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On the crystal structures of the polymorphs of manganese(II) chloride tetrahydrate: α -MnCl₂·4H₂O and β -MnCl₂·4H₂O

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Abstract - The manganese(II) chloride tetrahydrate MnCl₂·4H₂O (α -form) crystallizes in the space group $P2_1/n$ with $a = 6.1918(4)$ Å, $b = 9.5230(6)$ Å, $c = 11.1918(6)$ Å, $\beta = 99.757(3)^\circ$, and $V = 650.37(7)$ Å³ ($Z = 4$). A second polymorph of MnCl₂·4H₂O (β -form) is mentioned in the literature to be isomorphous with FeCl₂·4H₂O but its crystal structure was never confirmed. In this study, we report for the first time on the crystal structure of this second polymorph of manganese(II) chloride tetrahydrate, β -MnCl₂·4H₂O, using room temperature single-crystal X-ray diffraction. The β -form crystallizes in space group $P2_1/c$ with $a = 5.9893(5)$ Å, $b = 7.2877(6)$ Å, $c = 8.5838(7)$ Å, $\beta = 110.952(4)^\circ$, and $V = 349.89(5)$ Å³ ($Z = 2$), confirming that β -MnCl₂·4H₂O is isotype to Fe(II)Cl₂·4H₂O. To the best of our knowledge this is the first compound reported to crystallize in both MnCl₂·4H₂O-type (α -form) and FeCl₂·4H₂O-type (β -form) structures. The crystal structure of both α -form and β -form of MnCl₂·4H₂O consists of discrete octahedra complexes [MnCl₂(H₂O)₄] linked by O-H...Cl hydrogen bonds. However, chlorine atoms are in *trans*-configuration in the β -form (*trans*-[MnCl₂(H₂O)₄] complexes) and in *cis*-configuration in the α -form (*cis*-[MnCl₂(H₂O)₄] complexes). Moreover, the coordination polyhedra of the manganese(II) atoms are less distorted in the β -form. This leads to two different hydrogen bond networks and to a slightly more compact [MnCl₂(H₂O)₄] complexes arrangement in the α -form.

Keywords: Manganese chloride, Single-crystal X-ray diffraction, Crystal structure, Hydrogen bond

INTRODUCTION

MnCl₂·4H₂O has been widely studied in biology and medicine for its impact on biological activity [1-6], as a neuronal contrast agent for enhanced magnetic resonance imaging [7,8], and in materials and coordination chemistry as a precursor for the solvothermal synthesis of cathode materials [9,10], manganese titanite and ferrite [11,12], nanoparticles [13,14], polyoxometallates [15], metal-organic frameworks [16], single-molecule magnets [17], magnetic coordination polymers [18-20], magnetic coordination clusters [21,22], and other magnetic Mn(II) complexes [23]. Historically, this compound has been studied extensively for its magnetic properties [24-37] as a good example of simple uniaxial Heisenberg antiferromagnet.

α -MnCl₂·4H₂O is reported to crystallize in the space group $P2_1/n$ with $a = 11.186$ Å, $b = 9.513$ Å, $c = 6.186$ Å, and $\beta = 99.74^\circ$ [38]. This structure was reported as the stable room temperature form of the manganese(II) chloride tetrahydrate [39]. Indeed, a second polymorph described as a metastable room temperature form, β -MnCl₂·4H₂O, is reported in the literature to be isomorphous with FeCl₂·4H₂O [38-40]. Crystals of the β -form have been obtained from the slow evaporation, between 0°C and 6°C, of a supersaturated solution [40]. However, the crystals rapidly change in appearance when removed from their mother-liquor [39,40]. Consequently, the crystallographic structure of this second polymorph was never confirmed.

In this article, we report on the crystal structures of the two polymorphs of manganese(II) chloride tetrahydrate, α -MnCl₂·4H₂O and β -MnCl₂·4H₂O, both determined from single-crystal X-ray diffraction at room temperature. Crystals of β -MnCl₂·4H₂O were obtained from the slow evaporation of a concentrated ethanol solution in presence of K₂S. Herein, we confirm that β -MnCl₂·4H₂O is isostructural with FeCl₂·4H₂O and crystallizes in the space group $P2_1/c$ with $a = 5.9893(5)$ Å, $b = 7.2877(6)$ Å, $c = 8.5838(7)$ Å, and $\beta = 110.952(4)^\circ$.

