

# SYNTHESIS, CHARACTERIZATION, ELECTRON PARAMAGNETIC RESONANCE AND UV-VISIBLE STUDY OF PEROVSKITE LAYERED SYSTEM $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]_2\text{CuCl}_4$

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## ABSTRACT

Perovskite Layer compounds with the general formula  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MX}_4$  or  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3] \text{MX}_4$  where M is a divalent metal atom and X an halogen (M = Cu, Mn, Zn, Co, Cd...) (X = Cl, Br...) are lamellar type structures with a particular properties due to synergy between organic and inorganic parts. In this work, the synthesis and the structure by X-ray powder diffraction of the compound  $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]_2\text{CuCl}_4$  are presented. The studied compound crystallize in the monoclinic system with cell parameters:  $a = 5.3230(15) \text{ \AA}$ ,  $b = 13.4714(40) \text{ \AA}$ ,  $c = 5.1414(13) \text{ \AA}$ ,  $\beta = 91.832(32)^\circ$ . The compound is also investigated by means of Infra-Red spectroscopy, Electron Paramagnetic Resonance (Electron Spin Resonance ESR) and UV-Visible spectroscopy. The ESR study shows a typical signal for distorted octahedral site and for a Ferro Magnetic Resonance (FMR). The absorption spectrum of UV-Visible spectroscopy shows bands due to Charge Transfer Transitions from the ligand orbitals ( $p\sigma$  and  $p\pi$ ) to the half-occupied d orbital.

**Keywords:** X-Ray Diffraction, Spectroscopy and Electron Spin Resonance.

## 1. INTRODUCTION

The organic-inorganic perovskites are one of the most extensively studied crystalline families of hybrids which offers an important opportunity to combine useful properties from two chemical realms, organic and inorganic compounds, within a single molecular scale composite<sup>1,2</sup>. Among these compounds, the 2D layered perovskites:  $(\text{R-NH}_3)_2\text{MX}_4$  and  $(\text{NH}_3-\text{R-NH}_3)\text{MX}_4$ , where R is an aliphatic or aromatic ammonium cation, M is a divalent metal that can adopt an octahedral or tetrahedral coordination, and X is a halogen: Cl, Br or I. These bis (n-alkylammonium tetrahelo metallates) form lamellar type structures in which the sheets of corner-shared  $\text{MX}_6$  octahedral are sandwiched between a pair of layer of n-alkylammonium chains. The cavities between the octahedral are occupied by the  $\text{NH}_3$  groups which are attracted

to the  $\text{MX}_6$  by hydrogen bonds  $\text{N-H}\dots\text{X}$ . the organic groups R self-assemble via  $\pi$  - stacking interaction (when the organic group contains aromatic groups), through Van der Waals force or hydrogen bonding when the organic group contains acid function<sup>3</sup>. So, the perovskite layers are typical "Sandwich" system because of the regular alternation of inorganic and hydrocarbon regions that consist of long chain alkylammonium groups ionically bonded to an inorganic support<sup>3,4</sup> (figure 1).

These compounds are the origin of a number of useful and peculiar properties due to the organic layer, to the inorganic layer and to the organic inorganic hybrids<sup>1</sup>. In fact the studies have shown that these perovskite layers are among the Phase Change Material (PCM) good for Thermal Energy Storage (TES) because of the solid-solid transition<sup>6</sup>. In addition, Balamurugan

*et al.* and Wei Ning *et al.* have studied the electrical behavior and the magnetic properties for some layered organic inorganic hybrids<sup>7-9</sup>. Several papers studied structural characterization of some organic inorganic hybrids like perovskite system<sup>1,3,6,10,16,17</sup>. Indeed, as known the crystallography plays a crucial role to understand the structural behavior of materials and make relationship structure properties. In this manuscript, we present powder X-ray diffraction at room temperature of two (2D) organic inorganic like perovskite system  $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]_2\text{CuCl}_4$ , Infra-Red spectroscopy, Electron Paramagnetic Resonance (Electron Spin Resonance ESR) and UV-Visible spectroscopy.

