Supplementary Information for "**Three structural modifications in the series of layered solids $T(H_2O)_2[Ni(CN)_4]\cdot xH_2O$ with T = Mn, Co, Ni: Their Nature and Crystal Structures",** by J. Rodríguez-Hernández, A.A. Lemus-Santana, C.N. Vargas, E. Reguera

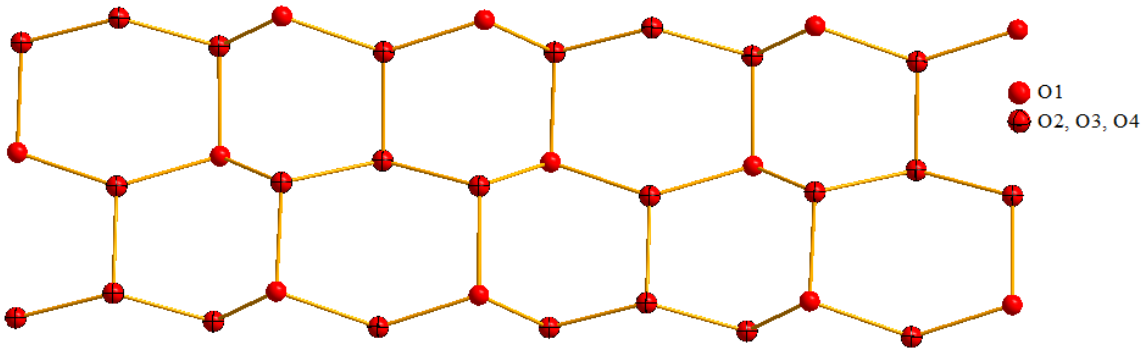

Figure S1: 2D ice-like structure for hydrogen bonded water molecules of L_0 phase: $T(H_2O)_2[Ni(CN)_4]\cdot 4H_2O$

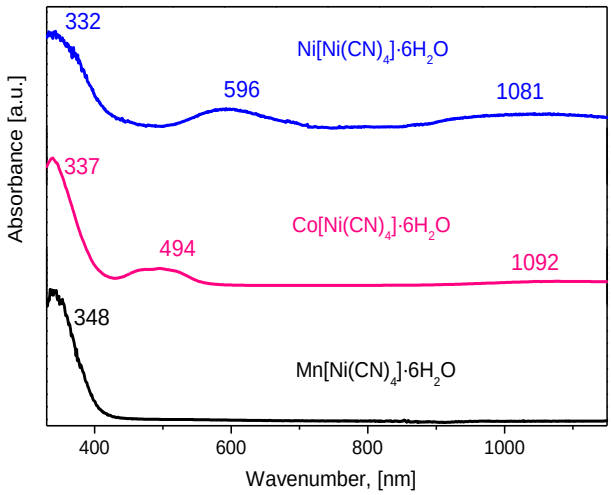

Figure S2: UV-vis spectra for $T[Ni(CN)_4]\cdot 6H_2O$; T=Ni, Co, Mn. These spectra correspond to octahedral coordination for T metals, respectively.

Table S1: XRD data collection and processing for L0 phase

	$Ni(H_2O)_2[Ni(CN)_4].4H_2O$	$Mn(H_2O)_2[Ni(CN)_4].4H_2O$	$Co(H_2O)_2[Ni(CN)_4].4H_2O$
Data collection			
Diffractometer	Bruker, D8 Advance	D10B-XPD LNLS (Brazil) beamline;	
Monochromator	graphite (secondary)	Ge(111) crystal analyzer	
Wavelength (Å)	CuKα, 1.54183	1.54995	1.54995
2θ range (°)	10-90	10-70	10-70
Step size (°)	0.02	0.008	0.02
Time per step (s)	15	1	1
Unit cell			
Space Group	Pnma	Pnma	Pnma
Parameter (Å)	a= 12.207(4) b= 13.860(5) c= 7.124(3)	a= 12.304(4) b= 14.125(6) c= 7.308(6)	a= 12.195(2) b= 13.885(3) c= 7.143(3)
V(Å^3)	1205.3(4)	1270.1(3)	1209.5(3)
Z	4	4	4
Refinement			
# of reflections	519	240	276
# of distance constraints	4	4	4
# of refined parameters			
Structural	29	29	29
Profile	10	10	10
R_{exp}	3.7	9.88	10.5
R_{wp}	7.2	14.3	19.2
R_B	5.17	10.9	16.6
S	1.95	1.44	1.82

