Soluble multiferroic hybrids
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Chapter 3. Multifunctional properties of the CuCl- and MnCl-based hybrids

3.1 Introduction

In this chapter we will demonstrate multifunctional properties of two-dimensional CuCl- and MnCl-based organic-inorganic perovskite-like hybrids. As discussed in Chapter 1, organic-inorganic hybrids are formed by the inorganic part, responsible for the magnetic and electronic properties and organic part, yielding ferroelectricity and structural flexibility. Tuning of the magnetic properties in CuCl-based hybrids is the subject of Chapter 4. This chapter will discuss the multiferroic properties of the Cu- and Mn-based 2D organic-inorganic hybrids. In particular, the detailed nature of the ferroelectric transition in CuCl₄(C₆H₅C₂H₄NH₃)₂ and a possible ferroelectric state in the MnCl₄(C₆H₅C₂H₄NH₃)₂ hybrid are discussed.

Multiferroics are the materials which have any type of long range magnetic order and are ferroelastic/ferroelectric¹⁻⁴. Therefore, multiferroicity is linked to the symmetry of the material⁵,⁶.

Currently several main types of the mechanisms, driving the multiferroicity are being explored⁷, namely: lone pair based multiferroics, geometric ferroelectrics, charge ordered compounds and magnetically driven multiferroics.

For every ordered state in a material, like ferromagnetism and ferroelectricity its own primary order parameter is defined. The useful multiferroics have coupling between its main order parameters. Therefore, it is of interest to predict and explore such a coupling in organic-inorganic hybrids, discussed in the present thesis.
D. Khomskii classified multiferroics in two types, depending on the nature of the magnetism and ferroelectricity, respectively. Type 1 multiferroics are materials in which the magnetic and electric ordering originates from different electrons. Thus the ordering temperatures are unrelated and completely different. As a consequence also, the magnetoelectric coupling is weak even though the polarization can be substantial.

Type “2” multiferroics, the order originate from the same type of electrons. The polarization is induced by inversion symmetry breaking magnetic order, such as spin spirals. These type 2 multiferroics have strong magnetoelectric coupling, and the ferroelectric polarization can be changed with an applied magnetic field. In this case the ferroelectric transition temperature is lower than the magnetic ordering temperature. These materials exhibit a weak ferroelectric polarization.

3.2 CuCl-hybrids

In this paragraph I will discuss the multifunctional properties of Cu-based hybrids. Existence of ferromagnetism and ferroelectricity in hybrid compounds is demonstrated using as example CuCl$_4$(C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$ (hereafter CuCl(PEA)). Magnetic properties of the compound are introduced by the inorganic part of the hybrid, while the organic moiety is responsible for ferroelectricity.

3.2.1 Structure of CuCl(PEA) hybrid

To determine structure of CuCl(PEA) hybrid, a fine crystal (clear, 0.60 x 0.40 x 0.20 mm size) was chosen. The selected crystal was mounted on a glass wire with varnish and the measurement was performed with a Bruker-Apex Single crystal diffractometer at 100K. Figure 1 displays the crystal structure of the CuCl(PEA) after refinement.
Refined data from the single crystal X-ray diffraction measurements show a two-dimensional layered structure consisting of CuCl₄ inorganic sheets formed by corner-sharing copper chloride octahedra. Inorganic sheets are intercalated by the double layers of phenylethylammonium molecules (Fig. 3.1).

**Figure 3.1.** Crystal structure of CuCl₄(C₆H₅CH₂CH₂NH₃)₂ determined by single crystal X-ray diffraction at 100 K.

CuCl(PEA) has a Pbcα space group at 100K with unit cell parameters $a = 7.2099(3)$, $b = 7.2664(4)$, $c = 38.238(18)$ Å. The resulting structural refinement using 2340 reflections provided the bond distances and angles, presented in Table 3.1. Obtained structure is similar to previously reported Cu-based compounds⁸⁻¹⁰. The distance between two adjacent inorganic planes is approximately 2 nm. The neighboring phenyl rings in the organic layers are perpendicular to each other with no significant π-π overlap. Due to the fact that Cu$^{2+}$ is a Jahn-Teller active ion, the CuCl₆ octahedra are distorted. The Cu-Cl bonds are analogous to those found in the alkane-based Cu-hybrids.
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3.2.2 Ferromagnetism in CuCl-based hybrids

In the organic-inorganic hybrids magnetism originates from the transition metal ions in the inorganic perovskite-like sheets. In the case of two-dimensional Mn- or Fe-based hybrids neighboring ions interact in-plane antiferromagnetically via a nearly 180° superexchange path through the Cl ions, situated between the metal ions.