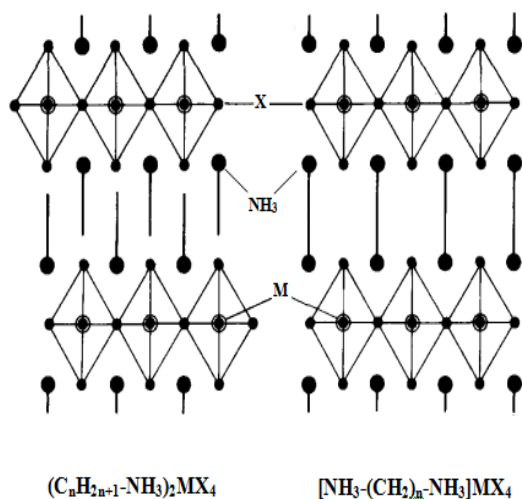


Fig. 1: Schematic representation of 2D-layered perovskites

## 2. Synthesis

A powder finely crushed of the diamine  $\text{NH}_2-(\text{CH}_2)_8-\text{NH}_2$  is prepared then 0,5g of the powder is dissolved in a small quantity of distilled water and the obtained solution is made under regular and weak agitation during at least half an hour. Gaseous HCl (obtained from concentrated  $\text{H}_2\text{SO}_4$  poured; drop with drop; on solid NaCl) is dissolved in the diamine solution in order to form the diamine chloride ( $\text{NH}_2-(\text{CH}_2)_8-\text{NH}_2, 2\text{HCl}$ ). Finally, the compound  $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]\text{CuCl}_4$  is prepared from 1M of the aqueous solution of ( $\text{NH}_2-(\text{CH}_2)_8-\text{NH}_2, 2\text{HCl}$ ) and 1M of an aqueous solution of  $\text{CuCl}_2$ .

## 3. X-ray Powder diffraction and Infrared spectroscopic investigation

The structure of the obtained compound is investigated by means of X-ray powder diffraction (XRD) and Infra-Red spectroscopy (FTIR).

### 3.1. X-ray powder diffraction

The indexed X-ray diffraction powder pattern of this compound is shown in Figure 2. The program Dicvol04 [18-20] is used to determine unit parameter cell. The best solution to index the well-defined peaks (10) in the range  $3^\circ - 38^\circ$  gives the monoclinic cell, with  $a = 5.3230(15) \text{ \AA}$ ,  $b = 13.4714(40) \text{ \AA}$ ,  $c = 5.1414(13) \text{ \AA}$ ,  $\beta = 91.832(32)^\circ$  and volume  $368.49 \text{ \AA}^3$ . The Figures of merit  $M(10) = 76.5$  and  $F(10) = 56.9(0.0068, 26)$ . The indexation of this diffractogram show layered structure in direction to the big axis  $c$ . To confirm this result structural resolution from X-ray single crystal diffraction is now in progress and will be published in a future paper.

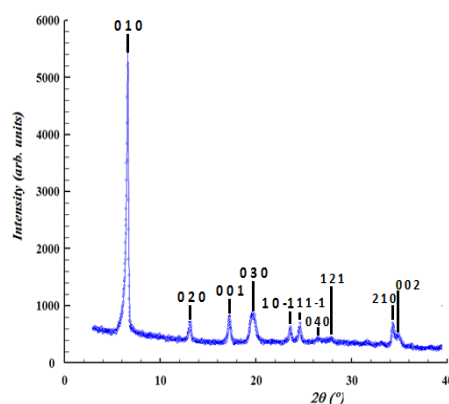


Fig. 2: Indexed Diffraction pattern of  $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]\text{CuCl}_4$

### 3.2. Infra-Red spectroscopy

The perovskite compound was also investigated by Fourier Transform Infra Red Spectroscopy (FTIR). The spectrum of the layer perovskite compound is divided in two ranges: Intern vibration modes of the organic cation in the range of frequency  $[4000 \text{ cm}^{-1} - 400 \text{ cm}^{-1}]$ , and extern vibration modes of the organic cation with the intern and extern vibration modes of the anion in the range  $[<400 \text{ cm}^{-1}]$ . Figure 3 present the intern vibration modes of the organic cation  $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]^{2+}$ . The principal vibrations are listed.

The strong peak at  $3332 \text{ cm}^{-1}$  is due to the asymmetric/symmetric N-H stretching vibration of secondary amine ( $>\text{NH}$ ). The asymmetric and symmetric stretching modes of  $(\text{NH}_3^+)$  peaks are located at  $2924$  and  $3063 \text{ cm}^{-1}$ . The peaks at  $2663$  and  $2887 \text{ cm}^{-1}$  are due to the asymmetric and symmetric stretching modes of  $-(\text{CH}_2)-$ , while the deformation modes of  $(\text{NH}_3^+)$  are presented on  $1646$  and  $1559 \text{ cm}^{-1}$  peaks. The twisting and the rocking modes of  $(\text{NH}_3^+)$  head groups are located in  $1063$  and  $1037 \text{ cm}^{-1}$ . The

band at  $820\text{ cm}^{-1}$  is due to stretching modes of C-C-C responsible of phase transition.

