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Structural Variations in Manganese Halide Chain Compounds Mediated by Methylimidazolium Isomers

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Supplementary Information

Figure S1. Raw and calculated PXRD data for [1MiH]$MnCl_3(H_2O)$ at room temperature.

Figure S2. Raw and calculated PXRD data for [4MiH]$MnCl_3(H_2O)$ at room temperature.

Figure S3. Unit cell packing and hydrogen bonding interactions along the chain direction for (a) (2-aminopyridinium)$MnCl_3(H_2O)$ (298 K) along the *c*-axis, (b) (pyrazolium)$MnCl_3(H_2O)$ (100 K) along the *a*-axis and (c) (pyridinium)$MnCl_3(H_2O)$ (153 K) along the *b*-axis.

Table S1. Unit cell parameters for (2-aminopyridinium)$MnCl_3(H_2O)$ (298 K), (pyrazolium)$MnCl_3(H_2O)$ (100 K) and (pyridinium)$MnCl_3(H_2O)$ (153 K).

Table S2. Crystal and structure refinement data for [1MiH]$MnCl_3(H_2O)$ and [4MiH]$MnCl_3(H_2O)$ at 298 K.

Table S3. Hydrogen bonds for [1MiH]$MnCl_3(H_2O)$ and [4MiH]$MnCl_3(H_2O)$ at 298 K (Å and °).

Table S4. Selected bond lengths (Å) and bond angles (°) versus temperature for [1MiH]$MnCl_3(H_2O)$.

Table S5. Selected bond lengths (Å) and bond angles (°) versus temperature for [4MiH]$MnCl_3(H_2O)$.

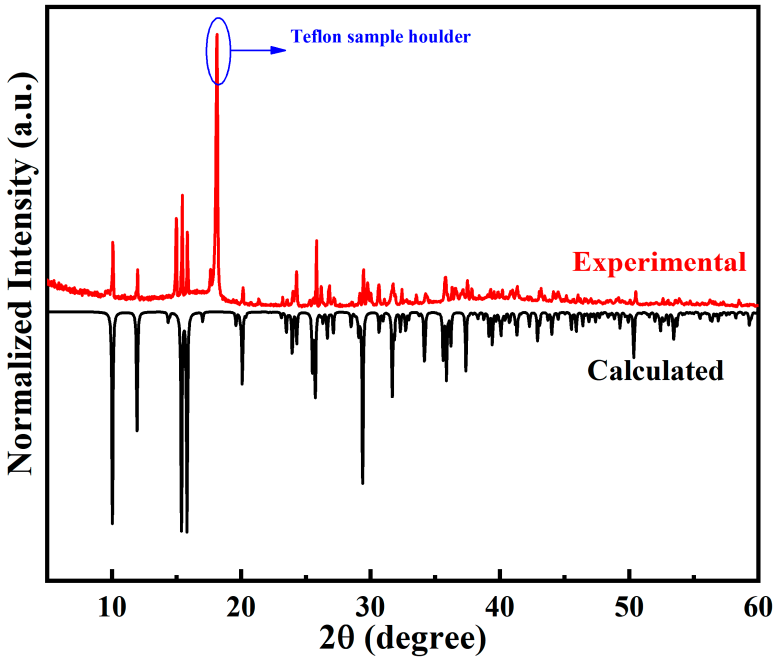

Figure S1. Raw and calculated PXRD data for [1MiH]$MnCl_3(H_2O)$ at room temperature.

