Synthesis, Structure and NH₃ Sorption Properties of Mixed Mg₁₋ₓMnₓ(NH₃)₆Cl₂ Ammines

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Abstract: This paper describes the synthesis, crystal structure, and NH₃ sorption properties of Mg₁₋ₓMnₓ(NH₃)₆Cl₂ (x = 0–1) mixed metal halide ammines, with reversible NH₃ storage capacity in the temperature range 20–350 °C. The stoichiometry (x) dependent NH₃ desorption temperatures were monitored using in situ synchrotron radiation powder X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry. The thermal analyses reveal that the NH₃ release temperatures decrease in the mixed metal halide ammines in comparison to pure Mg(NH₃)₆Cl₂, approaching the values of Mn(NH₃)₆Cl₂. Desorption occurs in three steps of four, one and one NH₃ moles, with the corresponding activation energies of 54.8 kJ·mol⁻¹, 73.2 kJ·mol⁻¹ and 91.0 kJ·mol⁻¹ in Mg₀.₅Mn₀.₅(NH₃)₆Cl₂, which is significantly lower than the NH₃ release activation energies of Mg(NH₃)₆Cl₂ (Eₐ = 60.8 kJ·mol⁻¹, 74.8 kJ·mol⁻¹ and 91.8 kJ·mol⁻¹). This work shows that Mg₁₋ₓMnₓ(NH₃)₆Cl₂ (x = 0 to 1, y = 0 to 6) is stable within the investigated temperature range (20–350 °C) and also upon NH₃ cycling.

Keywords: metal chlorides; solid solution; mixed hexammines; ammonia storage; in situ powder X-ray diffraction

1. Introduction

Energy storage materials and methods have gained high interest to ensure the transition to carbon-free future. Hydrogen, as a high-density energy carrier alternative to fossil fuels, is one of the promising solutions for energy storage systems via solid storage of hydrogen [1–4]. Several studies have highlighted the potential of hydrogen-based energy systems [5–8].

Metal halide ammines have been studied as indirect hydrogen and ammonia storage materials [9–11]. Particularly Mg(NH₃)₆Cl₂ has received significant attention due to its high gravimetric NH₃ and H₂ capacity of 51.8 wt% and 9.2 wt%, respectively [12–17]. Mg(NH₃)₆Cl₂ crystallizes in the cubic space group Fm-3m with a K₂PtCl₄-structure type and a = 10.1899(4) Å [18]. NH₃ is thermally released in three steps at the temperatures of 142 °C (4 moles of NH₃), 230 °C (1 mole of NH₃) and 375 °C (1 mole of NH₃), respectively against an ammonia pressure of 1 bar [15]. The phase-formation and thermodynamic properties of Mg(NH₃)₆Cl₂, Mg(NH₃)₄Cl₂ and Mg(NH₃)Cl₂ have been thoroughly studied, and the high temperatures necessary to release the two last moles of NH₃ hampers the application of Mg(NH₃)₄Cl₂ as an effective energy storage system [19–22]. However, the desorption temperatures of NH₃ may be tailored toward lower NH₃ desorption temperatures via the formation of
solid solutions, e.g., mixed cation metal halide ammines. Mn(NH₃)₆Cl₂ also exhibits a high gravimetric capacity of ammonia (44.8 wt%), and is isostructural to Mg(NH₃)₆Cl₂ with a slightly larger unit cell parameter: \( a = 10.249(3) \, \AA \) [23]. Similar to Mg(NH₃)₆Cl₂, NH₃ is released from Mn(NH₃)₆Cl₂ in three steps with desorption temperatures of 80 °C, 180 °C, and 354 °C, respectively, and thus lower than the desorption temperatures of Mg(NH₃)₆Cl₂ [13,15]. However, only the sorption cyclability of the four first moles of NH₃ in Mn(NH₃)₆Cl₂ has been considered for ammonia storage applications, which is found to be reversible for at least 10 cycles [10].