EXPERIMENTAL

Synthesis method

Single crystals of both structural α - and β -forms were obtained by solvent evaporation techniques. Two solutions were prepared from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ precursor: (i) 100 mg was solubilized in ethanol (3g) and (ii) 200 mg was solubilized in a 50% diluted ethanol solution (3g). Finally, 1g of K_2S saturated ethanol solution was added to both solutions prior to be heated under reflux at 110°C under argon flow for 2h and cooled to room temperature. Single crystals of β - and α -forms of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were obtained from the slow recrystallization in ambient atmosphere of the solutions (i) and (ii), respectively.

Single-crystal X-ray diffraction

Single-crystal X-ray data were acquired under ambient atmosphere at room temperature ($T = 293\text{ K}$) on an APEX II Bruker AXS diffractometer using $\text{Mo-K}\alpha$ wavelength ($\lambda = 0.71073\text{ \AA}$) at the Centre de Diffraction X of the Institut des Sciences Chimiques de Rennes. Crystals of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were picked up from the mother liquor and immediately submerged in PARATONE® oil in order to limit the exposure to air and avoid degradation, mainly caused by dehydration. Despite the weak stability of the β -form under ambient atmosphere, no degradation of the crystal was observed during the measurement. Measurements were processed with the APEX 2 program suite [41]. Frame integration and data reduction were carried out with the SAINT program [42]. The SADABS program [43] was employed for multiscan-type absorption corrections. The structures were solved by direct methods using the SIR97 program [44] and then refined with full-matrix least-square methods based on F^2 (SHELXL-2014) [45] through the WinGX platform [46]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were introduced in the structural model through Fourier difference maps analysis. The atomic coordinates for hydrogen atoms were refined and the equivalent isotropic displacement parameters were constrained to be equal to 1.2 times that of their parent atom. The weak residual electronic density peaks, obtained in the final refinements, indicate that no extra atoms were missing in the structural models. The conditions for the data collections and structure refinements are summarized in Table 1.

Table 1. Summary of single crystal data collection and structure refinement conditions at room temperature for β - and α - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

Structural Formula	β - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	α - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
Space group	$P2_1/c$	$P2_1/n$
Temperature (K)	293(2)	293(2)
Formula weight	197.90	197.90
Wavelength (\AA)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
a (\AA)	5.9893(5)	6.1918(4)
b (\AA)	7.2877(6)	9.5230(6)
c (\AA)	8.5838(7)	11.1918(6)
β ($^\circ$)	110.952(4)	99.757(3)
V (\AA^3)	349.89(5)	650.37(7)
Z	2	4
Calculated density ($\text{g}\cdot\text{cm}^{-3}$)	1.878	2.021
Absorption coefficient (mm^{-1})	2.578	2.774
F(000)	198	396
Crystal size (mm)	0.07 x 0.06 x 0.05	0.52 x 0.26 x 0.08
Crystal color	Colorless	Colorless
Theta range ($^\circ$)	3.643 / 27.516	2.826 / 27.454
h_min, h_max	-7, 6	-7, 7
k_min, k_max	-9, 9	-12, 12
l_min, l_max	-10, 11	-14, 9
R(int)	0.0560	0.0296
Collected reflections	3900	5956
Unique reflections [$I > 2\sigma$]	606	1269
Completeness	0.999	0.998
Data/restraints/parameters	805/0/47	1483/0/89
Goodness-of-fit	1.006	1.069
Final R_1 [$I > 2\sigma$]	0.0339	0.0213
Final wR_2 [$I > 2\sigma$]	0.0539	0.0384
Largest difference ($\text{e}^- \cdot \text{\AA}^{-3}$)	0.399 and -0.360	0.238 and -0.300