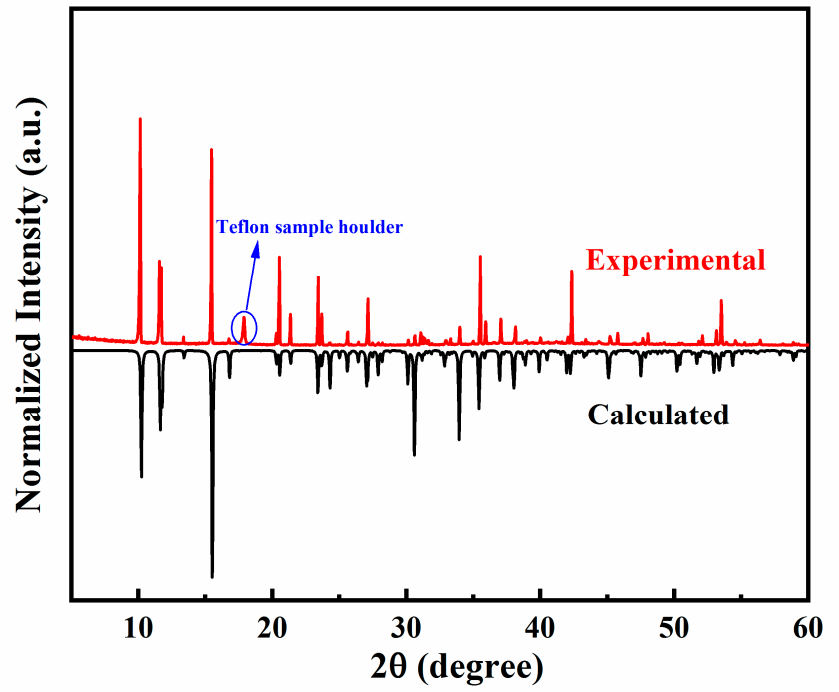

Figure S2. Raw and calculated PXRD data for [4MiH]$MnCl_3(H_2O)$ at room temperature.

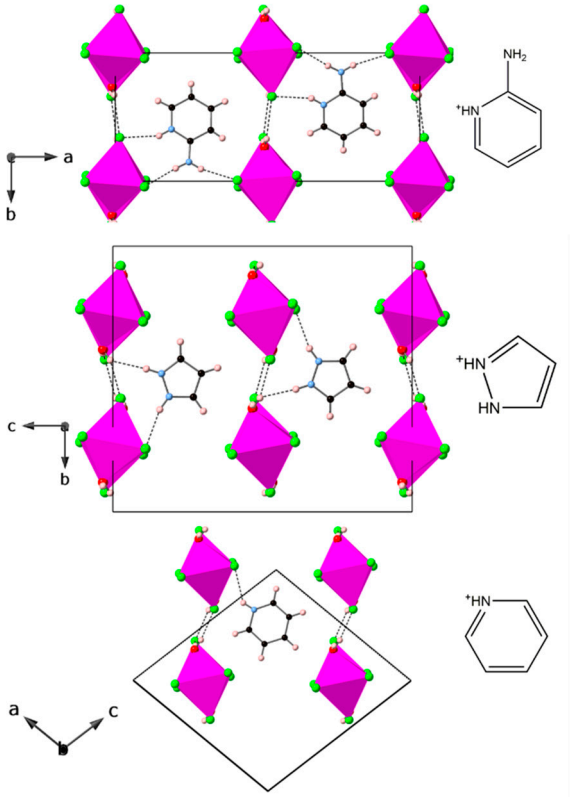

Figure S3. Unit cell packing and hydrogen bonding interactions along the chain direction for (**a**) (2-aminopyridinium)$MnCl_3(H_2O)$ (298 K) [1] along the *c*-axis, (**b**) (pyrazolium)$MnCl_3(H_2O)$ (100 K) [2] along the *a*-axis and (**c**) (pyridinium)$MnCl_3(H_2O)$ (153 K) [3] along the *b*-axis.

Table S1. Unit cell parameters for (2-aminopyridinium)$MnCl_3(H_2O)$ (298 K) [1], (pyrazolium)$MnCl_3(H_2O)$ (100 K) [2] and (pyridinium)$MnCl_3(H_2O)$ (153 K) [3].

Compound	(2-aminopyridinium) $MnCl_3(H_2O)$	(pyrazolium) $MnCl_3(H_2O)$	(pyridinium)* $MnCl_3(H_2O)$
Space group	*Pca*2$_1$	*Pbca*	*P*2$_1$/*n*
***a*/Å**	18.150 (1)	7.2477 (14)	11.417 (2)
***b*/Å**	7.659 (1)	14.614 (3)	7.2779 (15)
***c*/Å**	7.368 (1)	16.473 (3)	11.817(2)
α/°	90	90	90
β/°	90	90	102.83 (3)
γ/°	90	90	90

*Note that the unit cell metrics here are essentially comparable to those of [1MiH]$MnCl_3(H_2O)$, but an alternative cell setting has been used.

