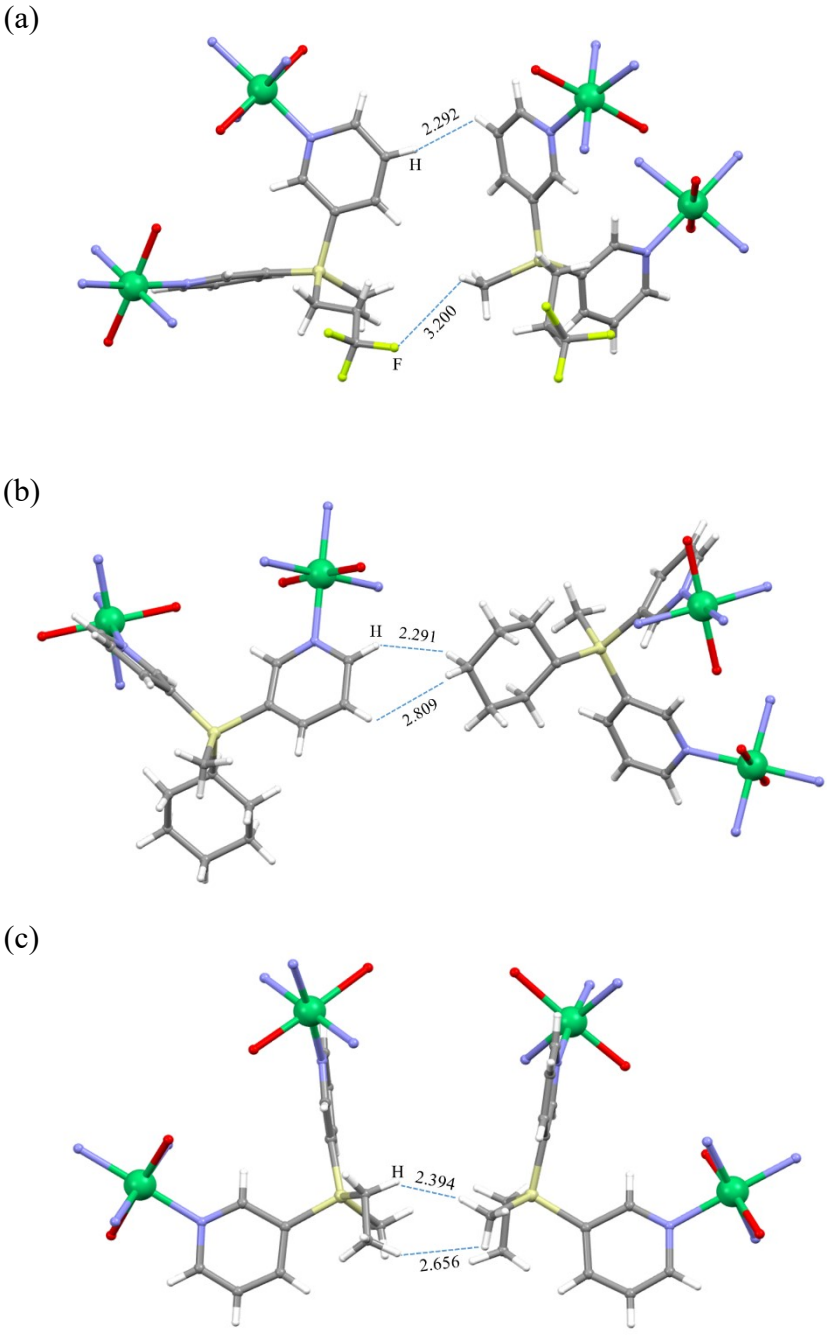

Fig. S6 Shortest inter-cage CH ⋯ HC or CF ⋯ HC distance (Å) for $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4{\cdot}34H_2O$ (a), $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4{\cdot}38H_2O$ (b), and $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4{\cdot}13H_2O$ (c).