The ammonia release temperatures are associated with the binding energy of NH₃ with its surrounding ions, which depends on the elements and crystal structures of the metal halides as elucidated in a recent study [24]. Formation of solid solutions has been suggested as an approach to tailor the NH₃ desorption temperatures and kinetics [25–27]. The NH₃ binding energies were investigated in SrCl₂-CaCl₂ solid solutions, and they were found to be intermediate those of the two precursors [28]. This led to studies on solid solutions of Sr₁₋ₓBaₓ(NH₃)₆Cl₂ and Sr₁₋ₓCaₓ(NH₃)₆Cl₂, and their respective NH₃ release properties. Sr₁₋ₓBaₓ(NH₃)₆Cl₂ solid solutions showed that varying the relative ratios of metal allowed tuning of the desorption temperature of ammonia. The gradual effect on the ammonia release temperature was observed with the optimal mixing condition of 37.5 % of BaCl₂ in Sr₁₋ₓBaₓ(NH₃)₆Cl₂ showing the full release of ammonia at temperature \( T < 100 \, \text{°C} \) of the final mixed metal halide ammine [25]. Similarly, it was demonstrated for Sr₁₋ₓCaₓCl₂ solid solutions and the corresponding Sr₁₋ₓCaₓ(NH₃)₆Cl₂ ammines that the NH₃ absorption and desorption properties could be enhanced by tuning the mixing ratio [26,27]. Additionally, the ammonia storage properties and crystal structures of the CaCl₂-CaBr₂, SrCl₂-SrBr₂ and SrCl₂-SrI₂ solid solutions have also been investigated, and intermediate ammonia storage properties of the mixed anion metal halides were observed [28–30]. These studies show the possibility of forming mixed metal halides with tunable ammonia sorption properties. Solid solutions of borohydride-based ammines have also been investigated as potential solid-state hydrogen storage materials. The solid solutions of Mgₓ₁₋ₓMnₓ(BH₄)₂·6NH₃ and structural similarities of Mg(BH₄)₂ and Mn(BH₄)₂ and their corresponding ammines were studied [31,32]. Similar to the present study it revealed temperature changes for ammonia release when compared to those of the pristine samples.

Inspired by the structural similarities between Mg(NH₃)₆Cl₂ and Mn(NH₃)₆Cl₂, this work addresses an investigation of solid solutions of Mgₓ₁₋ₓMnₓ(NH₃)₆Cl₂. Here we show the synthesis of these novel series of mixed metal halide ammines with tunable properties for the NH₃ desorption. We present the Mgₓ₁₋ₓMnₓ(NH₃)₆Cl₂ (\( x = 0.025, 0.05, 0.1, 0.3 \) and 0.5) solid solutions obtained by mechanical mixing of MgCl₂ and MnCl₂, followed by annealing and subsequent exposure to anhydrous NH₃ gas. The mixed metal halide ammines were systematically investigated with in situ powder X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and volumetric Sieverts techniques. The thermally induced ammonia release for the mixed metal halide ammines is discussed: three NH₃ desorption events are observed and the crystal structures of the intermediate ammine phases are identified and structurally characterized. The kinetics, absorption, and desorption properties of NH₃ are studied. The results presented in this work show that by changing the relative Mg/Mn ratio the NH₃ sorption properties can be tuned and optimized depending on the application.

2. Materials and Methods

2.1. Sample Preparation

Anhydrous MgCl₂ and MnCl₂ powders with a purity of 99.999% were purchased from Alfa Aesar and Sigma-Aldrich, respectively. Mg₁₋ₓMnₓCl₂ solid solutions (\( x = 0.025, 0.05, 0.1, 0.3 \) and 0.5) were obtained using a SPEX SamplePrep 8000D Dual Mixer high-energy ball mill. The powders were placed in a 25 mL hardened steel vial together with hardened steel balls (10 mm diameter) in a ball-to-powder mass ratio of 16:1 and sealed in an Ar-filled glove box (<1 ppm of O₂ and H₂O). The ball milling program was for one hour.
The as-milled powders were annealed to increase the crystallinity. Batches of ~0.5 g of the as-milled powders were sealed in a stainless-steel cylinder inside a glove box, and subsequently heated to 350 °C with a heating rate of 1 °C·sec⁻¹ and kept isothermal at 350 °C for 24 h. These samples are denoted “as-synthesized” samples. Subsequently, the as-synthesized samples were placed in a high temperature stainless-steel cylinder and connected to an in-house built Sieverts apparatus. The samples were then exposed to an NH₃ gas pressure of 2.5 bar at room temperature (RT) for at least 3 h. MnCl₂ was ammoniated for 3 h at T = −20 °C and 1 bar NH₃. It was then stored in a glovebox freezer at −34 °C prior to the experiments, due to instability of the Mn(NH₃)₆Cl₂ at ambient conditions. These samples are denoted “ammoniated” samples.