Table S2: XRD data collection and processing for L1 phase

	$Ni(H_2O)_2[Ni(CN)_4].H_2O$	$Mn(H_2O)_2[Ni(CN)_4].H_2O$	$Co(H_2O)_2[Ni(CN)_4].H_2O$
Data collection			
Diffractometer	Bruker, D8 Advance		
Monochromator	graphite (secondary)		
Wavelength (Å)	CuKα, 1.54183		
2θ range (°)	5-80	10-80	5-80
Step size (°)	0.025	0.02	0.02
Time per step (s)	15	15	20
Unit cell			
Space Group	Imma	Imma	Imma
Parameter (Å)	a= 7.091(4) b=14.135(3) c=8.876(5)	a= 7.303(2) b= 14.539(2) c= 9.044(2)	a= 7.115(2) b=14.264(3) c=8.898(1)
V($Å^3$)	889.6(3)	960.3(2)	903.0(2)
Z	4	4	4
Refinement			
# of reflections	163	178	166
# of distance constraints	2	2	2
# of refined parameters			
Structural	15	15	15
Profile	10	10	10
R_{exp}	7.10	8.75	8.21
R_{wp}	13.5	14.2	15.3
R_B	9.70	10.7	13.5
S	1.9	1.62	1.86

Table S3: XRD data collection and processing for K phase

	$Ni(H_2O)_2[Ni(CN)_4].2H_2O$	$Mn(H_2O)_2[Ni(CN)_4].2H_2O$	$Co(H_2O)_2[Ni(CN)_4].2H_2O$
Data collection			
Diffractometer	Bruker, D8 Advance		
Monochromator	graphite (secondary)		
Wavelength (Å)	CuKα, 1.54183		
2θ range (°)	10-80	10-80	10-80
Step size (°)	0.025	0.02	0.02
Time per step (s)	15	15	15
Unit cell			
Space Group	P4/mmm	P4/mmm	P4/mmm
Parameter (Å)	a= b= 7.145(2) c= 10.116(2)	a= b= 7.279(2) c= 10.291(2)	a= b= 7.182(3) c= 10.139(2)
V($Å^3$)	516.4(1)	545.3(2)	523.0(3)
Z	2	2	2
Refinement			
# of reflections	122	128	122
# of distance constraints	4	4	4
# of refined parameters			
Structural	12	12	12
Profile	10	10	10
R_{exp}	5.65	4.74	7.14
R_{wp}	11.0	9.48	12.1
R_B	11.5	8.45	9.1
S	1.94	2.0	1.69

Table S4: Refined atomic positions and thermal and occupation factors for L0 phase

Composition	site	x	y	z	B_{iso}	Occ
$Ni(H_2O)_2[Ni(CN)_4].4H_2O$						
Ni_{OH}	4a	0.5	0.5	0.5	1.78(2)	1
Ni_{CN}	4c	0.430(3)	0.25	0.036(3)	1.78(2)	1
C1	8d	0.433(3)	0.347(2)	0.218(3)	2.3(1)	1
N1	8d	0.434(2)	0.407(2)	0.329(3)	2.3(1)	1
C2	8d	0.456(4)	0.340(3)	-0.154(4)	2.3(1)	1
N2	8d	0.472(3)	0.396(3)	-0.272(3)	2.3(1)	1
O1	8d	0.663(2)	0.425(4)	0.460(2)	3.7(2)	1
O2	8d	0.684(2)	0.429(1)	0.023(2)	3.7(2)	1
O3	4c	0.728(1)	0.25	0.918(2)	3.7(2)	1
O4	4c	0.704(1)	0.25	0.566(2)	3.7(2)	1
$Mn(H_2O)_2[Ni(CN)_4].4H_2O$						
Mn	4a	0.5	0.5	0.5	2.05(2)	1
Ni	4c	0.434(2)	0.25	0.009(2)	1.94(2)	1
C1	8d	0.443(3)	0.346(4)	0.184(2)	2.5(1)	1
N1	8d	0.439(4)	0.398(3)	0.308(3)	2.5(1)	1
C2	8d	0.463(3)	0.341(3)	-0.171(2)	2.5(1)	1
N2	8d	0.477(4)	0.398(2)	-0.278(3)	2.5(1)	1
O1	8d	0.661(2)	0.439(3)	0.442(1)	3.1(3)	1
O2	8d	0.678(1)	0.432(4)	0.043(3)	3.1(3)	1
O3	4c	0.742(1)	0.25	0.936(2)	3.1(3)	1
O4	4c	0.707(1)	0.25	0.559(3)	3.1(3)	1

