

[MS28-P03] Unusual Structural Phenomena in the Reaction of Copper and Nickel Dihalides with NH_{3(g)} at Ambient Conditions.

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While many solid state reactions take place slowly at high temperatures (and in some cases high pressures), the reversible ammoniation – deammoniation of many metal halides is a process which occurs at near-ambient conditions. Given the potential of ammonia as a “clean” fuel, the facile NH₃ uptake and release in metal halides advocates the use of these compounds as solid state ammonia storage materials.[1,2] We present here work concerning the direct reaction between NiX₂ (X = Cl, Br, I) or CuX₂ (X = Cl, Br) and gaseous ammonia at ambient temperature and pressure. The reaction of NiX₂ with NH_{3(g)} produces the stoichiometric product [Ni(NH₃)₆]X₂ within one hour as nano-sized crystallites. Despite the ease of the ammonia sorption, it is noteworthy that the reaction is by no means topotactic. In fact, it demands a complete structural rearrangement from layered NiX₂ (CdCl₂ type, *R-3m*; e.g. with Ni–X distances of 243 pm for X = Cl)[3] to structures comprising isolated complex cations [Ni(NH₃)₆]²⁺ bound to halide anions (e.g. with Ni–X distances of 436 pm for X = Cl). Furthermore, NH₃ can be removed from [Ni(NH₃)₆]X₂ (cubic, *Fm-3m*) by simple thermal activation, which occurs in a two step process with NiX₂·2NH₃ (*Cmmm* for X = Cl, Br, I or *Pbam* for X = Br, I)[4] as an intermediate phase and finally yielding the original starting material, NiX₂. This reversible ammonia sorption coupled with a high gravimetric capacity (44 wt.-% NH₃ for X = Cl) places nickel halides among the most promising ammonia storage materials for use in mobile fuel cell applications. The case for copper amines is somewhat contrasting in that the structure of

copper complexes is mediated by the Jahn-Teller effect. As a result the hexammine exists as a (non-standard) *F4/mmm* structure with an elongated *c*-axis compared to the cubic Ni(NH₃)₆X₂ structure.[5] The reaction of NH₃ with CuX₂ (X = Cl, Br) to form the hexammines occurs readily at ambient temperature. Rietveld refinement against XRD data for the chloride revealed an ammonia deficit on the elongated axial sites leading to a composition of [Cu(NH₃)_{5.22(4)}]Cl₂. This ammonia deficit suggests that these amines should be defined as [CuL₄L_(2-x)]X₂ complexes.

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