2.2. Thermal Analysis

Combined thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the monometallic and mixed metal halide ammines were measured using a Netzsch STA 449 F3 Jupiter apparatus. The powders (~40 mg) were placed in an alumina crucible with a pierced lid under protective Ar atmosphere in a glove box. The alumina crucibles were shortly exposed to air (ca. 1 min) during mounting in the TGA-DSC apparatus. The powders were heated from RT to 455 °C with a heating rate of 5 °C·min⁻¹ in an Ar flow of 50 mL·min⁻¹. Additionally, the batches of Mg(NH₃)₆Cl₂, Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ and Mn(NH₃)₆Cl₂ powder (~10 mg) were measured at six different heating rates of 1, 2, 5, 10, 20 and 40 °C·min⁻¹ for Kissinger analyses [33].

2.3. Synchrotron Radiation Powder X-ray Diffraction

High resolution in situ temperature varied synchrotron radiation powder X-ray diffraction (SR-PXD) experiments were performed at the Swiss Light Source (SLS), Switzerland and at the Diamond Light Source, Oxford, UK. At SLS, data were obtained at the Material Science powder diffraction beamline X04SA [34] using a monochromatic beam in Debye–Scherrer geometry with a Mythen microstrip detector with a wavelength of λ = 0.709396 Å. At Diamond, data were obtained at the I11 beamline [35] using a wide angle position sensitive detector and a wavelength of λ = 0.82646 Å. In both cases, the samples were loaded into 0.5 mm borosilicate glass capillaries in an Ar-filled glove box (<1 ppm of O₂ and H₂O), sealed with grease and rotated during data acquisition. The samples were heated at 5 °C·min⁻¹ from RT to 500 °C using a heat blower. The temperature was calibrated using a NaCl standard prior to diffraction runs [36]. The powder diffraction data were normalized and reduced, then modeled and refined according to the Rietveld method as implemented in the TOPAS software [37].

The structural models of Mg(NH₃)₆Cl₂, Mg(NH₃)₂Cl₂ and Ni(NH₃)Cl₂ were used as starting points for Rietveld refinements of the hexammine, diammine, and monoammine phases of the mixed metal halide ammines, respectively. The diffraction peaks were modeled by a Thompson-Cox-Hastings pseudo-Voigt function. The scale factor, zero-shift, unit cell parameters, atomic positions and background were refined. The N-H and H-H distances were restrained using soft restraints function during the Rietveld refinements.

2.4. Sorption Kinetics and Cycling

The two pristine materials MgCl₂ and MnCl₂ and the mixed metal halides Mg₀.₉Mn₀.₁Cl₂ and Mg₀.₅Mn₀.₅Cl₂ (m = 0.1 g) were studied with regards to their NH₃ absorption and desorption kinetics. The absorption process was conducted under 2.5 bar of NH₃ at RT, while the desorption reaction was achieved by heating the samples up to 350 °C with a heating rate of 2 °C·min⁻¹ under 1 bar of NH₃. A calibrated volume consisting of a reference volume (V = 482.9 mL) and a sample chamber
(\(V = 23.25 \text{ mL}\)) was used during the experiments and the moles of absorbed and desorbed \(\text{NH}_3\) were calculated according ideal gas law using the formula below:

\[
\Delta n = \frac{\Delta P V}{RT},
\]

where \(\Delta n\) is the number of \(\text{NH}_3\) moles absorbed or desorbed, \(\Delta P\) is the pressure change in the system occurring due to absorption or desorption of \(\text{NH}_3\), \(V\) is the volume, \(R\) is the gas constant and \(T\) is the temperature. In all cases, the number of absorbed or desorbed moles was normalized by the molar weight of the corresponding compound. Each \(\text{NH}_3\) desorption was followed by evacuation of the released \(\text{NH}_3\) from the cylinder to avoid reabsorption of the \(\text{NH}_3\) gas during cooling to RT. The \(\text{NH}_3\) desorption/absorption was cycled four times for each sample.