Table S5: Refined atomic positions and thermal and occupation factors for L1 phase

Composition	site	x	y	z	B_{iso}	Occ
$Ni(H_2O)_2[Ni(CN)_4].H_2O$						
Ni_{OH}	4a	0	0	0	1.19(3)	1
Ni_{CN}	4e	0.5	0.25	0.053(3)	1.25(2)	1
C	16j	0.307(3)	0.156(3)	0.044(2)	3.2(3)	1
N	16j	0.192(2)	0.101(3)	0.039(2)	3.2(3)	1
O1	8h	0	0.035(3)	0.765(5)	3.8(3)	1
O2	4e	0	0.25	0.789(4)	3.8(3)	1
$Mn(H_2O)_2[Ni(CN)_4].H_2O$						
Mn	4a	0	0	0	1.56(2)	1
Ni	4e	0.5	0.25	0.046(2)	1.92(2)	1
C	16j	0.319(2)	0.158(3)	0.045(3)	2.5(1)	1
N	16j	0.208(2)	0.102(3)	0.044(3)	2.5(1)	1
O1	8h	0	0.028(3)	0.764(1)	3.4(2)	1
O2	4e	0	0.25	0.809(1)	3.4(2)	1
$Co(H_2O)_2[Ni(CN)_4].H_2O$						
Co	4a	0	0	0	1.43(1)	1
Ni	4e	0.5	0.25	0.058(2)	1.85(1)	1
C	16j	0.321(3)	0.156(1)	0.048(4)	2.8(1)	1
N	16j	0.204(2)	0.101(3)	0.030(2)	2.8(1)	1
O1	8h	0	0.030(2)	0.768(3)	3.2(2)	1
O2	4e	0	0.25	0.812(3)	3.2(2)	1

Table S6: Refined atomic positions and thermal and occupation factors for K phase

