

# Supporting Information

## The odd-even effect in *n*-carboxyalkylammonium-containing organic-inorganic hybrids of Mn(II) halides: Structural and magnetic characterisation

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### **Section 1: Calculated and experimental powder X-ray diffraction patterns of samples used for magnetic studies.**

Experimental powder X-ray diffraction patterns of bulk samples were compared with powder patterns calculated from the single crystal structures to determine if the single crystal is representative of the bulk sample, and to ensure that the samples used for the magnetic studies were pure. The experimental powder patterns are shown in black and the calculated patterns are given in red. The patterns were compared using the software DiffractWD.<sup>1</sup> Note that the simulated patterns were calculated from single crystal structures determined at 150 K, while the experimental powder X-ray diffraction patterns were measured at room temperature, resulting in a shift of some of the diffraction peaks relative to each other, due to the change of the unit cell with a change in temperature. The intensities of the peaks may be affected by preferred orientation, due to the use of a flat sample holder.

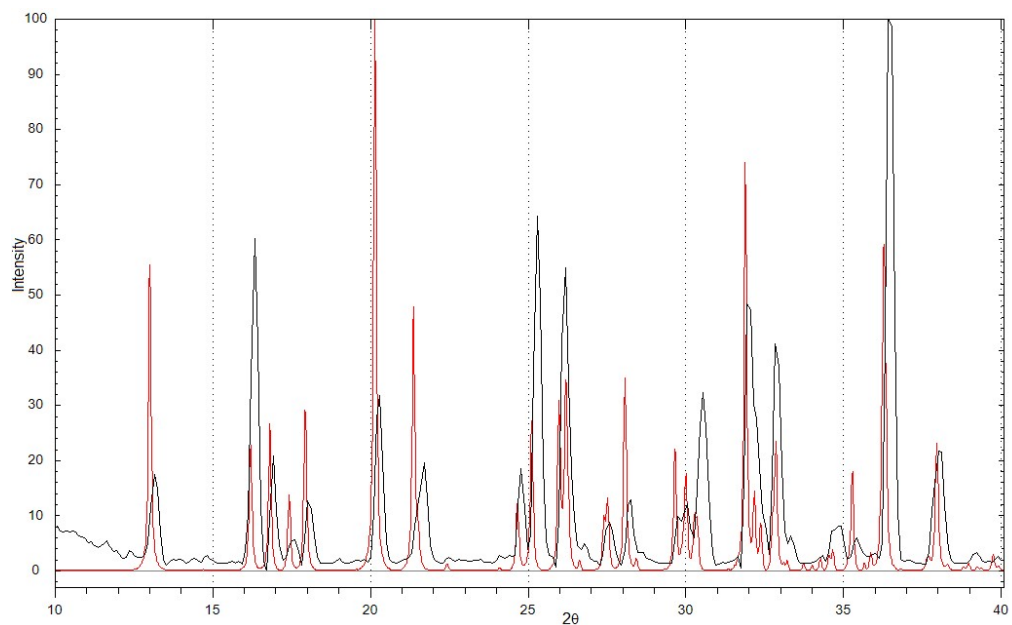


Figure S1.1: Calculated  $C_3MnClH_2O$  powder X-ray diffraction pattern (red) vs experimental pattern (black).