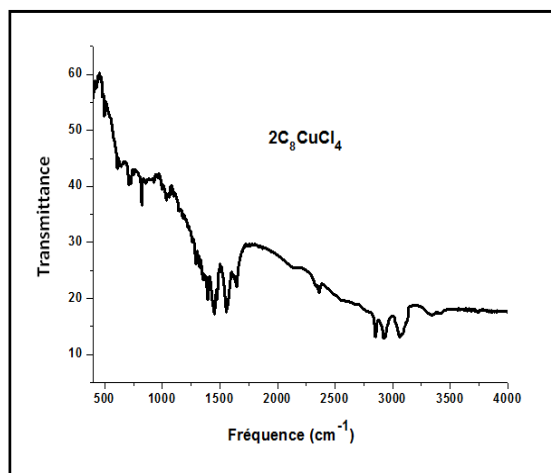


Fig. 3: IR spectrum of  $[\text{NH}_3\text{-(CH}_2)_8\text{-NH}_3]\text{CuCl}_4$

#### 4. Electron Spin Resonance

Electron Paramagnetic Resonance or Electron Spin Resonance (ESR) is a very sensitive tool that provides information about lattice symmetry and structure. It reflects the environment of the paramagnetic ion<sup>11</sup>. ESR has been proved to be a useful tool for the study of magnetic correlations in magnetic materials<sup>9</sup>. Our complex contains  $\text{Cu}^{2+}$  ions, which make it active to the ESR. In deed;  $\text{Cu(II)}$  has nine valence d electrons resulting in one unpaired electron in the  $d_{x^2-y^2}$  orbital in the ground state. This is perturbed by application of an external magnetic field and can be studied by Electron Spin Resonance<sup>12</sup>.

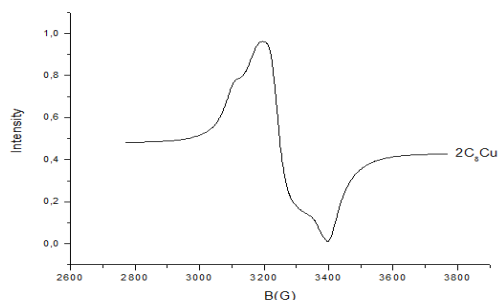


Fig. 4: ESR spectrum of  $[\text{NH}_3\text{-(CH}_2)_8\text{-NH}_3]\text{CuCl}_4$

The signal is large and asymmetric (figure 4), typical for distorted octahedral site<sup>13</sup>, also typical for a Ferro Magnetic Resonance (FMR). More, the FMR line split into two lines and the signal appears to be composed of two overlapped spectral lines. For the splitting, the appearance of an additional FMR line is similar to the FMR behavior of coupled FM layers separated by nonmagnetic spacer layers<sup>8</sup>, and it

is caused by the presence of relatively large local field ( $H_{\text{local}}$ ) of the ferromagnetic domain. In addition, the hyperfine structure doesn't show up, which means that the interaction between the single electron and the nucleus of the copper does not take place. So, the linking  $\text{Cu}\text{---Cl}$  has an ionic character. Indeed, these results were already observed in other papers<sup>14, 15</sup>.

#### 5. UV-Visible

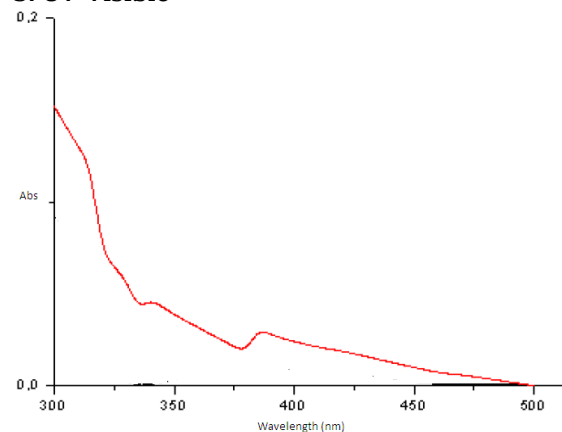


Fig. 5: UV-Visible absorption spectrum of  $[\text{NH}_3\text{-(CH}_2)_8\text{-NH}_3]\text{CuCl}_4$

The spectrum (figure 5) presents two absorption bands, the first one at 338 nm and the second one at 398 nm, these bands are due to the Charge Transfer Transitions. Indeed, at higher photon energy (UV-Vis), electrons are excited from the filled ligand-centred orbitals to the half-occupied d orbital, producing ligand to metal charge transfer transitions. The first band at 338nm represent the charge transfer transition from the  $p\sigma$  ligand to the half-occupied d orbital and the second band at 398nm represent the transition from the  $p\pi$  ligand to the half-occupied d orbital.

#### 6. CONCLUSION

In summary, we have synthesized an organic inorganic compound with a layer structure  $[\text{NH}_3\text{-(CH}_2)_8\text{-NH}_3]\text{CuCl}_4$ , we have started the structural investigation by X Ray powder diffraction, the compound crystallize in a monoclinic system and the cell parameters are  $a = 5.3230(15)\text{ \AA}$ ,  $b = 13.4714(40)\text{ \AA}$ ,  $c = 5.1414(13)\text{ \AA}$ ,  $\beta = 91.832(32)^\circ$ . It shows layered structure in direction to the big axis c. By Fourier Transform Infra Red Spectroscopy we have detected the principal vibrations. The obtained compound was also investigated by Electron Paramagnetic Resonance (Electron Spin Resonance ESR) and UV-Visible spectroscopy. The ESR study shows a typical signal for distorted octahedral site and for a Ferro Magnetic Resonance (FMR). The

absorption spectrum of UV-Visible spectroscopy shows bands due to Charge Transfer Transitions from the ligand orbitals ( $p\sigma$  and  $p\pi$ ) to the half-occupied d orbital.

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