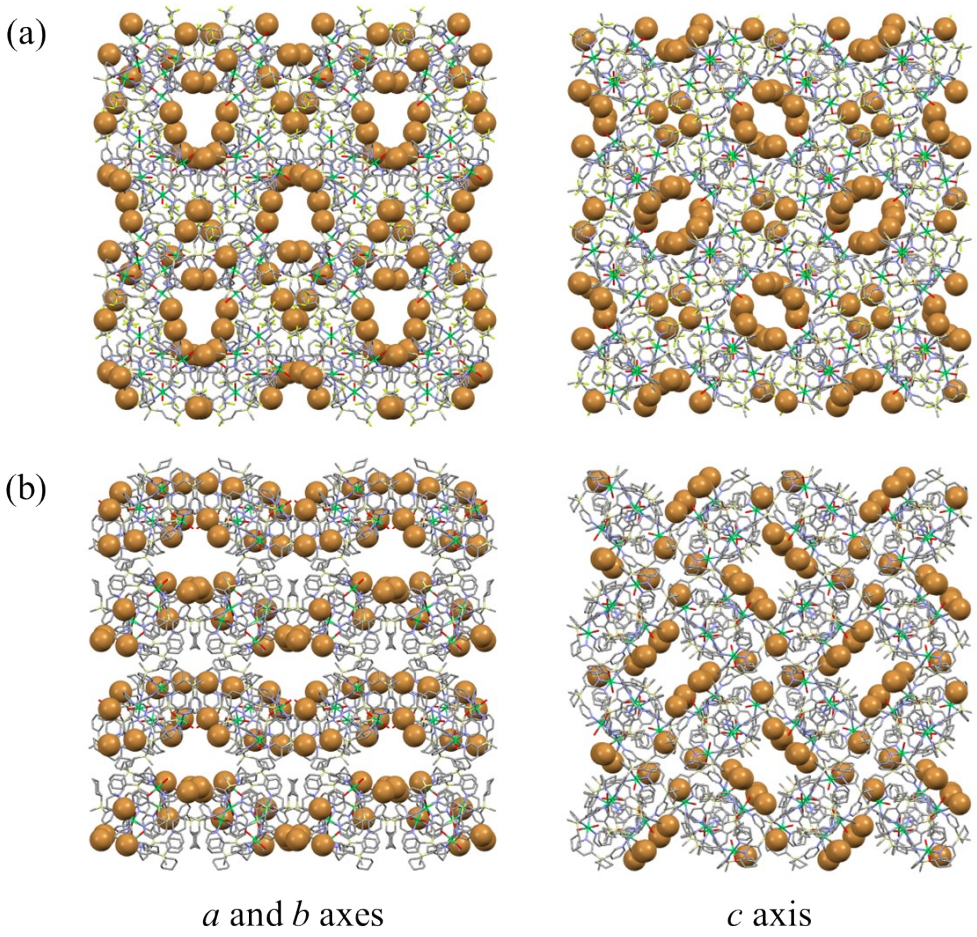

Fig. S7 The crystal structures showing the position of outside Br^- in $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4 \cdot 34H_2O$ (a) and $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4 \cdot 38H_2O$ (b).

