Chapter 1

GENERAL INTRODUCTION

Introduction

Organic compounds have structural diversity, ease of processing, efficient luminescence, good optical along with good electrical mobility and/or electrical behavior. Inorganic compounds have a distinct set of advantages, including mechanical and thermal stability, higher structural dimensionality along with interesting electrical and/or magnetic properties. Thus, organic-inorganic hybrid compounds (OIHCs) offer an important opportunity to combine useful properties from these two chemical areas (organic and inorganic) within a single molecule. One of the best strategies to make organic-inorganic hybrid compounds with multifunctional behavior is layered materials based on distortion of perovskite structure [1,2].

Materials which have crystal structure similar to calcium titanium oxide ($CaTiO_3$) called perovskite structure compounds [3]. The cubic AMX_3 perovskite structure (Figure 1.1) consists of an extended three-dimensional (3-D) network of corner-sharing MX_6 octahedra, where A = cation, X = halide and M = divalent metal. The larger A cations fill the 12-fold coordinated holes among the octahedra. For the 3-D perovskites the size of the A cation is limited by the size of the 3-D hole into which it must fit. For a perfectly packed perovskite structure the geometrically imposed condition for the A, M, and X ions to be in close contact is $(R_A + R_X) = t\sqrt{2}\,(R_M + R_X)$, where R_A, R_M, and R_X are the ionic radii for the corresponding ions and the tolerance factor must satisfy $t \approx 1$. Empirically it is found that $0.8 \leq t \leq 0.9$ for most cubic perovskites. Using $t = 1$ and essentially the largest values for R_M and R_X (*e.g.* R_{Pb} = 1.19, R_I = 2.20 Å), the limit on R_A is found to be approximately 2.6 Å. This calculation, tells us that the size of methyl ammonium or ammonium cation only will be useful for generating three dimensional continuous networked compounds.

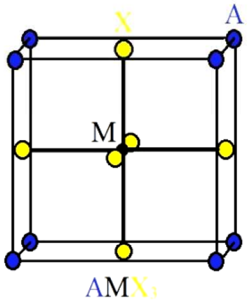

Figure 1.1 Structure of basic AMX_3 perovskite unit cell.

If one uses 'A cation' which is longer, then compounds with the molecular formula AMX_4 and A_2MX_4 [where A = organic ammonium cations (OACs), M = transition metal ion and X = halogen] can be obtained, which is well cited in literature [4]. Organic-inorganic perovskites are widely studied hybrid crystalline systems that exhibit interesting magnetic, optical and electrical properties [5,6,7,8]. We will concentrate more on A_2MX_4 class of compounds in this thesis.

In A_2MX_4 class of compounds, the inorganic component consists of more or less regular corner shared octahedral units. This extended MX_4^{2-} layer is exist as quasi two-dimensional (2-D) magnet, and alternating with OACs, bilayers (for monoammonium) or monolayer (for biammonium). The ammonium groups needs to be able to fit into the "holes" formed by terminal and bridging halogen within the distorted perovskite-sheets, without the rest of the molecule interfering with the sheets. That leads to extreme elongation of one semi-coordinate bond and allowing accommodation of OACs between the inorganic layers. That is why the structure of the MX_4 layers is characterized by two kinds of metal-halide distances equatorial (D_S) and axial (D_L) distances, a result of Jahn-Teller distortion. In these layered perovskites, Jahn-Teller elongated bonds of adjacent M^{2+} ions lie in the plane of the layer but are oriented at right angles to each other, thus defining an antiferrodistortive structure. The, OACs, are stabilized by the two distinct interactions:

(a) Hydrogen bonding to inorganic sheets at one or both end;
(b) van der Waals interactions amongst their tails.

The choice of OACs and hydrogen bonding scheme is important for determining the orientation and conformation of the organic molecule within the layered hybrid structure. For example when we take monofunctional OACs the inorganic layer of metal-halide is separated by bilayers, of organic part, and give staggered form. But when we take bifunctional OACs then inorganic layer of metal-halide is separated by monolayer, of organic part, and gives eclipsed form (Figure 1.2). In principle, the ammonium head(s) of the OACs can hydrogen bond to any of the eight halides (*i.e.* four bridging/four terminals) within the holes formed by the corner-sharing MX_6 octahedra (Figure 1.3). In practice, due to the geometric constraints of the ammonium group and the organic tail, the $N\text{-}H\cdots X$ interactions generally form either to two bridging halides and one terminal halide (bridging halide configuration) or to two terminal halides and one bridging halide (terminal halide configuration).