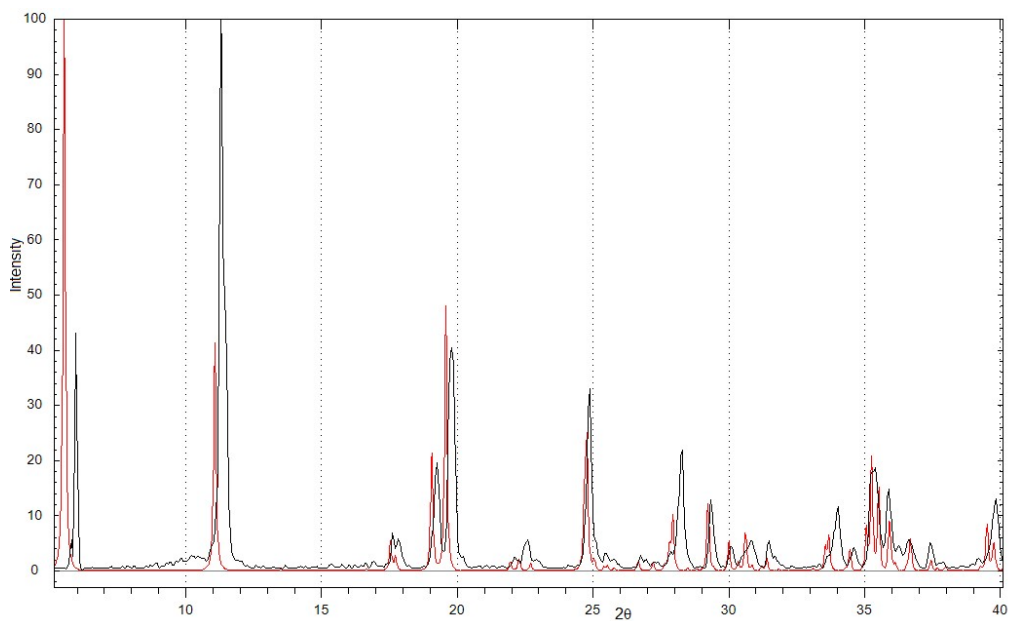


Figure S1.2: Calculated  $C_4MnCl$  powder X-ray diffraction pattern (red) vs experimental pattern (black).

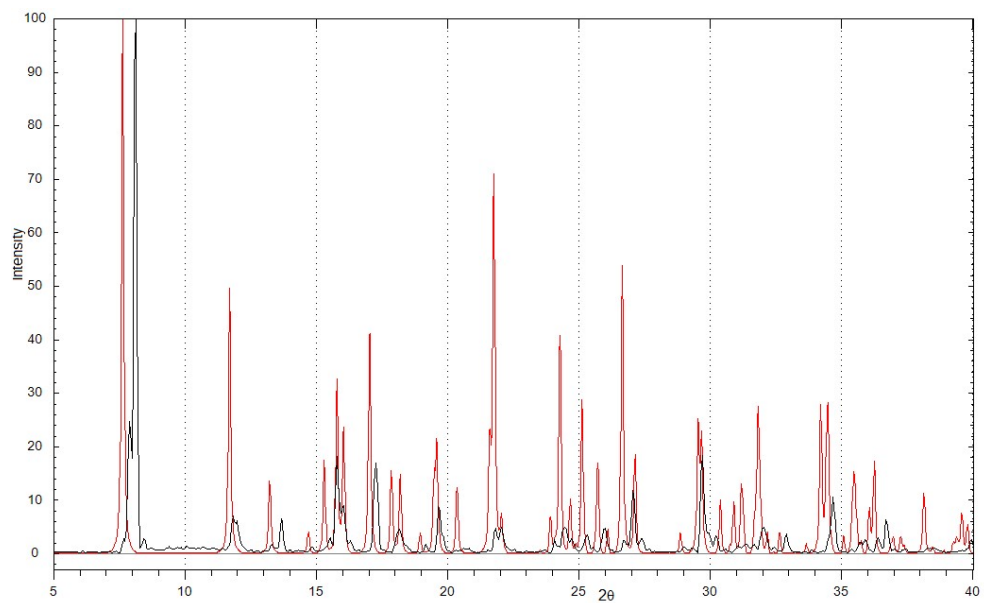


Figure S1.3: Calculated  $C_5MnCl$  powder X-ray diffraction pattern (red) vs experimental pattern (black).