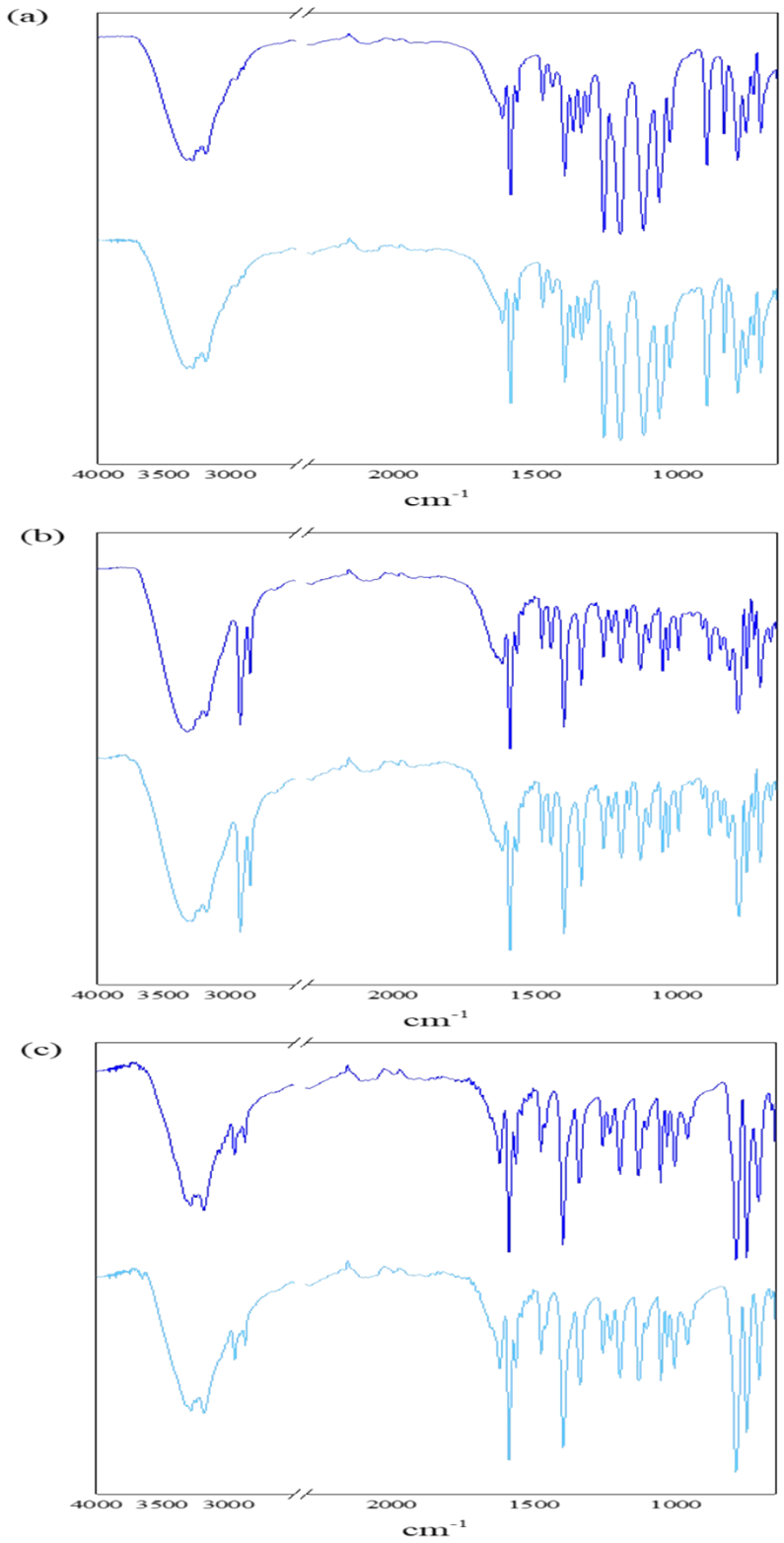

Fig. S8 IR spectra of $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4{\cdot}34H_2O$ (blue) and solvate H_2O readsorbed $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4{\cdot}34H_2O$ (light blue) (a), $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4{\cdot}38H_2O$ (blue) and solvate H_2O readsorbed $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4{\cdot}38H_2O$ (light blue) (b), $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4{\cdot}13H_2O$ (blue), and solvate H_2O readsorbed $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4{\cdot}13H_2O$ (light blue) (c).