Table S2. Crystal structure and refinement data for [1MiH]$MnCl_3(H_2O)$ and [4MiH]$MnCl_3(H_2O)$ at 298 K.

Compound	[1MiH]$MnCl_3(H_2O)$	[4MiH]$MnCl_3(H_2O)$
Formula	$C_4N_2H_7MnCl_3(H_2O)$	$C_4N_2H_7MnCl_3(H_2O)$
Formula weight	262.42	262.42
Crystal system	Monoclinic	Monoclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*c*
***a*/Å**	11.7462 (7)	8.6661 (5)
***b*/Å**	7.3437 (4)	15.1882 (11)
***c*/Å**	14.9054 (11)	7.3425 (5)
β/°	130.965 (4)	94.956 (2)
***V*/Å^3**	970.88 (12)	962.82 (11)
Z	4	4
Measured ref	11748	9097
Independent ref	3171 [R(int) = 0.058]	2194 [R(int) = 0.0277]
GOOF	1.127	1.025
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0735 wR_2 = 0.1150	R_1 = 0.0259 wR_2 = 0.0616

Further details of the crystal structures at two different temperatures (173 K and 298 K) may be obtained from the CCDC and FIZ Karlsruhe Deposition Teams (https://www.ccdc.cam.ac.uk) on quoting deposition numbers 2031437-2031440.

Table S3. Hydrogen bonds for [1MiH]$MnCl_3(H_2O)$ and [4MiH]$MnCl_3(H_2O)$ at 298 K.

Compound	D-H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)
[1MiH]$MnCl_3(H_2O)$	O1-H1A...Cl3_#1	0.73(5)	2.49(5)	3.215(4)	172(5)
	O1-H1B...Cl3_#3	0.92(8)	2.32(8)	3.224(4)	169(7)
	N2-H2...Cl1_#2	0.88	2.57	3.292(4)	139.3
	N2-H2...O1	0.88	2.39	3.037(6)	130.9
[4MiH]$MnCl_3(H_2O)$	O1-H1A…Cl3#1	0.93	2.45	3.241(2)	143.1
	O1-H1B…Cl3#2	0.93	2.58	3.198(2)	124.8
	N1-H1…Cl1#3	0.86	2.86	3.395(2)	122.0
	N1-H1…Cl3	0.86	2.50	3.283(2)	151.3
	N2-H2…Cl2#4	0.86	2.69	3.307(2)	129.6
	N2-H2…Cl3#5	0.86	2.65	3.365(2)	141.7

*Note: Symmetry transformations used to generate equivalent atoms: #1 -x+1, y-1/2, -z-1/2; #3 x, -y+3/2, z+1/2; #3 -x+1, y+1/2, -z-1/2 ([1MiH]$MnCl_3(H_2O)$). #1 −x, y+1/2, −z+1/2; #2 x, −y+3/2, z+1/2; #3 x, −y+3/2, z−1/2; #4 x+1, −y+3/2, z+1/2; #5 x+1, y, z ([4MiH]$MnCl_3(H_2O)$).

Table S4. Selected bond lengths (Å) and bond angles (°) versus temperature for [1MiH]$MnCl_3(H_2O)$.