However, in the case of Cu\(^{2+}\) s=1/2-based hybrids, alternation of long and short bonds due to the Jahn-Teller effect results into a specific orbital arrangement. The magnetic spin is located in the \(d_{x^2-y^2}\) orbital, which aligns with the long axis of the octahedron. Thus, the orbitals on neighboring metal ions are orthogonal to each other and the spins experience ferromagnetic superexchange via a 180° Cu-Cl-Cu pathway.
ferromagnetic coupling in-plane leads to in-plane 2D order and an apparent quasi 3D ferromagnetic ordering.

To measure magnetic properties of CuCl(PEA) hybrid, a fine crystal was selected, mounted in gelatin capsule and mounted in a plastic straw. Cotton was used to fix the crystal in the capsule. Then, measurements were performed at a MPMS XL Quantum Design magnetometer.

Figure 3.2 (reproduced from A. Arkenbout PhD thesis) displays the dependence of the magnetization versus temperature for the CuCl(PEA) hybrid, which indicates ferromagnetic order below 11K. The saturation magnetization value of 0.8 μB/f.u. (field of 100 Oe) shows 80% of the theoretical value. This behavior agrees with previous studies of this hybrid by Estes et al. Overall for Cu-based hybrids it is possible to tune magnetic properties such as transition temperature, preferential magnetization direction and coercivity by the introduction of the different organic blocks. This will be demonstrated in chapters 4 and 5.
3.2.3 Structural phase transitions

The high temperature phase transitions were analyzed by heat flow measurements using differential scanning calorimetry. Figure 3.3 (left) shows the heat flow above room temperature. The Cu-hybrid material decomposes at 460 K. Between room temperature and decomposition two phase transitions appear at 340 and 410 K. Both transitions show a peak in the heat flow caused by latent heat or a delta function in the specific heat, characteristic of first-order phase transitions. A detailed inspection of the heating and cooling curves near the phase transition at 340 K (Fig. 3b) provides evidence for hysteresis, also characteristic of a first-order phase transition. The different slopes before and after $T_c$ are the result of the first order nature: there is a different specific heat in both phases. This transition can be described as weakly first-order.

3.2.4 Ferroelectric transition in CuCl(PEA) hybrid

Ferroelectricity is a property of a material, which indicates existence of spontaneous electric polarization and possibility to change its direction with an applied external electric field. This phenomena was discovered for the ammonium Rochelle salt (ARS)\cite{ars}. Ferroelectric materials exhibit
spontaneous non-zero polarization in the absence of an external electric field. In analogy to the ferromagnetism, a material usually demonstrates ferroelectricity below a certain transition temperature, called Curie temperature, $T_c$. Due to symmetry requirements, ferroelectric materials also should be piezo- and pyroelectric. Thus, to proof ferroelectricity of the material, pyroelectric current measurements were performed for CuCl(PEA) hybrid.

First, silver contacts were placed on the surface of the CuCl(PEA) crystal sample. Then, the material was cooled down through the phase transitions while applying a poling voltage of +200 volts perpendicular to the c-axis. When the sample reached the low temperature phase, the electric field was switched off and contacts were shorted to redistribute (compensate) surface charges. Then, current was measured during the heating of the sample through phase transitions. The dependence of the pyroelectric current on the temperature is shown at Figure 3.4 (left).

![Pyrocurrent vs Temperature](image1)

**Figure 3.4.** Pyroelectric current measurement for CuCl(PEA) hybrid (left) and polarization versus temperature dependence (right), extracted by integration of the pyroelectric current over time.