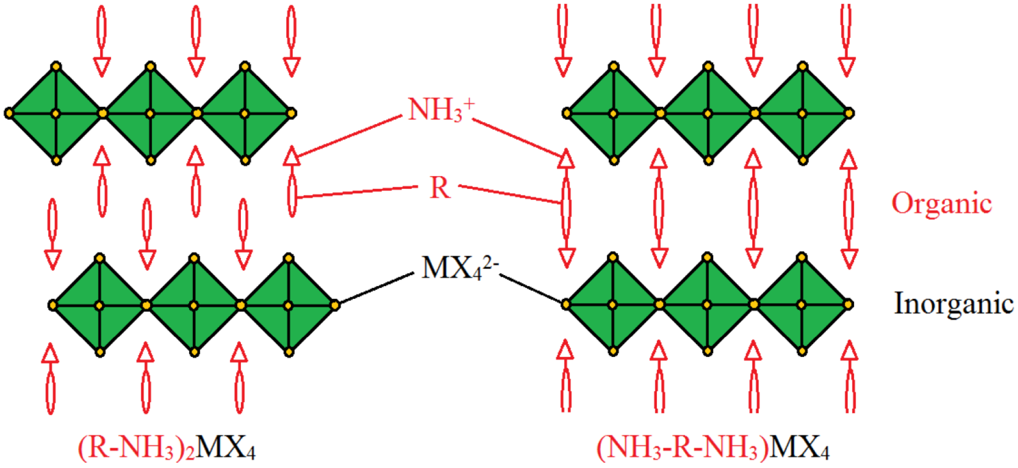

Figure 1.2 Schematic representation of single-layer perovskite with monoammonium ($R\text{-}NH_3^+$) (a) and biammonium ($^+NH_3\text{-}R\text{-}NH_3^+$) (b), organic cations.

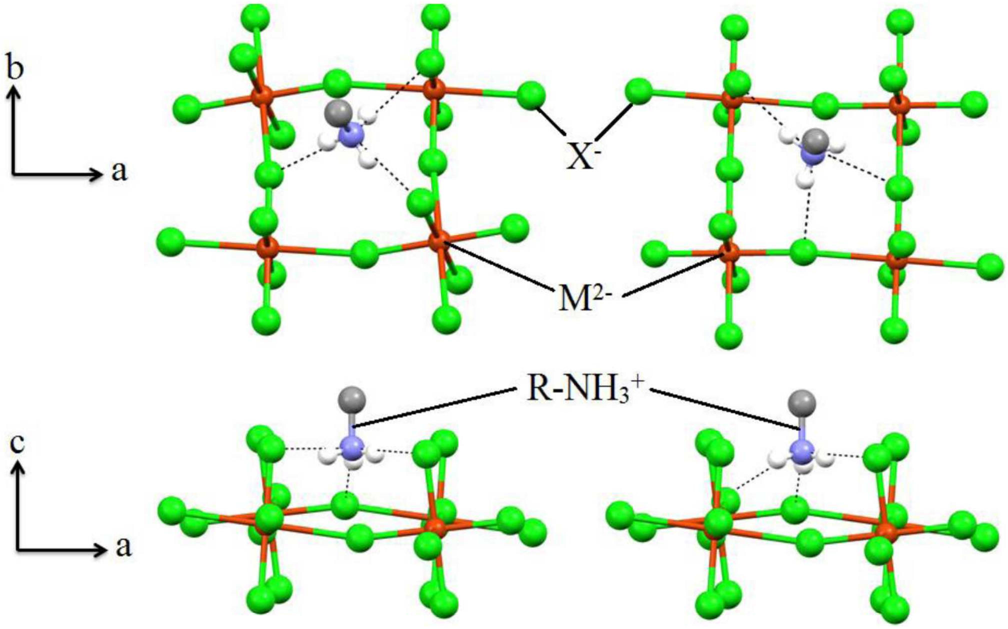

Figure 1.3 Two hydrogen bonding schemes observed in $(R\text{-}NH_3)_2MX_4$ and $(NH_3\text{-}R\text{-}NH_3)MX_4$ type structures: bridging halide configuration (a) and terminal halide configuration (b).

It is clear that the hydrogen bonding pattern of ammonium group with terminal halide, which always tilts the position of MX_4^{2-} along the axis, and bonding with bridging halide, always forcing the alternating layer halide atoms out of the plane, leading to decreases super exchange pathway through the two halides between interlayer metal. Therefore super exchange interaction through the two halides between interlayer metals normally decreases due to tilted position of MX_4^{2-}. The bridging halide bond angle seems to play an important role in controlling the magnetic coupling to be ferromagnetic or antiferromagnetic. Generally, bent M-X-M bond angle, smaller than 156º, is unfavourable for the ferromagnetic coupling between d_z^2 and d_{xz} of metal [9].