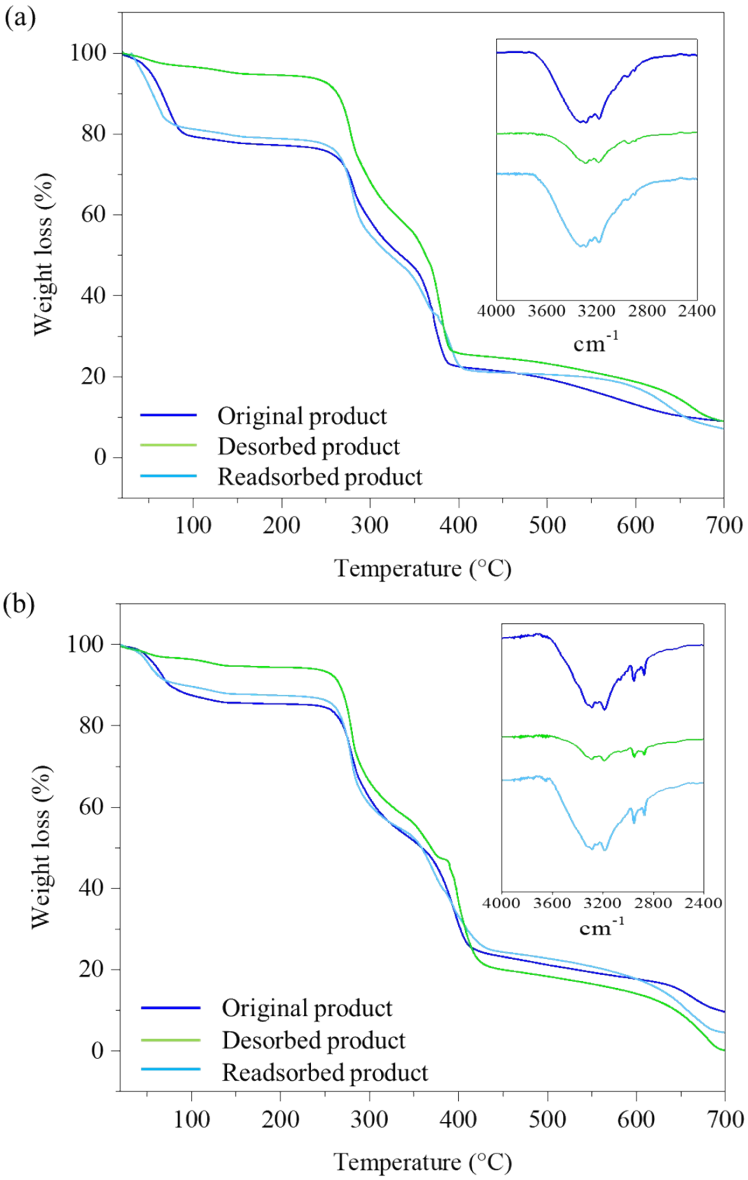

Fig. S9 TGA and FT-IR spectra (inset) for $Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4 \cdot 34H_2O$ (a) and $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4 \cdot 13H_2O$ (b). Original product (blue), after desorbed sample over P_2O_5 (green), and after readsorbed sample in H_2O (light blue). The curve (green) shows that all of the H_2O molecules within the channels excepting the coordinated water molecules evaporated. The light blue curve indicates that the water solvates are restored in H_2O.

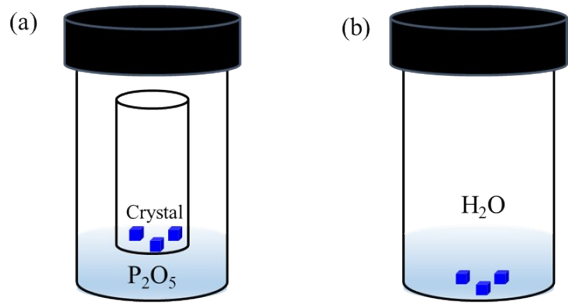

Fig. S10 Procedure of solvate H_2O desorption over P_2O_5 (a) and readsorption in water (b). The procedure was monitored by TGA.

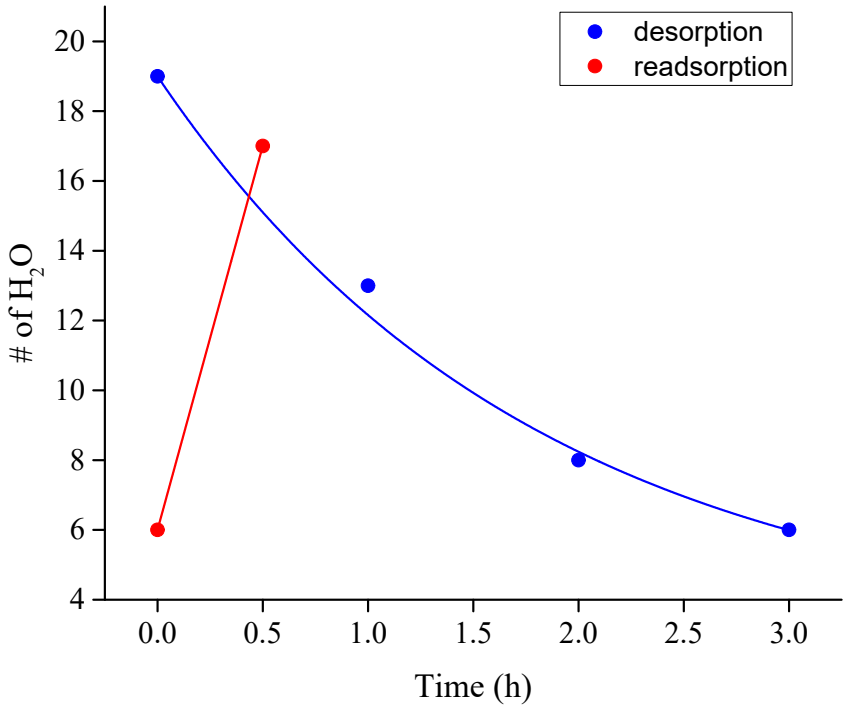

Fig. S11 Water-desorption/readsorption rate of $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4 \cdot 13H_2O$

