



ELECTRON SPIN RESONANCE (ESR) STUDY OF FOUR PEROVSKITE LAYER COMPOUNDS

$[\text{NH}_3-(\text{CH}_2)_3-\text{COOH}]_2\text{CuCl}_4$, $[\text{CH}_3-(\text{CH}_2)_7-\text{NH}_3]_2\text{CuCl}_4$,
 $[\text{NH}_3-(\text{CH}_2)_8-\text{NH}_3]\text{CuCl}_4$, AND $[\text{NH}_3-(\text{CH}_2)_{10}-\text{NH}_3]\text{CuCl}_4$

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ABSTRACT

Perovskite Layer compounds with the general formula $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MX}_4$ (C_nMX_4 for short) or $[\text{NH}_3-(\text{CH}_2)_n-\text{NH}_3]\text{MX}_4$ (Short notation $2\text{C}_n\text{MX}_4$) where M is a divalent metal atom and X an halogen ($M = \text{Cu}, \text{Mn}, \text{Zn}, \text{Co}, \text{Cd} \dots$) ($X = \text{Cl}, \text{Br} \dots$) are lamellar type structures and 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. Perovskite Layer compounds are Phase Change Material which have solid-solid transitions and thermal properties good for Thermal Energy Storage. Electron Spin Resonance (ESR) study was done to some of the perovskite layers that we have synthesized. It shows a Ferromagnetic Resonance line (FMR) that split into two overlapped spectral lines for $2\text{C}_8\text{CuCl}_4$. The observed splitting of the FMR signal has been observed in other layered compounds.

Keywords: Perovskite layer, ESR, Ferromagnetic, Thermal energy storage.

1. INTRODUCTION

The organic–inorganic perovskites are one of the most extensively studied crystalline families of nano-hybrids which offers an important opportunity to combine useful properties from two

chemical realms, organic and inorganic compounds, within a single molecular scale composite (Elmebrouki *et al.*, 2011). Among these compounds, the perovskite layers organometallics which exist on two types. The Monoammonium type with the general formula $[C_nH_{2n+1}NH_3]_2MX_4$ (C_nMX_4 for short) and the Diammonium type with the general formula $[NH_3-(CH_2)_n-NH_3] MX_4$ (Short notation $2C_nMX_4$) where M is a divalent metal atom and X an halogen (M = Cu, Mn, Zn, Co, Cd...) (X = Cl, Br...). These compounds are lamellar type structures in which the sheets of corner-shared MX_6 octahedra are sandwiched between a pair of layer of n-alkylammonium chains. The cavities between the octahedra are occupied by the NH_3 groups which are attracted to the MX_6 by hydrogen bonds N-H...X. 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 (Tamsamani *et al.*, 2011)

These compounds are the origin of a number of useful and peculiar properties due to the organic layer or to the inorganic one or to the organic inorganic hybrids (Elmebrouki *et al.*, 2011). 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 (Tamsamani *et al.*, 2011). In addition, these materials have a distinct set of advantages, including good electric mobility, tunable band gap property, magnetic property, but only few studies have been done to the electrical behaviour and the magnetic properties for this kind of perovskite layers when the same studies were already known for other layered compounds (Balamurugan *et al.*, 2009) Wei Ning *et al.* (2009a ;2009b).

In our lab, we have synthesized several composites in both types (monoammonium and diamonium). In this work we try to study by means of Electron Spin Resonance (ESR) four samples, two monoammonium $[NH_3-(CH_2)_3-COOH]_2CuCl_4$ (*acid Cu* for short) and $[CH_3-(CH_2)_7-NH_3]_2CuCl_4$ (*mono Cu* for short) and two diamonium $[NH_3-(CH_2)_8-NH_3]CuCl_4$ (*2C8Cu* for short) and $[NH_3-(CH_2)_{10}-NH_3]CuCl_4$ (*2C10Cu* for short)