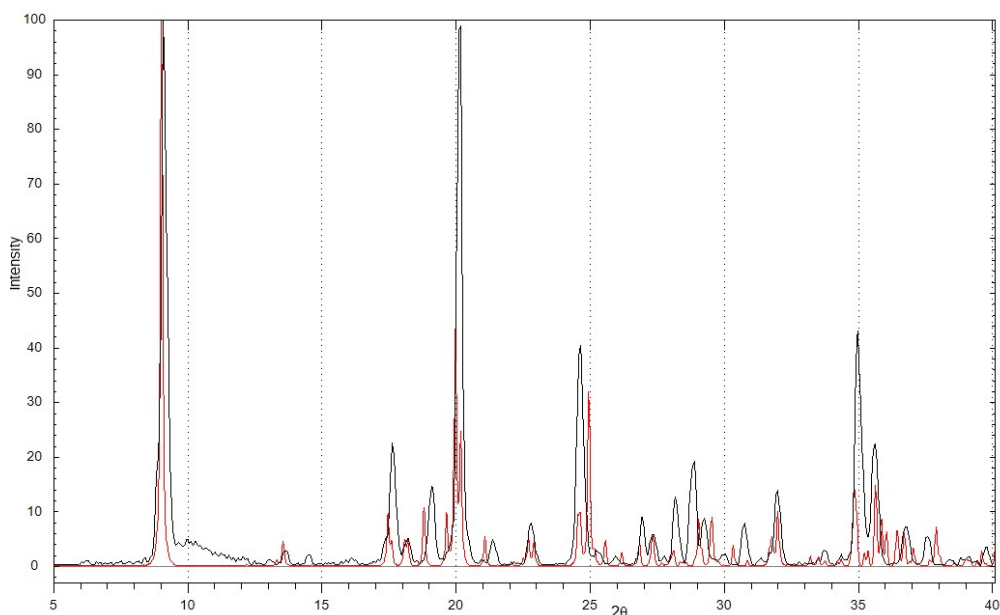


Figure S1.4: Calculated **C6MnCl** powder X-ray diffraction pattern (red) vs experimental pattern (black).

## **Section 2: Structural Discussion: Additional Information.**

This section presents additional information on the structural features of the four compounds structurally characterised.

### **C3MnClH<sub>2</sub>O**

In this structure, four asymmetric units comprise the unit cell. The Mn-Cl bonds lengths are 2.4732(4) Å and 2.5656(4) Å and are longer than the M-O bonds lengths of 2.2248(9) Å. The layers in the structure are parallel to the *bc*-plane. In the inorganic sheet, the Mn···Mn metal ion distance is 5.572 Å along the *c*-direction, and 7.070 Å along the *b*-direction. Even though the cation exhibits an all-*trans* conformation, a slight deviation from 180° is observed in the N-C-C-C torsion angle, with a value of 174.58(11)°. The C-O-H···Cl-Mn and Mn-O-H···O=C hydrogen bonding interactions have D···A distances of 3.1003(11) Å and 2.7335(14) Å, respectively. The D···A distances of the N-H<sup>+</sup>···Cl-Mn hydrogen bonding interactions are 3.1741(12) Å and 3.3211(12) Å and that of the N-H<sup>+</sup>···O-Mn interaction, 2.9677(15) Å. The Mn-O-H···Cl-Mn hydrogen bonding interactions have a D···A distance of 3.1666(10) Å. The hydrogen bonded ribbons between the anions extend in the *c*-direction.

### **C5MnClH<sub>2</sub>O**

In this structure, two asymmetric units comprise the unit cell. In the cation, The N-C-C-C torsion angle is -173.10(12)°. The Mn-Cl bond lengths are 2.5672(4) Å and 2.5034(4) Å, while the Mn-O bond length is 2.1872(11) Å. The M···M distance is 5.905 Å in the *a*-direction and 7.819 Å in the *b*-direction. In this structure, the layers are parallel to the *ab*-plane. The Mn-O-H···Cl-Mn hydrogen bonding interactions have D···A distances of 3.1799(11) Å, and connect anions to form a hydrogen bonded ribbon extending in the *a*-direction. The shortest

and longest D···A distances for the N-H···Cl-Mn hydrogen bonding interactions are 3.1612(13) Å and 3.4316(14) Å.

#### C4MnCl

In this structure, two asymmetric units make up the unit cell. The inorganic layer is parallel to the *bc*-plane. The Mn-Cl bond lengths are 2.5632(3) Å, 2.5571(3) Å, 2.4853(3) Å and 2.5632(3) Å. The longest and shortest D···A N-H···Cl-Mn hydrogen bonding distances are 3.4710(12) Å and 3.1973(11) Å.

#### C6MnCl

In this structure, the inorganic layer is parallel to the *ab*-plane. Six chlorido ligands are coordinated to the Mn<sup>2+</sup> metal ion with Mn-Cl bond lengths ranging from 2.4920(4) Å to 2.6025(4) Å. In the layered structure inorganic layers are separated by bilayers of tilted, non-interdigitated 5-carboxypentylammonium cations. The shortest and longest D···A hydrogen bond distances are 3.2473(16) Å and 3.2978(18) Å, respectively.