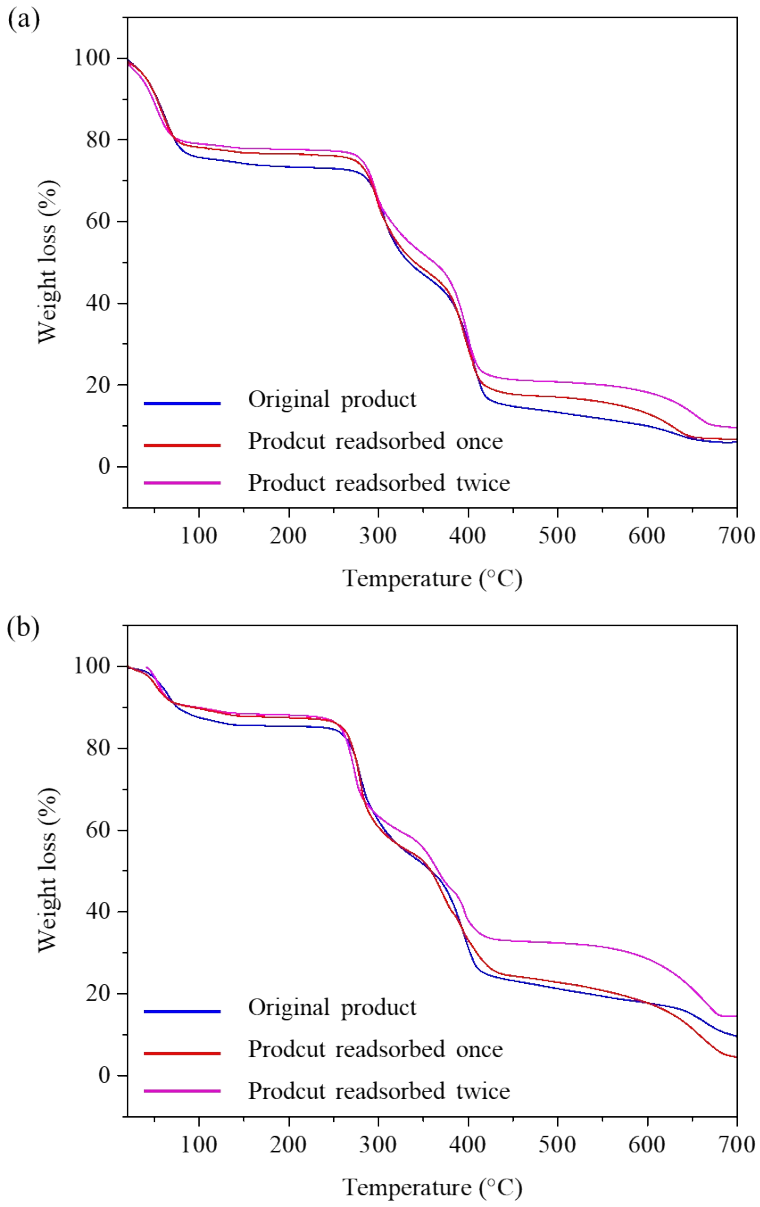

Fig. S12 TGA results of recyclability test for $Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4 \cdot 38H_2O$ (a) and $Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4 \cdot 13H_2O$ (b).

Table S1 Crystallographic data

	$Br_2@[Ni_3L^1{}_6(H_2O)_6]Br_4\cdot 34H_2O$	$Br_2@[Ni_3L^2{}_6(H_2O)_6]Br_4\cdot 38H_2O$	$Br_2@[Ni_3L^3{}_6(H_2O)_6]Br_4\cdot 13H_2O$	$Cl_2@[Ni_3L^3{}_6Cl_3(H_2O)_3]Cl\cdot 5C_4H_8O_2$
Formula	$Ni_3Br_6C_{84}H_{170}O_{40}N_{12}F_{18}Si_6$	$Ni_3Br_6C_{102}H_{220}O_{44}N_{12}Si_6$	$Ni_3Br_6C_{78}H_{134}O_{19}N_{12}Si_6$	$Ni_3Cl_6C_{98}H_{141}O_{13}N_{12}Si_6$
M_w	3154.44	3143.02	2368.09	2252.59
Cryst. sys.	Tetragonal	Tetragonal	Tetragonal	Monoclinic
Space group	$P\text{-}42_1c$	$P\text{-}42_1c$	$I4_122$	$C2/c$
a (Å)	30.232(4)	31.291(4)	23.0816(4)	26.434(5)
b (Å)	30.232(4)	31.291(4)	23.0816(4)	15.826(3)
c (Å)	30.935(6)	31.796(6)	39.4683(13)	27.998(6)
β (°)	90	90	90	105.26(3)
V (Å^3)	28273(10)	31132(11)	21027.1(10)	11300(4)
Z	8	8	8	4
ρ (g cm^{-3})	1.482	1.341	1.496	1.324
μ (mm^{-1})	2.638	2.542	2.945	0.726
R_{int}	0.0973	0.0970	0.0827	0.1308
GoF on F^2	0.941	0.989	1.049	0.903
R_1 [$I>2\sigma(I)$][a]	0.0663	0.0579	0.0436	0.0844
wR_2 (all data)[b]	0.2096	0.1850	0.1234	0.2776