Fig.1. Monoammonium type of Perovskite layer compounds $[C_nH_{2n+1}NH_3]_2MX_4$

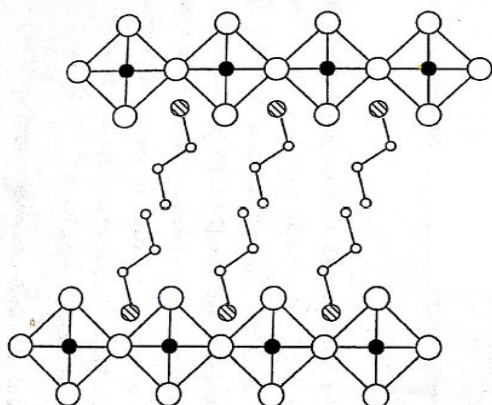


Fig.2. Diammonium type of Perovskite layer compounds $[NH_3(CH_2)_nNH_3]MX_4$

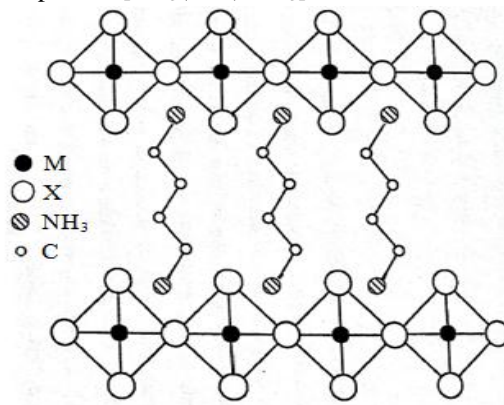
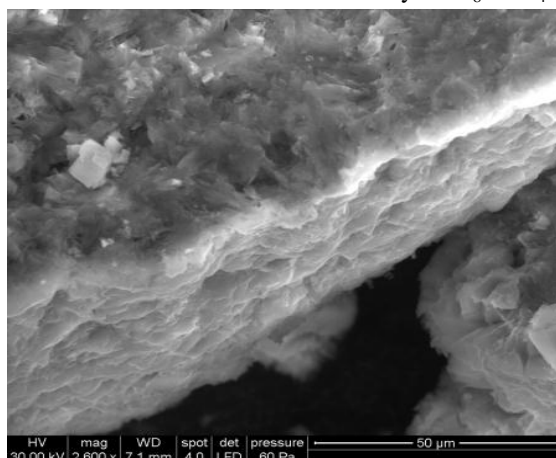
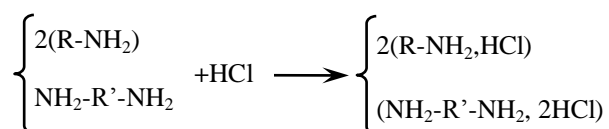


Fig.3. Lamellar structure of a Perovskite Layer $2C_8CuCl_4$ by MEB

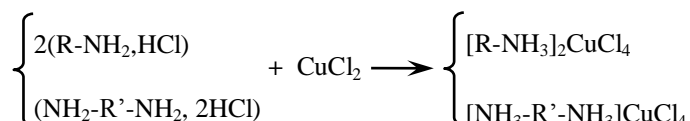
1.1. Synthesis of the compounds

The first step in the synthesis is adding gaseous HCl to the diamine or monoamine organic chain



(Gaseous HCl is obtained by adding drop by drop H_2SO_4 acid to solid NaCl)

Next, we complete the synthesis of the complexes by mixing stoichiometric quantities of the products of the first reaction and aqueous solution of $CuCl_2$.



The acquired solution is clear, homogeneous and uncolored. It is left in dark at room temperature several days to obtain single crystals (Elmebrouki *et al.*, 2011), (Elmebrouki *et al.*, 2013).

1.2. Electron Spin Resonance

ESR is a very sensitive tool that provides informations about lattice symmetry and structure. It reflects the environment of the paramagnetic ion (Glinchuk and Kuzian, 2007). ESR has been proved to be a useful tool for the study of magnetic correlations in magnetic materials (Wei Ning *et al.*, 2009b). Our complexes contain Cu^{2+} ions, which make them active to the ESR. In deed; 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 (Edward, 2006).