Temperature	173 K	298 K
Mn(1)-O(1)	2.240(3)	2.247(3)
Mn(1)-Cl(3)	2.5109(9)	2.5152(12)
Mn(1)-Cl(2)	2.5201(9)	2.5327(12)
Mn(1)-Cl(2)#1	2.5289(9)	2.5408(12)
Mn(1)-Cl(1)	2.5640(9)	2.5742(12)
Mn(1)-Cl(1)#2	2.5784(9)	2.5903(12)
O(1)-Mn(1)-Cl(3)	178.24(6)	178.07(10)
O(1)-Mn(1)-Cl(2)	86.84(6)	86.54(11)
Cl(3)-Mn(1)-Cl(2)	94.03(3)	94.12(4)
O(1)-Mn(1)-Cl(2)#1	85.64(6)	85.72(11)
Cl(3)-Mn(1)-Cl(2)#1	93.49(3)	93.61(4)
Cl(2)-Mn(1)-Cl(2)#1	172.48(2)	172.27(3)
O(1)-Mn(1)-Cl(1)	87.03(6)	87.18(10)
Cl(3)-Mn(1)-Cl(1)	94.46(3)	94.59(4)
Cl(2)-Mn(1)-Cl(1)	92.03(3)	92.29(4)
Cl(2)#1-Mn(1)-Cl(1)	87.54(3)	87.21(4)
O(1)-Mn(1)-Cl(1)#2	85.63(6)	85.27(10)
Cl(3)-Mn(1)-Cl(1)#2	92.88(3)	92.96(4)
Cl(2)-Mn(1)-Cl(1)#2	87.41(3)	87.03(4)
Cl(2)#1-Mn(1)-Cl(1)#2	92.05(3)	92.45(4)
Cl(1)-Mn(1)-Cl(1)#2	172.66(2)	172.45(3)
Mn(1)-Cl(1)-Mn(1)#1	90.73(2)	91.12(3)
Mn(1)-Cl(2)-Mn(1)#2	92.90(2)	93.24(3)

*Note: Symmetry transformations used to generate equivalent atoms: #1 -x-1,y+1/2,-z-3/2 #2 -x-1,y-1/2,-z-3/2 (173 K); #1 -x+1,y-1/2,-z-1/2 #2 -x+1,y+1/2,-z-1/2 (298 K).

Table S5. Selected bond lengths (Å) and bond angles (°) versus temperature for [4MiH]$MnCl_3(H_2O)$.

Temperature	173 K	298 K
Mn(1)-O(1)	2.1997(14)	2.2032(14)
Mn(1)-Cl(2)	2.5281(5)	2.5327(6)
Mn(1)-Cl(1)	2.5399(5)	2.5409(5)
Mn(1)-Cl(1)#1	2.5476(5)	2.5531(6)
Mn(1)-Cl(3)	2.5636(5)	2.5580(6)
Mn(1)-Cl(2)#2	2.5536(5)	2.5602(6)
O(1)-Mn(1)-Cl(2)	89.90(4)	89.58(4)
O(1)-Mn(1)-Cl(1)	85.60(4)	85.62(4)
Cl(2)-Mn(1)-Cl(1)	175.496(19)	175.194(19)

O(1)-Mn(1)-Cl(1)#1	91.73(4)	91.60(4)
Cl(2)-Mn(1)-Cl(1)#1	87.682(16)	87.432(18)
Cl(1)-Mn(1)-Cl(1)#1	92.211(18)	92.480(18)
O(1)-Mn(1)-Cl(3)	176.79(4)	176.91(4)
Cl(2)-Mn(1)-Cl(3)	92.252(17)	92.289(18)
Cl(1)-Mn(1)-Cl(3)	92.252(17)	92.517(18)
Cl(1)#1-Mn(1)-Cl(3)	90.740(16)	90.943(17)
O(1)-Mn(1)-Cl(2)#2	86.37(4)	86.14(4)
Cl(2)-Mn(1)-Cl(2)#2	92.659(19)	92.795(19)
Cl(1)-Mn(1)-Cl(2)#2	87.299(16)	87.103(18)
Cl(1)#1-Mn(1)-Cl(2)#2	178.076(18)	177.723(19)
Cl(3)-Mn(1)-Cl(2)#2	91.139(17)	91.312(18)
Mn(1)-Cl(1)-Mn(1)#2	92.038(18)	92.333(18)
Mn(1)-Cl(2)-Mn(1)#1	92.177(18)	92.355(19)

*Note: Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z-1/2 #2 x,-y+1/2,z+1/2 (173 K); #1 x,-y+1/2,z+1/2 #2 x,-y+1/2,z-1/2 (298 K).

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