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$

Table S2 Bond lengths (Å) and angles (°)

$Br_2@[Ni_3L^1{}_6(H_2O)_6]$ $Br_4\cdot 34H_2O$		$Br_2@[Ni_3L^2{}_6(H_2O)_6]$ $Br_4\cdot 38H_2O$		$Br_2@[Ni_3L^3{}_6(H_2O)_6]$ $Br_4\cdot 13H_2O$		$Cl_2@[Ni_3L^3{}_6Cl_3(H_2O)_3]$ $Cl\cdot 5C_4H_8O_2$	
Ni(1)-O(6)	2.065(9)	Ni(1)-O(4)	2.098(6)	Ni(1)-O(4)	2.079(5)	Ni(1)-N(5)	2.115(5)
Ni(1)-N(3)	2.085(9)	Ni(1)-O(3)	2.098(7)	Ni(1)-O(3)	2.087(5)	Ni(1)-N(5)$^{\#1}$	2.115(5)
Ni(1)-N(12)	2.088(9)	Ni(1)-N(1E)	2.104(7)	Ni(1)-N(1)$^{\#2}$	2.114(5)	Ni(1)-O(3)	2.127(5)
Ni(1)-O(1)	2.109(8)	Ni(1)-N(2D)	2.109(7)	Ni(1)-N(1)	2.114(5)	Ni(1)-N(4)$^{\#1}$	2.129(6)
Ni(1)-N(9)	2.118(9)	Ni(1)-N(2B)	2.116(7)	Ni(1)-N(3)$^{\#2}$	2.116(5)	Ni(1)-N(4)	2.129(6)
Ni(1)-N(13)	2.15(1)	Ni(1)-N(1A)	2.118(8)	Ni(1)-N(3)	2.116(5)	Ni(1)-Cl(2)	2.404(2)
Ni(2)-O(4)	2.08(1)	Ni(2)-O(5)	2.072(6)	Ni(2)-N(4)	2.092(4)	Ni(2)-N(6)$^{\#1}$	2.118(6)
Ni(2)-N(10)	2.084(9)	Ni(2)-N(1D)	2.090(9)	Ni(2)-N(6)$^{\#2}$	2.097(5)	Ni(2)-N(1)	2.118(5)
Ni(2)-N(2)	2.100(9)	Ni(2)-N(2F)	2.105(5)	Ni(2)-O(1)	2.102(4)	Ni(2)-N(2)	2.123(6)
Ni(2)-N(4)	2.111(9)	Ni(2)-N(2E)	2.111(9)	Ni(2)-O(2)	2.103(3)	Ni(2)-O(1)	2.124(4)
Ni(2)-O(2)	2.125(9)	Ni(2)-N(2C)	2.115(8)	Ni(2)-N(2)	2.103(4)	Ni(2)-N(3)	2.146(6)
Ni(2)-O(4)	2.08(1)	Ni(2)-O(6)	2.161(8)	Ni(2)-N(5)	2.109(4)	Ni(2)-Cl(1)	2.372(2)
Ni(3)-O(5)	2.063(7)	Ni(3)-O(2)	2.083(5)			N(5)-Ni(1)-N(5)$^{\#1}$	173.2(3)
Ni(3)-O(3)	2.110(9)	Ni(3)-N(1F)	2.083(9)	O(4)-Ni(1)-O(3)	180.0	N(5)-Ni(1)-O(3)	86.6(1)
Ni(3)-N(11)	2.12(1)	Ni(3)-O(1)	2.109(6)	O(4)-Ni(1)-N(1)$^{\#2}$	90.7(1)	N(5)$^{\#1}$-Ni(1)-O(3)	86.6(1)
Ni(3)-N(7)	2.123(1)	Ni(3)-N(1C)	2.112(8)	O(3)-Ni(1)-N(1)$^{\#2}$	89.3(1)	N(5)-Ni(1)-N(4)$^{\#1}$	88.6(2)
Ni(3)-N(6)	2.14(1)	Ni(3)-N(1B)	2.113(8)	O(4)-Ni(1)-N(1)	90.7(1)	N(5)$^{\#1}$-Ni(1)-N(4)$^{\#1}$	91.4(2)
Ni(3)-N(5)	2.15(1)	Ni(3)-N(2A)	2.132(8)	O(3)-Ni(1)-N(1)	89.3(1)	O(3)-Ni(1)-N(4)$^{\#1}$	89.5(1)