At the phase transition the polarization disappears and a current is generated to compensate the charge displacement, which is represented by the peak at 340K (Fig. 3.4 left). When the sign of the poling electric field is reversed, it results in a current in the opposite direction. The polarization as a function of temperature was obtained by integrating the pyroelectric
current with respect to time. Figure 3.4(right) displays the disappearance of the polarization above $T_c$. The magnitude of the measured polarization is approximately 250 $\mu$C/m$^2$ perpendicular to the c-axis. The pyroelectric current measurements prove that the Cu-hybrid is polar below 340 K.

Another evidence for ferroelectricity of CuCl(PEA) below 340K is measurement of capacitance. Figure 3.5 display capacitance of the sample versus temperature. Measurement was performed at 1 kHz frequency. A sharp jump of the capacitance at the 340K phase transition is evidence for polar order below 340K. It should be noted that for proper ferroelectrics divergence of the dielectric constant is observed at $T_c$.

The classical method to prove ferroelectricity of the material is to measure the ferroelectric hysteresis loop$^{16,17}$. Above the coercive field the polarization reverses, which results in a peak in the displacement current. The integration of such current curves for both negative and positive electric field sweeps would then result in a ferroelectric hysteresis loop. However, all measurements performed on CuCl(PEA) hybrid have not been successful, probably due to the low magnitude of polarization. At high voltages, leakage currents dominate the measurements and any small current due to a polarization reversal remained undetected. The classic example of a hydrogen-bond-type improper ferroelectric, Ammonium Rochelle Salt$^{15,18}$, displays a ferroelectric transition at 110 K with a polarization of 2200 $\mu$C/m2, which is 10 times larger than the polarization observed in CuCl(PEA) hybrid.
The weakly first-order nature of the transition suggests that the material is an improper ferroelectric\textsuperscript{19,20}. In this case the polarization is not the primary order parameter of the phase transition but is instead a side-effect of a transition that is initiated by the primary order parameter.

3.2.5 Discussion and origin of multiferroic properties

We showed that at 100K CuCl(PEA) hybrid can be described by the centrosymmetric \textit{Pbca} spacegroup, which is not polar. However, in the previous section, pyroelectric and capacitance data prove the polar nature of the transition. The spacegroup Pbca is inconsistent with ferroelectric properties of the material. Thus, CuCl(PEA) hybrid should have lower symmetry. However, the breaking of inversion symmetry by a change in the hydrogen bonding pattern can be not manifested in our diffraction data due to a consequence of the crystallographic ‘phase problem’, where to a first approximation the intensities of Friedel reflection pairs I(hkl) and I(−h−k−l) are always equal. When anomalous dispersion corrections are included in the atomic scattering factors such that $f = f_0 + \Delta f' + i\Delta f''$, the imaginary term $\Delta f''$ can become significant and the intensities of Friedel pairs are unequal for polar structures. Nevertheless, such differences are typically difficult to measure experimentally, often being obscured by absorption corrections. In our case the breaking of inversion symmetry involves light hydrogen and nitrogen atoms, with low scattering factors and large thermal motion that makes their contribution to the intensity at large scattering vectors small. Furthermore, in polar samples with near-equal populations of opposite ferroelectric domains, the difference between $I_{(hkl)}$ and $I_{(−h−k−l)}$ vanishes. Therefore, X-ray diffraction is often an unconvincing method to determine the presence or absence of inversion symmetry and is particularly problematic in the case of our Cu-hybrid. Although the space group Pbca that we use in our analysis forbids a macroscopic polarization, it does allow local dipole moments and is an accurate approximation of the structure.
based on electron density, capturing most of the structural degrees of freedom involved in the ferroelectric ordering.