Composition	site	x	y	z	Biso	Occ
$Ni(H_2O)_2[Ni(CN)_4].2H_2O$						
$Ni1_{CN}$	1c	0.5	0.5	0	1.05(1)	1
$Ni2_{CN}$	1b	0	0	0.5	1.05(1)	1
$Ni1_{OH}$	1a	0	0	0	1.05(1)	1
$Ni2_{OH}$	1d	0.5	0.5	0.5	1.05(1)	1
C1	4j	0.311(2)	0.311(2)	0	3.3(2)	1
N1	4j	0.198(3)	0.198(3)	0	3.3(2)	1
C2	4k	0.189(2)	0.189(2)	0.5	3.3(2)	1
N2	4k	0.302(2)	0.302(2)	0.5	3.3(2)	1
O1	2g	0	0	0.232(3)	3.7(2)	1
O2	4h	0.5	0.5	0.271(2)	3.7(2)	1
O3	4i	0.5	0	0.248(3)	3.7(2)	1
$Mn(H_2O)_2[Ni(CN)_4].2H_2O$						
Ni1	1c	0.5	0.5	0	1.53(2)	1
Ni2	1b	0	0	0.5	1.53(2)	1
Mn1	1a	0	0	0	1.62(2)	1
Mn2	1d	0.5	0.5	0.5	1.62(2)	1
C1	4j	0.315(2)	0.315(2)	0	2.8(3)	1
N1	4j	0.204(2)	0.204(2)	0	2.8(3)	1
C2	4k	0.185(1)	0.185(1)	0.5	2.8(3)	1
N2	4k	0.296(2)	0.296(2)	0.5	2.8(3)	1
O1	2g	0	0	0.229(5)	3.6(3)	1
O2	4h	0.5	0.5	0.270(5)	3.6(3)	1
O3	4i	0.5	0	0.247(4)	3.6(3)	1
$Co(H_2O)_2[Ni(CN)_4].2H_2O$						
Ni1	1c	0.5	0.5	0	1.32(1)	1
Ni2	1b	0	0	0.5	1.32(1)	1
Co1	1a	0	0	0	1.26(1)	1
Co2	1d	0.5	0.5	0.5	1.26(1)	1
C1	4j	0.312(2)	0.312(2)	0	2.4(2)	1
N1	4j	0.200(3)	0.200(3)	0	2.4(2)	1
C2	4k	0.187(1)	0.187(1)	0.5	2.4(2)	1
N2	4k	0.301(2)	0.301(2)	0.5	2.4(2)	1
O1	2g	0	0	0.236(5)	3.2(2)	1
O2	4h	0	0	0.272(4)	3.2(2)	1
O3	4i	0.5	0	0.246(5)	3.2(2)	1

Table S7. Calculated interatomic distances (in Å) and bond angles (in ^{o}) for L0 phase.

Bond distance (Å)	Angles (°)	
$Ni(H_2O)_2[Ni(CN)_4].4\ H_2O$		
Ni_{CN}-C1= 1.869(1)	C1-Ni_{CN}-C2= 91.0(5)	N1-Ni_{OH}-N2´=91.7(2)
Ni_{CN}-C2= 1.872(2)	C1-Ni_{CN}-C1´=92.3(2)	N1- Ni_{OH}-O1= 90.9(2)
Ni_{OH}-N1= 1.936(1)	C1-Ni_{CN}-C2´= 168.5(3)	N1- Ni_{OH}-O1´= 89.1(2)
Ni_{OH}-N2= 2.189(2)	C2-Ni_{CN}-C2´= 83.8(2)	N2- Ni_{OH}-O1= 85.9(2)
Ni_{OH}-O1= 2.258(1)	Ni_{CN}-C1-N1= 179.6(3)	N2- Ni_{OH}-O1´= 94.1(1)
C1-N1= 1.153(1)	Ni_{CN}-C2-N2= 179.7(3)	Ni_{OH}-N1-C1= 156.9(3)
C2-N2= 1.167(1)	N1-Ni_{OH}-N2= 88.3(4)	Ni_{OH}-N2-C2= 178.2(3)
$Mn(H_2O)_2[Ni(CN)_4].4H_2O$		
Ni-C1= 1.871(2)	C1-Ni-C2= 88.4(1)	N1- Mn-N2´=89.8(3)
Ni-C2= 1.870(3)	C1-Ni-C1´=93.2(1)	N1- Mn-O1= 85.9(3)
Mn-N1= 2.138(2)	C1-Ni-C2´= 166.1(1)	N1- Mn-O1´= 94.1(3)
Mn-N2= 2.180(2)	C2-Ni-C2´= 86.8(1)	N2- Mn-O1= 90.3(2)
Mn-O1= 2.201(5)	Ni-C1-N1= 171.0(2)	N2- Mn-O1´= 89.7(1)
C1-N1= 1.169(4)	Ni-C2-N2= 177.4(2)	Mn-N1-C1= 156.7(2)
C2-N2= 1.144(4)	N1-Mn-N2= 90.2(1)	Mn-N2-C2= 175.2(2)

Table S8. Calculated interatomic distances (in Å) and bond angles (in ^{o}) for L1 phase.