O(6)-Ni(1)-N(3)	88.5(4)	O(4)-Ni(1)-O(3)	178.7(3)	N(1)$^{\#2}$-Ni(1)-N(1)	178.7(3)	N(5)-Ni(1)-N(4)	91.4(2)
O(6)-Ni(1)-N(12)	91.7(4)	O(4)-Ni(1)-N(1E)	89.8(3)	O(4)-Ni(1)-N(3)$^{\#2}$	91.7(1)	N(5)$^{\#1}$-Ni(1)-N(4)	88.6(2)
N(3)-Ni(1)-N(12)	90.2(4)	O(3)-Ni(1)-N(1E)	89.1(3)	O(3)-Ni(1)-N(3)$^{\#2}$	88.3(1)	O(3)-Ni(1)-N(4)	89.5(1)
O(6)-Ni(1)-O(1)	178.2(4)	O(4)-Ni(1)-N(2D)	90.8(3)	N(1)$^{\#2}$-Ni(1)-N(3)$^{\#2}$	90.6(2)	N(4)$^{\#1}$-Ni(1)-N(4)	178.9(3)
N(3)-Ni(1)-O(1)	90.5(3)	O(3)-Ni(1)-N(2D)	90.0(3)	N(1)-Ni(1)-N(3)$^{\#2}$	89.3(2)	N(5)-Ni(1)-Cl(2)	93.4(1)
N(12)-Ni(1)-O(1)	86.8(4)	N(1E)-Ni(1)-N(2D)	89.1(3)	O(4)-Ni(1)-N(3)	91.7(1)	N(5)$^{\#1}$-Ni(1)-Cl(2)	93.4(1)
O(6)-Ni(1)-N(9)	91.3(4)	O(4)-Ni(1)-N(2B)	90.7(3)	O(3)-Ni(1)-N(3)	88.3(1)	O(3)-Ni(1)-Cl(2)	180.0
N(3)-Ni(1)-N(9)	178.4(4)	O(3)-Ni(1)-N(2B)	90.3(3)	N(1)$^{\#2}$-Ni(1)-N(3)	89.3(2)	N(4)$^{\#1}$-Ni(1)-Cl(2)	90.5(1)
N(12)-Ni(1)-N(9)	91.4(4)	N(1E)-Ni(1)-N(2B)	179.2(3)	N(1)-Ni(1)-N(3)	90.6(2)	N(4)-Ni(1)-Cl(2)	90.5(1)
O(1)-Ni(1)-N(9)	89.8(4)	N(2D)-Ni(1)-N(2B)	91.4(3)	N(3)$^{\#2}$-Ni(1)-N(3)	176.7(2)	N(6)$^{\#1}$-Ni(2)-N(1)	88.4(2)
O(6)-Ni(1)-N(13)	92.9(4)	O(4)-Ni(1)-N(1A)	88.7(3)	N(4)-Ni(2)-N(6)$^{\#2}$	178.7(2)	N(6)$^{\#1}$-Ni(2)-N(2)	173.7(2)
N(3)-Ni(1)-N(13)	90.0(4)	O(3)-Ni(1)-N(1A)	90.6(3)	N(4)-Ni(2)-O(1)	89.5(2)	N(1)-Ni(2)-N(2)	90.6(2)
N(12)-Ni(1)-N(13)	175.5(4)	N(1E)-Ni(1)-N(1A)	90.6(3)	N(6)$^{\#2}$-Ni(2)-O(1)	89.5(2)	N(6)$^{\#1}$-Ni(2)-O(1)	86.6(2)
O(1)-Ni(1)-N(13)	88.7(4)	N(2D)-Ni(1)-N(1A)	179.4(3)	N(4)-Ni(2)-O(2)	89.8(2)	N(1)-Ni(2)-O(1)	89.9(1)
N(9)-Ni(1)-N(13)	88.5(4)	N(2B)-Ni(1)-N(1A)	88.8(3)	N(6)$^{\#2}$-Ni(2)-O(2)	91.2(2)	N(2)-Ni(2)-O(1)	87.2(1)
O(4)-Ni(2)-N(10)	90.8(4)	O(5)-Ni(2)-N(1D)	90.9(3)	O(1)-Ni(2)-O(2)	177.9(2)	N(6)$^{\#1}$-Ni(2)-N(3)	92.5(2)
O(4)-Ni(2)-N(2)	90.8(4)	O(5)-Ni(2)-N(2F)	89.7(3)	N(4)-Ni(2)-N(2)	90.3(2)	N(1)-Ni(2)-N(3)	178.9(2)