To reveal the nature of structural transition at 340K we performed single X-ray diffraction measurements of CuCl(PEA) hybrid below and above $T_c$. Measurements were performed in the temperature ranges from 100K to 220K (30K step), from 295K to 358K (~20K step) and at 398K. Refined data can be found in Appendix 1. At high temperatures, in $Cmca$ symmetry the Cu, Cl and various C atoms are located on special positions, in contrast to $Pbca$ where only Cu occupies a special position. Most of the inter-atomic distances increase with temperature, in line with the increase in lattice parameters. The only distance that significantly decreases above $T_c$ is the Cu-Cl distance parallel to the c-axis, which exhibits a reduction of ~0.6%.

The most striking difference between the high and the low temperature structures is the disappearance of the mirror plane that lies in the inorganic layer above $T_c$. This becomes a glide plane in the $Pbca$ structure and allows buckling of the CuCl$_6$ octahedra to occur as shown. The dependence of the buckling angle on the temperature is presented at Figure 3.6. As demonstrated, there is a discontinuous transition for the dependence of the buckling angle with temperature. Above $T_c=340K$ the buckling of the CuCl$_6$ octahedra completely disappears.

![Figure 3.6. Temperature dependence of the buckling angle for CuCl(PEA) hybrid.](image)
Raman spectroscopic analysis of the low frequency librational modes of the organic cation confirms the weakly first-order character of the transition. This part of the project was performed together with A.Caretta. As shown in figure 3.7, the intensity of a Raman active $A_g$ mode at $\sim 15 \text{ cm}^{-1}$ at room temperature decreases above 270 K and becomes essentially zero at 340 K. Measurement was performed by A. Caretta. This observation can be explained by an orientational melting of the organic molecules. The pronounced temperature dependence of the intensity between $\sim 270$ K and $T_c$ is due to the presence of fluctuations, which clearly demonstrates the weak character of the phase transition\textsuperscript{21}.

![Figure 3.7](image)

**Figure 3.7.** Amplitude of a Raman-active $A_g$ organic libration mode at $\sim 15 \text{ cm}^{-1}$ as a function of temperature. The inset shows low-frequency Raman spectra above and below $T_c$\textsuperscript{10,21}.

The weakly first-order nature of the transition suggests that the material is an improper ferroelectric. In this case the polarization is not the primary order parameter of the phase transition but is instead a side-effect of a transition that is initiated by the primary order parameter. The origin of the electric polarization is a cooperative reorientation of the ammonium cations. Hydrogen-bond ordering model can describe the transition at $T_c \sim 340$K, based on crystallographic data. As mentioned in the introduction, hydrogen-bonded-related multiferroic behavior is common for the
perovskite-like hybrids. However the origin of ferroelectricity is still under debate due to its mixed nature: both order-disorder arising from the rotation of the NH$_3$ organic group$^{10}$ and displacive disorder$^{21}$, originating from the dipole moment of the A-group cation$^{22}$.

The present model describes hydrogen-bond reorientation related ferroelectric transition. This model is based on the fact that ammonium groups have several different, but energetically equivalent orientations in the non-polar phase above Tc=340K. An average of those positions is observed by diffraction and an ordered network of hydrogen bonds is absent.

The buckling of the octahedra below Tc results in a displacement of the ammonium groups and a cooperative hydrogen-bond ordering as shown at Figure 3.8. Each ammonium then occupies a fixed position and the hydrogen bonds form an ordered network. The nitrogen atom is located exactly in the middle of the cavity, formed by the CuCl$_6$ octahedra, connected to corresponding chlorine atoms with three hydrogen bonds. The first hydrogen bond is formed with an in-plane chlorine. From our X-ray diffraction data, this bond exhibits the shortest bond length (2.321Å) and a favorable N-H-Cl angle (172.28°). We therefore propose that this bond is the strongest, too strong to be influenced by the applied poling electric field. The second hydrogen bond is formed with out-of-plane chlorine and is weaker due to the larger distance (2.368Å) and less favorable angle (168.69°). There are two chlorine atoms available for this hydrogen bond.

Figure 3.8.
Representation of the buckling of the CuCl$_6$ octahedra, causing cooperative hydrogen bonds reordering.
These chlorine atoms are crystallographically inequivalent due to the buckling of the inorganic sheet and the resulting hydrogen bonds do not have the same energy. The ammonium group thus sees an asymmetric double potential well. Therefore, one hydrogen bond can be reoriented to the less favorable position with poling by applied electric field. The third hydrogen atom of the ammonium forms a weaker hydrogen bond, and in our model we neglect its role.