Bond distance (Å)	Angles (°)	
$Ni(H_2O)_2[Ni(CN)_4].1H_2O$		
Ni_{CN}-C=1.909(2)	C-Ni_{CN}-C´=88.2(2)	N- Ni_{OH} -N´=94.3(2)
Ni_{OH}-N=2.003(2)	C-Ni_{CN}-C´´=175.0(3)	N- Ni_{OH} -N´´=180
Ni_{OH}-O1=2.144(2)	C-Ni_{CN}-C´´´=91.6(3)	N- Ni_{OH} -N´´´=85.6(3)
C-N=1.127(1)	Ni_{CN}-C-N=179.4(4)	N- Ni_{OH} -O1=90.2(4)
	Ni_{OH}-N-C=171.8(4)	N- Ni_{OH} -O1´=89.8(3)
$Mn(H_2O)_2[Ni(CN)_4].1H_2O$		
Ni-C=1.881(2)	C-Ni-C´= 90.7(2)	N- Mn-N´=90.6(2)
Mn-N=2.160(2)	C-Ni-C´´=179.4(3)	N- Mn-N´´=180.0
Mn-O1= 2.173(2)	C-Ni-C´´´=89.3(3)	N- Mn-N´´´=89.4(3)
C-N=1.149(1)	Ni-C-N=179.7(4)	N- Mn-O1=93.0(4)
	Mn-N-C=169.8(4)	N- Mn-O1´= 87.0(3)
$Co(H_2O)_2[Ni(CN)_4].1H_2O$		
Ni-C=1.852(2)	C-Ni-C´=86.9(3)	N-Co-N´=89.5(3)
Co-N=2.062(2)	C-Ni-C´´=174.1(3)	N-Co-N´´=180.0
Co-O1= 2.108(2)	C-Ni-C´´´=92.8(2)	N-Co-N´´´=90.5(2)
C-N=1.155(1)	Ni-C-N=174.1(4)	N-Co-O1=90.8(4)
	Co-N-C=178.4(4)	N-Co-O1´= 89.2(4)

Table S9. Calculated interatomic distances (in Å) and bond angles (in ^{o}) for K phase.

Bond distance (Å)	
$Ni(H_2O)_2[Ni(CN)_4].2H_2O$	
$Ni2_{CN}$-C2= 1.910(2)	$Ni1_{OH}$-O1= 2.350(2)
$Ni1_{CN}$-C1= 1.909(2)	$Ni2_{OH}$-O2= 2.308(2)
$Ni2_{OH}$-N2= 2.000(2)	C1-N1= 1.142(3)
$Ni1_{OH}$-N1= 2.001(2)	C2-N2= 1.142(1)
$Mn(H_2O)_2[Ni(CN)_4].2H_2O$	
Ni2-C2= 1.900(2)	Mn1-O1= 2.360(2)
Ni1-C1= 1.904(2)	Mn2-O2= 2.369(2)
Mn2-N2= 2.102(2)	C1-N1= 1.143(1)
Mn1-N1= 2.100(2)	C2-N2= 1.145(1)
$Co(H_2O)_2[Ni(CN)_4].2H_2O$	
Ni2-C2= 1.905(2)	Co1-O1= 2.397(2)
Ni1-C1= 1.909(2)	Co2-O2= 2.304(2)
Co2-N2= 2.024(2)	C1-N1= 1.138(1)
Co1-N1= 2.031(2)	C2-N2= 1.149(1)

Table S10: Relevant bond distances and angles for the series of layer solids under study

Phase	O_C-O_{HB1} (Å)	$O_{HB1-HB2}$ (Å)	T-N-C angle (^{o})
K (Mn)	3.64(2)	---	180
L_0 (Mn)	2.89(4)	2.78(5)	166.0(3)
L_1 (Mn)	3.19(2)	---	169.8(4)
K (Co)	3.60(3)	---	180
L_0 (Co)	2.79(5)	2.82(4)	169.2(2)
L_1 (Co)	3.19(2)	---	174.9(4)
K (Ni)	3.574(2)	---	180
L_0 (Ni)	2.91(1)	2.53(2)	167.4(2)
L_1 (Ni)	3.16(4)	---	171.8(4)

O_C: Oxygen of coordinated water molecules; O_{HB}: Oxygen of hydrogen bonded water molecules