

High Pressure Raman Spectroscopic Studies of (*p*-chloroanilinium)₂CuCl₄

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Abstract: (*p*-chloroanilinium)₂CuCl₄ has a corner shared layered structure of CuCl₆⁴⁻ octahedra with *p*-chloroanilinium cation sandwiched between the layers. The CuCl₆ octahedra are irregular due to Jahn-Teller distortion. We report our high pressure Raman results on this compound in the present manuscript. Our results indicate significant changes in Raman spectra at ~ 3 GPa and ~ 8 GPa. The changes at 3 GPa can be attributed to a reduction in puckering of the CuCl₄²⁻ layer and the transition at 8 GPa, which also leads to a colour change of this sample to deep red, could be due to delocalization of the e_g electrons along with a reduction of the cooperative Jahn-Teller distortion in this layer. These changes were found to be reversible.

Keywords: organic-inorganic hybrid layered structures, high pressure, Raman spectroscopy.

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INTRODUCTION

In recent years, crystalline families of organic-inorganic hybrid compounds (OIHCs) having general formula A₂CuCl₄, (A: alkyl or aromatic ammonium cation) have gained a lot of importance for their potential as multifunctional materials [1-3]. These compounds crystallize with distorted octahedra of CuCl₆⁴⁻ in layers sandwiched between organic ammonium cation (A). The tetrahalocuprate complexes having different A's show varieties of phase transitions, mainly driven by (a) Jahn-Teller distortion (J-T) of Cu²⁺ ion and/or (b) combination of terminal and bridging type hydrogen bonding (H-bonding). The structure of CuCl₄²⁻ layer gets affected by J-T distortion resulting in two types of Cu-Cl distances, longer (D_L) and shorter (D_S) in addition to slight puckering in the layered structure. Antiferromagnetic insulating compound (*p*-chloroanilinium)₂CuCl₄ (**1**) shows two distinct types of NH⁺...Cl hydrogen bonding interactions one with a terminal Cl and the other one with a bridging Cl atom (Fig. 1), as revealed from single crystal X-ray diffraction studies [4]. In this class of compounds, the cation anion angles, cation-cation

distances and the hydrogen bond play a crucial role in their multifunctional behavior. Thus, to tune the interplay between lattice and electronic degrees of freedom and to explore the roles of J-T distortion and H-bonding towards high pressure phase transitions in compound (**1**), we carried out Raman spectroscopic studies upto ~ 25 GPa.

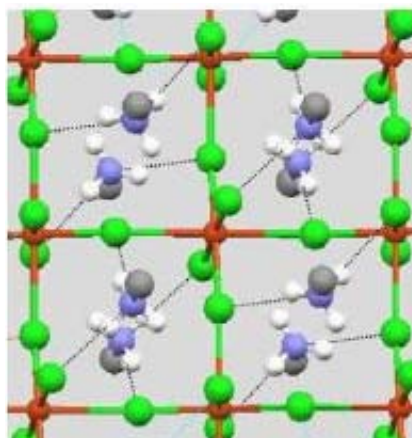


FIGURE 1. NH⁺...Cl hydrogen bonding interaction in (**1**)

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