If the material is not poled or strained, it is expected that all the second hydrogen bond will adopt the favorable configuration, lower in energy. This would result in an exact cancellation of all the local moments and no macroscopic polarization would be observed. However, when a poling field is applied the ammonium group can adopt different configuration, and a net polarization can be generated. Therefore, the local displacement of nitrogen atoms introduces an internal electric field that tends to align the surrounding dipoles in the same direction. As a result of this cooperative distortion, the dipole moments do not exactly cancel, but give rise to a macroscopic polarization along the direction of the poling field in the plane. For other directions of the electric poling field, this model will also result in a macroscopic polarization.

As described above, the shift of the positively charged nitrogen atoms with respect to the negatively charged inorganic backbone generates a local dipole. In the Pbca space group, the displacements on both sides of the inorganic sheet are opposite and hence these local moments cancel. However, the pyroelectric current data provide evidence that the true symmetry is lower, allowing finite polarization. In the next sections we will demonstrate the same phenomena for Mn-based hybrid, but with a polar spacegroup. The key parameter for the generation of macroscopic polarization is the introduction of hydrogen-bond order by buckling of the perovskite-like sheet. The Jahn-Teller distortion present in the Cu-hybrid, where atomic displacements within the inorganic layer are caused by d-orbital degeneracy, does not seem to play any role in this mechanism. X-ray diffraction data indicate that the displacement of the ammonium group is
~0.01 nm below Tc, which results in an in-plane polarization of a magnitude consistent with the pyroelectric current measurements.

3.3 MnCl-hybrids

3.3.1 Structure of MnCl(PEA) hybrid

Single crystals of MnCl₄(C₆H₅C₂H₄NH₃)₂ (MnCl(PEA)) were synthesized according to the procedure, described in Chapter 2, similar to CuCl(PEA) hybrid. MnCl(PEA) has a Pbc2₁ space group at 100K with unit cell parameters a=7.1140(8) Å b=7.2139(8) Å c=39.1534(43) Å. Refined pattern details can be found in Appendix 1. Refinements were performed by G.Blake.

The resulting structural refinement provided the general structural parameters. The structure of MnCl(PEA) is also layered, similar to the previously reported Mn-based organic-inorganic hybrids¹¹,¹³,²³–²⁵ and to the general layout of 2D hybrids, discussed in the present thesis, like CuCl(PEA).

Figure 3.9. Crystal structure of MnCl₄(C₆H₅C₂H₄NH₃)₂ determined by single crystal X-ray diffraction at 100 K.
Analogous to CuCl(PEA), the MnCl(PEA) hybrid represents a layered crystal structure, with alternating inorganic and double organic layers. Inorganic monosheets are formed by MnCl$_6$ corner shared octahedra, intercalated by double layers of PEA organic ligands in tail-to-tail geometry (Figure 3.9). Due to the fact that Mn$^{2+}$ is non a Jahn-Teller active ion, Mn-Cl distances in-plane are the same. However, similar to the CuCl(PEA) hybrid the MnCl$_6$ octahedra are buckled. Therefore, it is of interest to investigate phase transitions in order to find the polar transition.

### 3.3.2 Antiferromagnetism in MnCl(PEA) hybrid

As discussed earlier, 2D hybrids with non Jahn-Teller active magnetic ions exhibit antiferromagnetic interactions in-plane. This is caused by superexchange interactions via Mn-Cl-Mn 180$^0$ pathway$^{11,12}$. Thus, magnetic spins couple antiferromagnetically. Figure 3.10 represents magnetization versus temperature and magnetization versus magnetic field of the MnCl(PEA) hybrid, measured perpendicular to the c-axis (out-of-plane). Magnetic spins of the Mn-hybrid are not aligned perpendicular to the inorganic plane, but exhibit canting. Therefore, a small ferromagnetic moment is present, which causes divergence of the correlation length in-plane, leading to quasi-3D order.