3. Results and Discussion

3.1. Structural Characterization of the As-Synthesized and Ammoniated Samples at RT

SR-PXD data were collected for the pristine samples, MgCl\(_2\) and MnCl\(_2\), and for the as-synthesized Mg\(_{1-x}\)Mn\(_x\)Cl\(_2\) \((x = 0, 0.025, 0.05, 0.1, 0.3, 0.5 \text{ and } 1)\) samples. The unit cell parameters are presented in Table S1 in the Supporting Information. The diffraction patterns in Figure 1 confirm the formation of a MgCl\(_2\)-MnCl\(_2\) solid solutions, as only a single set of Bragg diffraction peaks belonging to Mg\(_{1-x}\)Mn\(_x\)Cl\(_2\) are observed, which is positioned in between that of MgCl\(_2\) and MnCl\(_2\). MgCl\(_2\) and MnCl\(_2\) are isostructural and crystallize in the trigonal CdCl\(_2\)-type structure with space group symmetry \(R\)-3\(m\) [38,39].

![Figure 1: SR-PXD patterns of Mg\(_{1-x}\)Mn\(_x\)Cl\(_2\) \((x = 0, 0.025, 0.05, 0.1, 0.3, 0.5 \text{ and } 1)\) obtained at RT. All peaks belong to the same CdCl\(_2\)-type phase.](image)

The MgCl\(_2\)-MnCl\(_2\) solid solution follows Vegard’s law approximately, as the volume is a function of the relative content of cations and in between that of the two pristine compounds, see Figure 2a. The larger ionic radius of Mn\(^{2+}\) (0.83 Å) as compared to Mg\(^{2+}\) (0.72 Å) results in an increase of the unit cell volume [40]. The deviation from Vegard’s law might be due to a localized strain field caused by difference in Mg and Mn sizes, as well as to the different outer electronic structures of the mixing components (Mg and Mn in our case) [41]. The solid solution is maintained after ammoniation and the deviation from Vegard’s law remains. It should be noted that a negative deviation from Vegard’s law should be also expected if contamination from iron contained in the milling media results in the form...
Mg\textsubscript{1-x-y}Mn\textsubscript{x}Fe\textsubscript{y}Cl\textsubscript{2}. Indeed, the ionic radius for Fe\textsuperscript{2+} (0.63 Å) is smaller than the radii of both Mg\textsuperscript{2+} and Mn\textsuperscript{2+} [40]. However, even if slight contaminations from the milling media and metallic Fe cannot be ruled out, they are expected to be very limited due to the relatively short milling time (1 h) used in this work. Additionally, metallic Fe must be oxidized to Fe\textsuperscript{2+} in order to substitute Mg\textsuperscript{2+}/Mn\textsuperscript{2+} and form Mg\textsubscript{1-x-y}Mn\textsubscript{x}Fe\textsubscript{y}Cl\textsubscript{2}. Therefore, it is most likely that the deviation from Vegard’s law observed here might be due to the different outer electronic structures of Mg and Mn. Rietveld refinement and structural characterization of the ammoniated samples confirm the cubic Mg(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} structure for all mixed cation hexammines (Supporting Information, Figure S1–S5). Figure 2b illustrate Vegard’s law (blue dotted line) for Mg\textsubscript{1-x}Mn\textsubscript{x}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2}. Surprisingly, the unit cell volume for samples with x < 0.05 are lower than that of Mg(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2}.

![Figure 2](image-url)

Figure 2. Unit cell volumes (V) of (a) Mg\textsubscript{1-x}Mn\textsubscript{x}Cl\textsubscript{2} and (b) Mg\textsubscript{1-x}Mn\textsubscript{x}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} at RT divided by the number of formula units (Z), plotted as a function of the Mn amount in the formula unit (x = 0, 0.025, 0.05, 0.1, 0.3, 0.5 and 1). The blue dotted line represents Vegard’s law. The standard deviations are within the data points.