### Section 3: Summary of literature structures containing *cis*- or *trans*-[MCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>x-</sup> anions.

Table S3.1: Structures reported in the literature containing a *cis*-[MCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>x-</sup> anion of any metal ion and any other species.

Structure Number	Structure CSD reference code	Type of [MCl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>x-</sup> anion	Metal ion	Reference
1	BOGHOV	<i>cis</i>	Rh <sup>3+</sup>	2
2	CIMWIE CIMWIE01 CIMWIE02	<i>cis</i>	Sn <sup>4+</sup>	3, 4, 5
3	COCLUB	<i>cis</i>	Sn <sup>4+</sup>	6
4	FETHOC	<i>cis</i>	Sn <sup>4+</sup>	7
5	FOSRIQ	<i>cis</i>	Sn <sup>4+</sup>	8
6	ODAFOO	<i>cis</i>	Sn <sup>4+</sup>	9
7	RODTOU	<i>cis</i>	Sn <sup>4+</sup>	10
8	XIHNEH	<i>cis</i>	Sn <sup>4+</sup>	11
9	ZUCJEM	<i>cis</i>	Sn <sup>4+</sup>	12
10	FOFBEJ	<i>cis</i>	In <sup>3+</sup>	13
11	GOJRAZ	<i>cis</i>	In <sup>3+</sup>	14
12	ZIJYIC	<i>cis</i>	In <sup>3+</sup>	15
13	LEGDOQ	<i>cis</i>	Pt <sup>4+</sup>	16
14	MAZFEZ	<i>cis</i>	Tc <sup>4+</sup>	17
15	OSAKAW	<i>cis</i>	Mn <sup>2+</sup>	18
16	TPASRU	<i>cis</i>	Ru <sup>3+</sup>	19

Table S3.2: Structures reported in the literature containing a *trans*-[MCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>x-</sup> anion of any metal ion and any other species.

Structure Number	Structure CSD reference code	Type of $[\text{MCl}_2(\text{H}_2\text{O})_2]^x$ anion	Metal ion	Reference
1	DILXOL	<i>trans</i>	$\text{Ca}^{2+}$	20
2	FANRUH	<i>trans</i>	$\text{Sn}^{4+}$	21
3	GEJHUA	<i>trans</i>	$\text{Sn}^{4+}$	5
4	GADWUD	<i>trans</i>	$\text{Cu}^{2+}$	22
5	GOPSOT	<i>trans</i>	$\text{Fe}^{3+}$	23
6	VOBYEQ	<i>trans</i>	$\text{Fe}^{3+}$	24
7	XAKHOI	<i>trans</i>	$\text{Fe}^{2+}$	25
8	GUMWEQ	<i>trans</i>	$\text{In}^{3+}$	26
9	KAGLUA	<i>trans</i>	$\text{Co}^{2+}$	27
10	EHIWIC	<i>trans</i>	$\text{Mn}^{2+}$	28
11	JURXOM	<i>trans</i>	$\text{Mn}^{4+}$ and $\text{Mn}^{2+}$	29
12	SUXXUF	<i>trans</i>	$\text{Mn}^{2+}$	30
13	TAKZOV	<i>trans</i>	$\text{Mn}^{2+}$	31
14	UZURIT	<i>trans</i>	$\text{Mn}^{2+}$	31
15	TMAARH	<i>trans</i>	$\text{Rh}^{3+}$	32
16	WUQHIZ	<i>trans</i>	$\text{Cd}^{2+}$	33