N(10)-Ni(2)-N(2)	177.8(5)	N(1D)-Ni(2)-N(2F)	179.2(4)	N(6)$^{\#2}$-Ni(2)-N(2)	88.9(2)	N(2)-Ni(2)-N(3)	88.4(2)
O(4)-Ni(2)-N(4)	90.9(5)	O(5)-Ni(2)-N(2E)	89.4(3)	O(1)-Ni(2)-N(2)	94.2(2)	O(1)-Ni(2)-N(3)	89.6(1)
N(10)-Ni(2)-N(4)	90.7(4)	N(1D)-Ni(2)-N(2E)	91.1(3)	O(2)-Ni(2)-N(2)	87.8(2)	N(6)$^{\#1}$-Ni(2)-Cl(1)	92.8(1)
N(2)-Ni(2)-N(4)	90.7(4)	N(2F)-Ni(2)-N(2E)	89.4(3)	N(4)-Ni(2)-N(5)	89.3(2)	N(1)-Ni(2)-Cl(1)	90.6(1)
O(4)-Ni(2)-N(1)	91.3(4)	O(5)-Ni(2)-N(2C)	88.9(3)	N(6)$^{\#2}$-Ni(2)-N(5)	91.6(2)	N(2)-Ni(2)-Cl(1)	93.4(1)
N(10)-Ni(2)-N(1)	90.0(4)	N(1D)-Ni(2)-N(2C)	90.7(4)	O(1)-Ni(2)-N(5)	91.2(2)	O(1)-Ni(2)-Cl(1)	179.3(1)
N(2)-Ni(2)-N(1)	88.5(4)	N(2F)-Ni(2)-N(2C)	88.8(3)	O(2)-Ni(2)-N(5)	86.8(2)	N(3)-Ni(2)-Cl(1)	89.9(1)
N(4)-Ni(2)-N(1)	177.7(5)	N(2E)-Ni(2)-N(2C)	177.5(4)	N(2)-Ni(2)-N(5)	174.6(2)		
O(4)-Ni(2)-O(2)	178.9(4)	O(5)-Ni(2)-O(6)	178.0(3)				
N(10)-Ni(2)-O(2)	88.2(3)	N(1D)-Ni(2)-O(6)	88.3(4)				
N(2)-Ni(2)-O(2)	90.1(4)	N(2F)-Ni(2)-O(6)	91.1(3)				
N(4)-Ni(2)-O(2)	89.6(4)	N(2E)-Ni(2)-O(6)	88.7(4)				
N(1)-Ni(2)-O(2)	88.2(4)	N(2C)-Ni(2)-O(6)	93.0(4)				
O(5)-Ni(3)-O(3)	178.8(5)	O(2)-Ni(3)-N(1F)	89.0(3)				
O(5)-Ni(3)-N(11)	89.6(3)	O(2)-Ni(3)-O(1)	178.9(3)				
O(3)-Ni(3)-N(11)	89.8(5)	N(1F)-Ni(3)-O(1)	89.9(3)				
O(5)-Ni(3)-N(7)	88.7(3)	O(2)-Ni(3)-N(1C)	90.8(3)				
O(3)-Ni(3)-N(7)	91.9(5)	N(1F)-Ni(3)-N(1C)	89.9(3)				
N(11)-Ni(3)-N(7)	176.7(4)	O(1)-Ni(3)-N(1C)	89.6(3)				
O(5)-Ni(3)-N(6)	89.9(4)	O(2)-Ni(3)-N(1B)	90.4(3)				
O(3)-Ni(3)-N(6)	89.1(4)	N(1F)-Ni(3)-N(1B)	178.2(3)				
N(11)-Ni(3)-N(6)	91.6(4)	O(1)-Ni(3)-N(1B)	90.7(3)				
N(7)-Ni(3)-N(6)	91.2(4)	N(1C)-Ni(3)-N(1B)	91.7(3)				

O(5)-Ni(3)-N(5)	90.9(4)	O(2)-Ni(3)-N(2A)	90.5(3)		
O(3)-Ni(3)-N(5)	90.1(5)	N(1F)-Ni(3)-N(2A)	90.5(3)		
N(11)-Ni(3)-N(5)	90.0(4)	O(1)-Ni(3)-N(2A)	89.1(3)		
N(7)-Ni(3)-N(5)	87.2(4)	N(1C)-Ni(3)-N(2A)	178.7(3)		
N(6)-Ni(3)-N(5)	178.2(4)	N(1B)-Ni(3)-N(2A)	87.9(3)		

[#1] x, -y+3/2, -z+5/4
[#2] -x+1, -y+1, z

[#1] -x+1,y,-z+3/2