2. RESULTS AND DISCUSSION

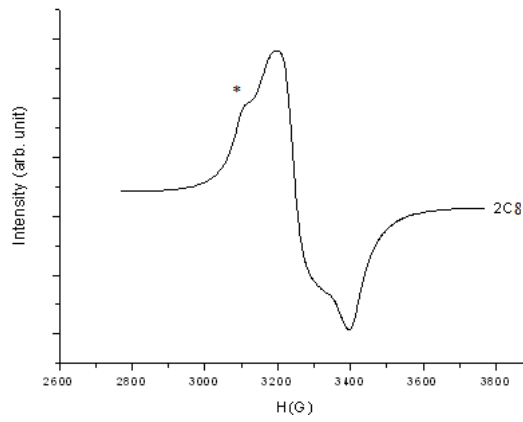


Fig 4

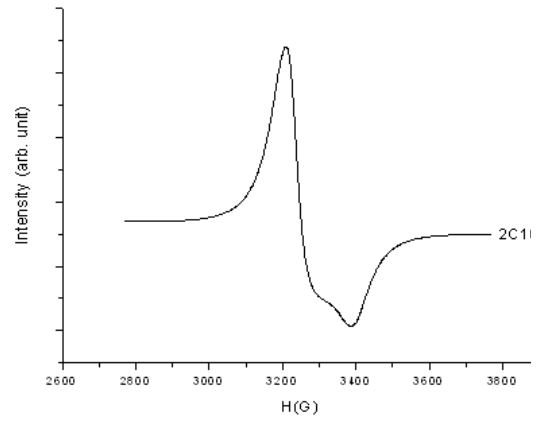


Fig 5

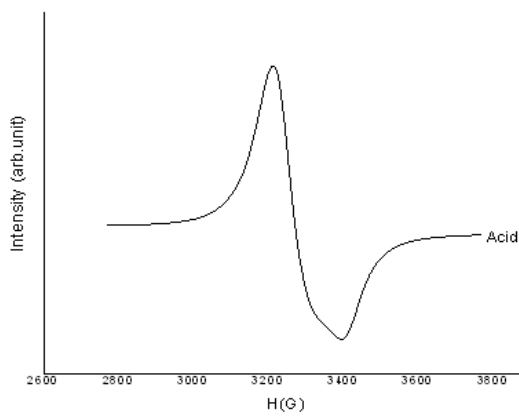


Fig 6

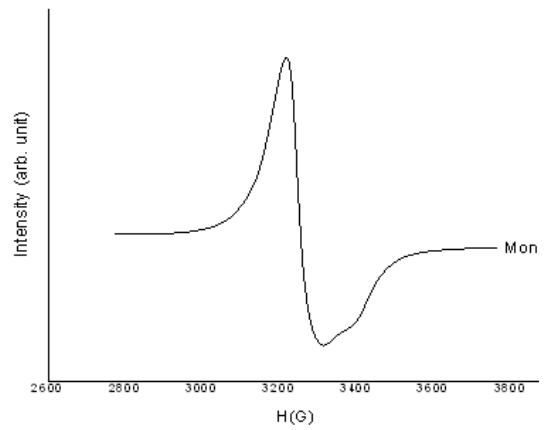


Fig 7

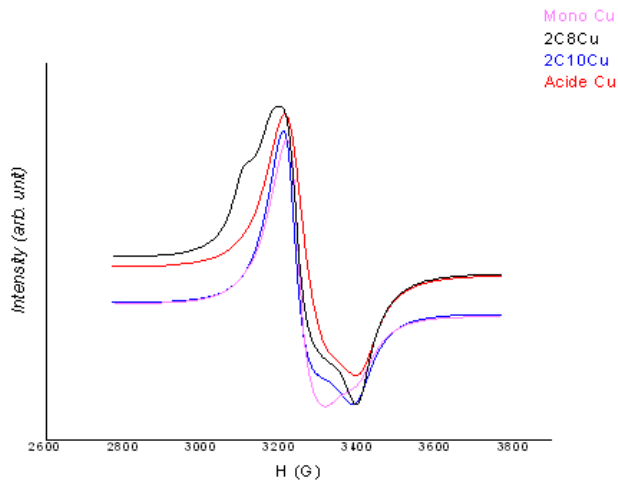


Fig 8

Fig 4,5,6 and 7 show the ESR spectra of $2C_8CuCl_4$, $2C_{10}CuCl_4$, acid Cu and mono Cu, they were recorded for $H=3270$, and for all spectra $\Delta H=1000G$. In Fig 8 we have grouped all spectra to make comparison.

The spectra are wide and asymmetric, which is typical for ferromagnetic resonance (FMR). The lines have Gaussian shape, also characteristic for FMR (Oleg *et al.*, 2007). This ferromagnetic resonance (FMR) is known to be anisotropic in layered compounds (Wei Ning *et al.*, 2009a); (Niang *et al.*, 1993).

More, for $2C_8CuCl_4$, 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 behaviour of coupled FM layers separated by nonmagnetic spacer layers (Wei Ning *et al.*, 2009a), and it is caused by the presence of relatively large local field (H_{local}) of the ferromagnetic domain.

Several papers have studied the ESR spectrum of this kind of perovskite layer compounds as a function of temperature and they have showed the existence of a conformational transition or an order-disorder transition of the $CuCl_4^{2-}$ matrix plane, which may correspond to the dynamic Jahn-Teller distortions (Lee *et al.*, 2009).

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