![Figure 3.10](image.png)

**Figure 3.10.** Temperature dependent magnetization measurements for MnCl(PEA) organic-inorganic hybrid. Magnetization versus temperature (left) and magnetization versus magnetic field, measured at 5K. Picture is taken from A.Arkenbout PhD thesis$^{14}$. 

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3.3.3 Structural phase transitions

To analyze the phase transitions of the MnCl(PEA) hybrid, DSC measurements were performed. Heat flow versus temperature (Fig. 3.11) displays two reversible phase transitions at 368 and 416K.

![Differential scanning calorimetry measurements for MnCl(PEA) organic-inorganic hybrid.](image)

The transition at 368K is accompanied by fluctuations, resulting in different slopes before and after the peak. Therefore this transition is assigned to a weak first order type of transition, similar to the one, observed in CuCl(PEA) hybrid at 340K. As seen in figure 3.11, the second phase transition at 416K is a second order transition because of the clear divergent type of the peak. The phase transition at 368K is of particular interest due to its similarity with
the 340K phase transition in CuCl(PEA) hybrid, previously assigned to the ferroelectric transition.

3.3.4 Polar phase transition in MnCl(PEA) hybrid

In order to find the structural changes at phase transition in MnCl(PEA) hybrid, X-ray single crystal measurements were performed at 320K and 380K. Refined data display spacegroup *Pbc21* below $T_c=363K$ at 100K and 320K changing to spacegroup *Cmca* at 380K. Importantly, the buckling-to-unbuckling transition, discussed earlier in this chapter is present for MnCl(PEA) at 363K. Therefore, the weak first-order nature of the transition suggests that the material is an improper ferroelectric, similar to the one discussed for CuCl(PEA).

![Image, demonstrating buckling-to-unbuckling transition for MnCl(PEA) hybrid at the T= 363K phase transition.](image)

**Figure 3.12.** Image, demonstrating buckling-to-unbuckling transition for MnCl(PEA) hybrid at the T= 363K phase transition.

Figure 3.12 represent structural changes of the inorganic part of the MnCl(PEA). As seen in the figure, below $T_c=363K$ MnCl$_6$ octahedra are buckled with the angle value of 7,33° relatively to the c-axis. However, after the phase transition MnCl$_6$ octahedra become unbuckled, when the imaginary line connecting the top-apical Cl with Mn and the bottom apical Cl atom is perfectly parallel to the c-axis.
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Figure 3.13 displays patterns of powder x-ray diffraction measurements of MnCl(PEA) hybrid measured at 303-423K (20K step) temperature range by A. Everhardt. The plot is zoomed in at the 24-25° of 2-theta range, where splitting of the (001) peak can be observed below the transition at 368K. This splitting reflects structural changes in-plane and represents the polar to non-polar state transition.

![Figure 3.13 X-ray powder diffraction pattern in the 24-25 degrees 2-theta range for the MnCl(PEA) hybrid (measured by A.Everhardt).](image)

As discussed in section 3.2.4 of the present chapter, Raman spectroscopic analysis of the low frequency librational modes of the organic cation confirms the weakly first-order character of the transition at 340K for CuCl(PEA) hybrid. Figure 3.14 shows the comparison of the Raman spectra of CuCl(PEA) and MnCl(PEA) hybrids. As seen in the figure, at low frequencies the spectral intensity of a Raman active A_g modes are quite similar for both compounds.
Raman spectroscopy measurements of MnCl(PEA) were performed at different temperatures below and above the 363K transition (performed by A. Caretta)\textsuperscript{21} (Fig 3.15). Analysis of the data revealed a decrease of the Raman active A\textsubscript{g} modes at \textasciitilde19 cm\textsuperscript{-1} and \textasciitilde42 cm\textsuperscript{-1} while heating. Eventually the mode becomes zero intensity at T\textsubscript{c}=363K. As described before, such an phenomenon is typically assigned to translation symmetry breaking due to an orientational melting of the organic molecules. Therefore, the transition at 363K can be assigned to a weakly first order transition which suggests that the material is also an improper ferroelectric below T\textsubscript{c}.