RESULTS AND DISCUSSION

Analysis of the single-crystal X-ray diffraction data recorded at room temperature (Table 1) confirms that the second polymorph of the manganese(II) chloride tetrahydrate, β - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, crystallizes in the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -type structure [47-49]. Its structure consists of discrete octahedral complexes $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ (Figure 1), where each manganese(II) atom is coordinated by 4 H_2O molecules in quasi-square configuration (Mn-O distances of 2.160 Å and 2.163 Å, Table 2) and 2 chlorine atoms in *trans*-configuration (Mn-Cl distances of 2.549 Å, Table 2). Manganese atoms are located on the special $2a$ position (*i.e.* on an inversion center) leading to *trans*- $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complexes (Figure 1). The crystal packing of these *trans*- $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complexes is ensured by O-H...Cl hydrogen bonds (Figure 2). Each hydrogen atom (*i.e.* H1A, H1B, H2A, and H2B) is involved in a single hydrogen bond (Figure 3) and each chlorine is a fourfold hydrogen-bond acceptor. Hence, each *trans*- $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complex forms 16 hydrogen bonds with its surrounding complexes: 8 from acceptive chlorine atoms and 8 from dative oxygen atoms. However, due to the localization of Mn atom on the inversion center, only 4 different hydrogen bonds occur in the β -form (Table 3). The determined hydrogen bond geometries of β - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ are in reasonable agreement with those reported by Verbist *et al.* for $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ [49]. The only difference resides in the O-H distances, and consequently the H...Cl distances, which are shorter and longer, respectively, in our structural model.

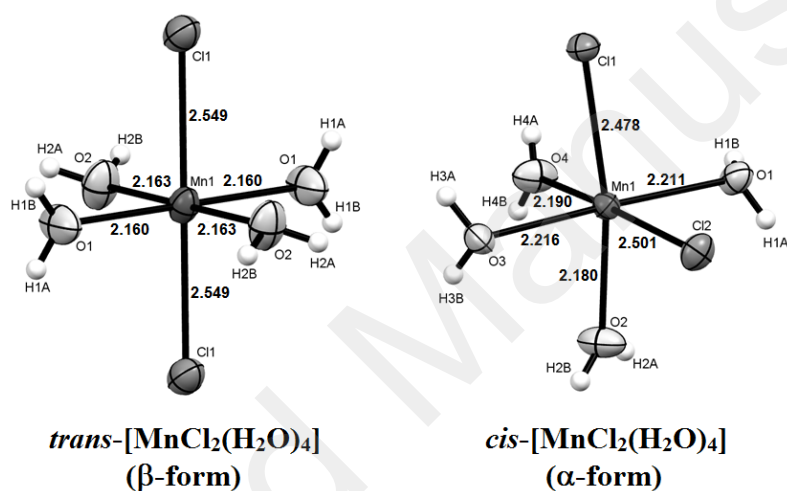


Figure 1. Representation of the *trans*- and *cis*- $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complexes in the β -form (left) and α -form (right) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, respectively. Displacement ellipsoids are shown at the 50% probability level. H atoms are represented as spheres of arbitrary radius.

Table 2. Selected bond lengths (Å) and angles (°) of β - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

Mn1-O1	2.160(2)	O1-Mn1-O2	89.7(1)
Mn1-O2	2.163(2)	O1-Mn1-Cl1	90.1(1)
<Mn-O>	2.162	O2-Mn1-Cl1	92.1(1)
Mn1-Cl1	2.549(1)	H1A-O1-H1B	108(1)
O1-H1A	0.75(3)	H2A-O2-H2B	104(1)
O1-H1B	0.75(3)		
O2-H2A	0.78(3)		
O2-H2B	0.78(3)		

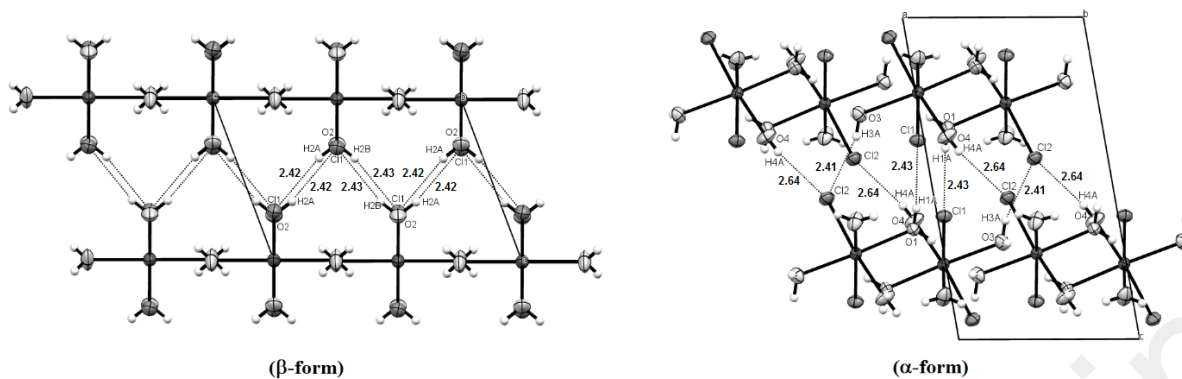


Figure 2. Representation of the O-H...Cl hydrogen bonds network encountered in the β -form (left) and in the α -form (right) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Displacement ellipsoids are shown at the 50% probability level. H atoms are represented as spheres of arbitrary radius.