Furthermore, OACs not only separate the layer of metal-halide but it can also vary the distance between the inorganic sheet and properties of the compounds. Smaller size of OACs decreases the distance of inorganic sheet and larger size of OACs increases the distance of inorganic sheet. The type of magnetic order ranges from ferromagnetic to antiferromagnetic also depends on the organic component and transition metals that are used. The highest ordering temperatures are observed for the Fe (II) based OIHCs [10]. Moreover, the ordering temperatures do also depend on the organic component. They are highest when short biammonium, R-groups, are used. For example $(NH_3CH_2CH_2NH_3)CuBr_4$ shows long range ferromagnetic ordering below T_c = 72 K and the $(CH_3CH_2NH_3)_2CuBr_4$ below T_c = 11 K [11]. Thus by changing the OACs and/or metal ions we can get a variety of OIHCs with different properties [12,13]. These OIHCs are generally stable up to the decomposition point. In a few cases the hybrids melt before decomposition [14].

The crystal structures of (ammonium)$_2$CuCl$_4$ and (ethyl ammonium)$_2$CuCl$_4$ were reported by Willett *et. al.* [15,16]. The structure of (propyl ammonium)$_2$CuCl$_4$ has been determined by Barendregt and Schenk [17]. The possible mechanisms for magnetic exchange have been a major area of study for decades and numerous empirical and theoretical descriptions have been presented [18]. A variety of pathways are known to propagate the exchange, including single atoms or ions, such as halides, bridging between metal species [19]. Subsequently, Snively *et al.* discovered that magnetic exchange could propagate through non-bonding contacts between halide ions which attached to different metal ions, the pathway, M-X···X-M, described as a double halide bridge [20]. In their studies for $(NH_3CH_2CH_2NH_3)CuCl_4$ consisting of sheets of square planar $CuCl_4^{2-}$ ions linked into square layers by Cu-Cl-Cu bridges, they observed that the antiferromagnetic exchange between the layers.

Subsequent work by the same group with a series of alkyl biammonium salts clearly showed that the effect was not unique to $(NH_3CH_2CH_2NH_3)CuCl_4$ and that the strength of the exchange was a function of the distance between the halide ions, rather than the distance between the metal ions [21].

Banks *et al.* report detailed examination of the magnetic structure of anhydrous cupric chloride, $CuCl_2$. Anhydrous $CuCl_2$ shows one-dimensional antiferromagnetic behavior and long range antiferromagnetic ordering below a Neel temperature of 23.9 K [22]. The behavior of magnetic susceptibility of anhydrous chlorides at low temperature (LT) is described by the Starr *et al.* [23]. Thus, by 'incorporating' OACs one can 'tune' the structure of $CuCl_2$ and hence explore technologically important properties such as magnetism.

The structural and calorimetric investigations of the OIHCs showed existence of a large number of phases and phase transitions [24,25]. These phase transitions are due to OACs. By properly choosing OACs with ferroelectric and/or ferroelastic phases one can generate OIHCs with multifunctionality, along with the magnetism [26]. Recently Polyakov *et al.* have found ferromagnetic order, below 13 K, and ferroelectric order, below 340 K, in OIHCs, $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$ [2]. Thus, it is possible to make multifunctional compounds using this strategy, which a topic of this thesis.

In this thesis we describe the syntheses and characterization of OACSs (**Chapter 3**) and their complexes, OIHCs, (**Chapter 4 - 7**). Investigation deals with (a) synthesis, (b) characterization using spectroscopic techniques and single crystal and/or powder X-ray diffraction (XRD) studies (c) study of phase transitions using thermal investigations (d) magnetic measurements where ever possible.

The thesis is focused on exploring role of OACs on OIHCs. With this motive we have synthesized 'novel' OIHCs by using different OACSs and mainly $CuCl_2$. **Chapter 4** include use of monofunctional achiral OACSs. While, **Chapter 5** is devoted for chiral monoammonium and biammonium OACSs. **Chapter 6** and **7** uses different metal halides in the form of $CoCl_2$ and $MnCl_2$, respectively. These OIHCs are also studied for thermochromic behavior.

Mn(II) based layered compound showed promise of ‘adsorption-desorption’ for polar solvent molecules is documented in **Chapter 7**. During the process of crystals growth of these compounds, we came across novel route to synthesis of organic nitrate salt which is a topic of **Chapter 8**.

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