Temperature-dependent birefringence measurements display a domain structure of the Mn-hybrid. After heating up to T\textsubscript{C}= 368K the observed domain pattern has totally changed. Figure 3.16 display pictures of a MnCl(PEA) crystal, made with an optical microscope with polarization filters. The sample was placed between two polarizers that make an angle of 45° (upper images) and 90° (lower images). The left picture shows the crystal at 300K in the initial domain structure.

\textbf{Figure 3.14.} Raman spectra for Mn(PEA) (upper curve) and CuCl(PEA)(lower curve) hybrids. Measurements are performed by A.Caretta.
Then, the crystal was heated to ~383K (above $T_c=368K$), where the color becomes darker and difference in colors within the main piece of the crystal disappears. Then, after cooling the sample back to 300K (Fig. 16 right picture) a domain structure re-appears in a completely different

**Figure 3.15.** Low-frequency Raman spectra of the Mn(PEA) hybrid, measured at different temperatures. Measurements are performed by A.Caretta.

**Figure 3.16.** Birefringence in the MnCl(PEA) hybrid below and above the polar phase transition. Left image at 300 K: sample in the polar phase before heating showing specific domains pattern. Middle images at 383 K: sample after heating through $T_c$. Right picture: compound at 300K with different domain pattern then in the initial state. Pictures and measurements are done by A. Everhardt.
configuration.

The proposed nature of these domains can be ferroelastic. If we consider that the second phase transition at 416K is a-b twinning and we heat up the sample to the maximum temperature point before $T_{c2}=416K$, but after $T_{c1}=368K$, the domain walls, observed on the picture may appear conductive\textsuperscript{26}. Therefore, it could be very hard to measure pyroelectric current or capacitance, due to high leakage currents at the domain walls. I propose that this is the main reason for capacitance and pyroelectric current measurements to fail.

Overall we conclude that MnCl(PEA) perovskite-like hybrid exhibits a polar-to-non-polar phase transition at $T_c=363K$. We also showed the buckling-to-unbuckling mechanism exists in MnCl(PEA) at $T_c$, previously described as the cause for hydrogen-bond ordering in CuCl(PEA) hybrid, resulting in finite polarization. Overall we propose that MnCl(PEA) is also improper ferroelectric below 363K. This should still be confirmed by pyroelectric current or P-E loop measurements.

### 3.4 Conclusions

We showed multiferroic properties in the hybrid CuCl$_4$(C$_6$H$_5$CH$_2$CH$_2$NH$_3$)$_2$, where the ferromagnetism originates from the inorganic part and ferroelectricity from the organic moiety. The CuCl$_4$(C$_6$H$_5$CH$_2$CH$_2$NH$_3$)$_2$ hybrid is polar below $T_c = 340 K$, as evidenced by the observation of a macroscopic polarization below $T_c$. The hydrogen-bond ordering results in a shift of the positively charged ammonium group with respect to the negatively charged inorganic backbone, generating a local dipole moment. Both capacitance measurements and the structural changes in the Cu-hybrid show a striking resemblance with the electrical properties of other improper ferroelectrics such as ARS.\textsuperscript{10,27,33} Magnetic susceptibility measurements reveal ferromagnetic ordering below 11K. Therefore, we provide evidence that this
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material constitutes a novel type of multiferroic behavior involving the coexistence of ferroelectricity originating from the organic block and ferromagnetism originating from the inorganic block.

We provide evidence that \( \text{MnCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2 \) is polar below 363K. We find agreement with the “buckling model”, introduced for \( \text{CuCl}_6(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2 \).

X-ray diffraction measurements show that the polarization in Cu- and Mn-based hybrids is possible due to a buckling of the perovskite blocks that leads to ordering of the hydrogen bonds below \( T_c \). This model is general and not restricted to the hybrids that are studied in this thesis. The electrical polarization and magnetic superexchange are both directly coupled to the buckling of the octahedra, and therefore the magnetoelectric coupling induced by this mechanism is potentially large.
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