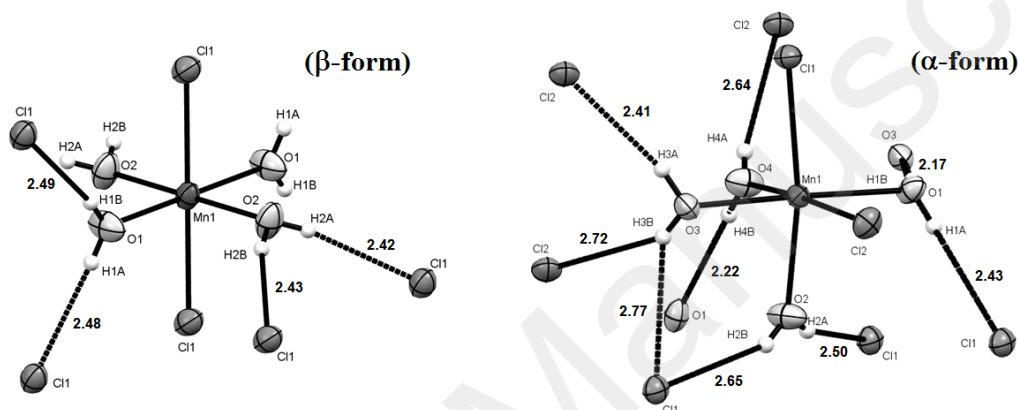


Figure 3. Representation of the hydrogen bonds between H_2O molecules and chlorine atoms in the β -form (left) and α -form (right) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Displacement ellipsoids are shown at the 50% probability level. H atoms are represented as spheres of arbitrary radius.

Table 3. Hydrogen bond geometries of β - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

D-H...A	D...A (Å)	D-H (Å)	H...A (Å)	D-H...A (°)
O1-H1A...Cl1 ^a	3.231(3)	0.75(3)	2.48(3)	174(3)
O1-H1B...Cl1 ^b	3.231(3)	0.75(3)	2.49(3)	172(3)
O2-H2A...Cl1 ^c	3.190(3)	0.78(3)	2.42(3)	168(3)
O2-H2B...Cl1 ^d	3.190(3)	0.78(3)	2.43(3)	166(3)

Symmetry codes: (a) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (b) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (c) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (d) $1 - x, -y, -z$.

Single-crystal X-ray diffraction data acquisition was also carried out on the well-known polymorph (α -form) of manganese(II) chloride tetrahydrate (Table 1). Our results are in agreement with the crystal structure previously determined from both single-crystal neutron diffraction [50] and single-crystal X-ray diffraction data [51]. Similarly to β - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, the α -form is built on discrete octahedra complexes $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ linked to one another by O-H...Cl hydrogen bonds (Figures 2 and 3). Nevertheless, in the α -form, chlorine atoms are in *cis*-configuration as opposed to the *trans*-configuration observed in the β -form (Figure 1). Moreover, in the α -form the *cis*- $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complexes are highly distorted (Table 4) in comparison to the almost regular *trans*- $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complexes encountered in the β -form (Figure 1). The average interatomic distances $\langle \text{Mn-O} \rangle$ and $\langle \text{Mn-Cl} \rangle$ are slightly longer and shorter, respectively, in the α -form (Table 4) compared to the β -form (Table 2). Due to its different chlorine atoms configuration and more distorted octahedra $[\text{MnCl}_2(\text{H}_2\text{O})_4]$ complexes, the α -form possess a more complex O-H...Cl hydrogen bonds network (Figure 3 and Table 5) and a slightly more compact crystal packing (*i.e.* 162.6 \AA^3 per formula unit) in comparison to the β -form (*i.e.* 174.9 \AA^3 per formula unit).

Table 4. Selected bond lengths (Å) and angles (°) of α -MnCl₂·4H₂O.