#### Section 4: $M$ vs $H$ plots

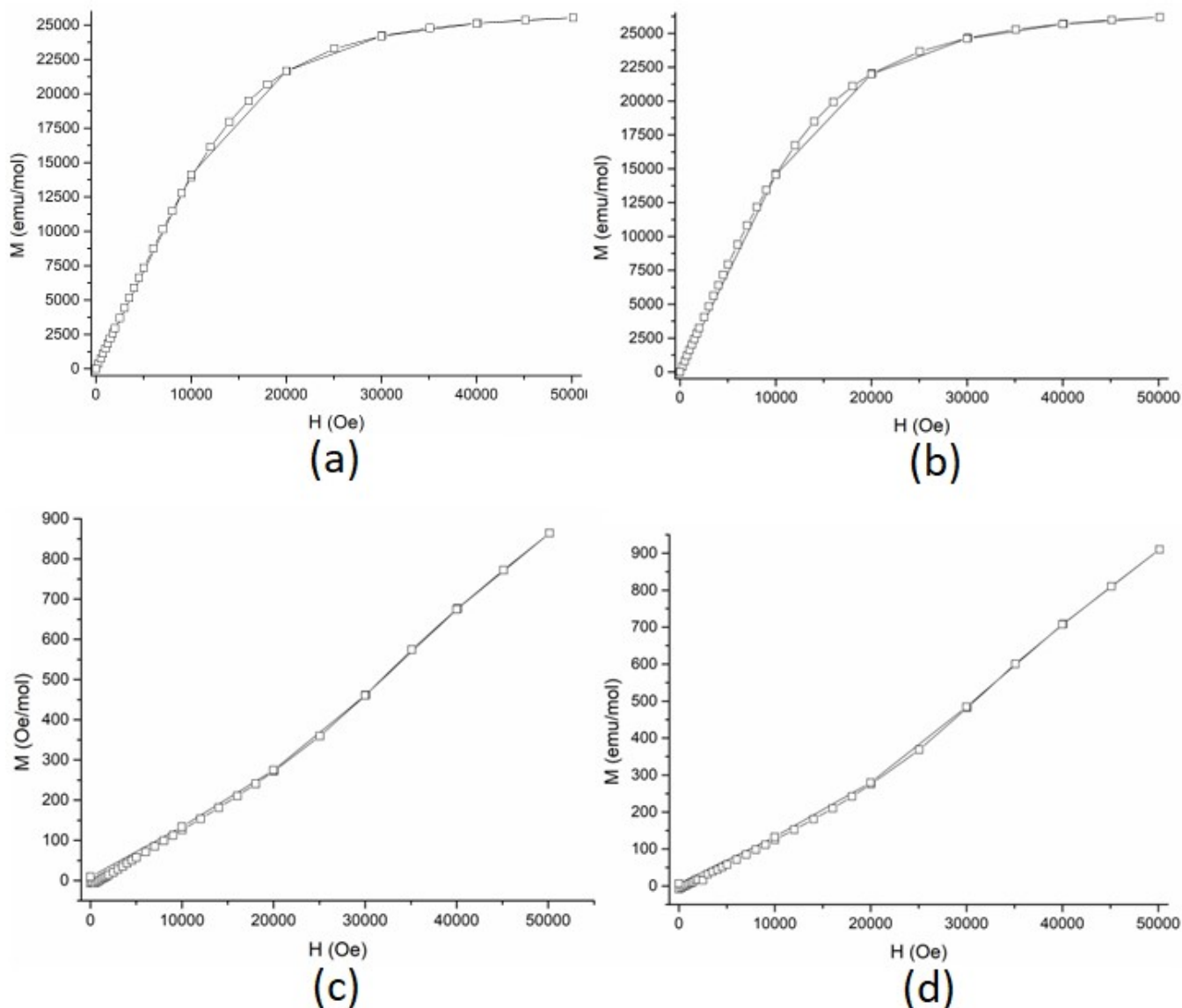


Figure S4.1: The  $M$  vs  $H$  plots measured at 1.8 K for (a)  $\text{C3MnClH}_2\text{O}$ , (b)  $\text{C5MnClH}_2\text{O}$ , (c)  $\text{C4MnCl}$  and (d)  $\text{C6MnCl}$ .

The  $M$  vs  $H$  plots of the four compounds under investigation are shown in Fig. S4.1 (a) to (d).

The  $M$  vs  $H$  plots of  $\text{C3MnClH}_2\text{O}$  and  $\text{C5MnClH}_2\text{O}$  are linear to a field of at least 10 kOe, and show saturation at 50 kOe, indicating weak, long-range AFM ordering.

The  $M$  vs  $H$  plots of  $\text{C4MnCl}$  and  $\text{C6MnCl}$  show an upward curvature, which is indicative of a low-dimensional AFM lattice, and are well below saturation at 50 kOe, indicating that the interactions are significant.

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