Mn1-O1	2.211(2)	O1-Mn1-O2	91.7(1)
Mn1-O2	2.180(2)	O1-Mn1-O4	89.9(1)
Mn1-O3	2.216(2)	O1-Mn1-Cl1	94.2 (1)
Mn1-O4	2.190(2)	O1-Mn1-Cl2	86.5(1)
<Mn-O>	2.199	O2-Mn1-O3	87.0(1)
Mn1-Cl1	2.478(1)	O2-Mn1-O4	81.7(1)
Mn1-Cl2	2.501(1)	O2-Mn1-Cl2	93.3(1)
<Mn-Cl>	2.489	O3-Mn1-O4	92.1(1)
O1-H1A	0.76(2)	O3-Mn1-Cl1	87.5(1)
O1-H1B	0.77(2)	O3-Mn1-Cl2	91.4(1)
O2-H2A	0.73(2)	O4-Mn1-Cl1	89.0(1)
O2-H2B	0.73(2)	Cl1-Mn1-Cl2	96.3(2)
O3-H3A	0.79(2)	H1A-O1-H1B	104(1)
O3-H3B	0.70(2)	H2A-O2-H2B	116(1)
O4-H4A	0.68(2)	H3A-O3-H3B	106(1)
O4-H4B	0.75(2)	H4A-O4-H4B	106(1)

Table 5. Hydrogen bond geometries of α -MnCl₂·4H₂O.

D-H...A	D...A (Å)	D-H (Å)	H...A (Å)	D-H...A (°)
O1-H1A...Cl1 ^a	3.175(1)	0.76(2)	2.43(2)	173(2)
O1-H1B...O3 ^b	2.930(2)	0.77(2)	2.17(2)	173(2)
O2-H2A...Cl1 ^c	3.209(2)	0.73(2)	2.50(2)	164(2)
O2-H2B...Cl1 ^d	3.322(2)	0.73(2)	2.65(2)	154(2)
O3-H3A...Cl2 ^e	3.180(1)	0.79(2)	2.41(2)	163(2)
O3-H3B...Cl1 ^d	3.301(1)	0.70(2)	2.77(2)	134(2)
O3-H3B...Cl2 ^d	3.294(1)	0.70(2)	2.72(2)	141(2)
O4-H4A...Cl2 ^f	3.303(2)	0.68(2)	2.64(2)	166(2)
O4-H4B...O1 ^c	2.969(2)	0.75(2)	2.22(2)	172(2)

Symmetry codes: (a) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (b) $-1 + x, y, z$; (c) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (d) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (e) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (f) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

From a crystal chemistry point of view, MnCl₂·4H₂O stands out as being the only divalent metal tetrahydrate halogenide to crystallize in both α - and β -form (Table 6). However, it is worth noting that other crystal structures can be found among MX₂·4H₂O compounds, as recently reported by Falkowski *et al.* on the orthorhombic form of MnBr₂·4H₂O (*Cmcm* space group) [61].

Table 6. Compilation of the divalent metal tetrahydrate halogenides MX₂·4H₂O reported to crystallize in either MnCl₂·4H₂O-type (α -form) or FeCl₂·4H₂O-type (β -form) structures.

	Cl	Br	I	References
Be	α			[52]
Ca	β		β	[53,54]
Cr	β			[55]
Mn	$\alpha + \beta$	α	β	[38,49,50,56,57], this work
Fe	β	β		[47-49,58]
Co	α	β		[58,59]
Ni	α			[58,60]

Finally, as the α -form of MnCl₂·4H₂O was extensively studied for its magnetic properties, β -MnCl₂·4H₂O undoubtedly offers some similarly interesting prospects. In such coordination complexes materials, the magnetic ordering is related to strong indirect exchange coupling occurring between the nearest-neighbor metal atoms through Mn-O-H...Cl-Mn and Mn-Cl...Cl-Mn interactions. Hence, by considering (i) that the arrangements of discrete octahedra complexes [MnCl₂(H₂O)₄] are different, with the α -form having two short Mn...Mn distances of 5.637(1) Å while the β -form has four short Mn...Mn distances of 5.630(1) Å, and (ii) that the isotype compound FeCl₂·4H₂O exhibits antiferromagnetic ordering around 1 K [62-67], we can expect magnetic ordering to occur in β -MnCl₂·4H₂O, which should be different from the α -form.

SUPPLEMENTARY MATERIAL

The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC-1941799 and CCDC-1941800 for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in its β -form and α -form, respectively).

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