The atomic positions of the monometallic and mixed hexammines obtained from Rietveld refinement are presented in Table 1. During the Rietveld refinements Mg and Cl atoms are fixed in the 4a and 8c positions, respectively, while the x-coordinate of N atom (24e position) is refined. N-H and H-H distances are restrained at ~1.107 Å and ~1.345 Å, respectively. Mg-N and Mn-N bond distances for the monometallic hexammines are 2.1564(7) Å and 2.2100(14) Å and thus similar to those previously reported values (2.197(5) and 2.270(15), respectively). Mg\textsubscript{1-x}Mn\textsubscript{x}-N bond distances are intermediate between the Mg-N and Mn-N bond distances. The unit cell parameters of Mg\textsubscript{1-x}Mn\textsubscript{x}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} and Mn(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} obtained in this study are a = 10.19579(9) Å and a = 10.26017(2) Å which correspond to the values reported previously [18,23]. The unit cell parameters for Mg\textsubscript{1-x}Mn\textsubscript{x}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} are also intermediate between the unit cell parameters of the monometallic hexammines.

![Table 1](image-url)

| Compound                  | N (x-coordinate) |
|---------------------------|------------------|
| Mg(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.21150(7), 0, 0 |
| Mg\textsubscript{0.975}Mn\textsubscript{0.025}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.21268(15), 0, 0 |
| Mg\textsubscript{0.95}Mn\textsubscript{0.05}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.2132(2), 0, 0 |
| Mg\textsubscript{0.9}Mn\textsubscript{0.1}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.21563(8), 0, 0 |
| Mg\textsubscript{0.7}Mn\textsubscript{0.3}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.21269(9), 0, 0 |
| Mg\textsubscript{0.5}Mn\textsubscript{0.5}(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.21267(10), 0, 0 |
| Mn(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} | 0.21540(14), 0, 0 |

* The data are obtained at RT.
3.2. Thermal Analysis

Figure 3 shows the TGA-DSC measurements performed on Mg(NH3)6Cl2, Mn(NH3)6Cl2 and Mg0.5Mn0.5(NH3)6Cl2. The DSC measurements for the other mixed amines are shown in the Supporting Information (Figure S6). All the hexamine compounds are relatively stable at RT, except for Mn(NH3)6Cl2, which slowly releases NH3 in the glove box at RT. Thus, Mn(NH3)6Cl2 was kept at T = −34 °C in a glovebox freezer prior to the TGA-DSC measurements.

TGA-DSC data shows the desorption process of the monometallic and mixed chloride amines which consists of three events. With a heating rate of 5 °C min⁻¹, the onset temperatures of the initial ammonia desorption of 4 NH3 moles from Mg(NH3)6Cl2 and Mn(NH3)6Cl2 are observed at 121 °C and 79 °C, respectively. For the solid solution Mg0.5Mn0.5(NH3)6Cl2, the onset temperature for the first desorption is 116 °C. The onset temperature for the next NH3 release is at 179 °C for Mg0.5Mn0.5(NH3)2Cl2, significantly lower as compared to 211 °C in Mg(NH3)2Cl2 and similar to 179 °C in Mn(NH3)2Cl2. The onset temperature of the last NH3 desorption of Mg0.5Mn0.5(NH3)2Cl2 is 276 °C, which is lower than the last desorption event onset temperature of Mg(NH3)2Cl2 ~ 289 °C. Mn(NH3)Cl2 starts desorbing the last mole of NH3 at 257 °C.

Each NH3 desorption step is followed by mass loss. In the first desorption step, 4 NH3 moles are released and Mg0.5Mn0.5(NH3)6Cl2 experience a 30.2% mass loss, while the next two desorption events reduce the mass of the sample by 8.3% and 8.1%, respectively. The mass loss ratio 4:1:1 of the monometallic and mixed hexamines (Supporting Information, Table S2) corresponds to the moles of NH3 desorbed in each desorption event, i.e., four moles of NH3 released in the first desorption step, and 1 mole of NH3 released in the second and third step, respectively, and agrees well with the theoretical weight loss expected from the NH3 desorption. The gravimetric NH3 capacities for the monometallic and the mixed cation hexamines are presented in Table S3. SR-PXD data measured of Mg1−xMnx(NH3)6Cl2, (x = 0, 0.025, 0.05, 0.1, 0.3 and 0.5) after the TGA-DSC measurements confirm the reformation of Mg1−xMnxCl2 after full NH3 release, thus confirming the stability of the solid solution (Supporting Information, Figure S7).

Kissinger analysis was performed on the DSC heat flow signals for the three desorption events measured for Mg(NH3)6Cl2, Mn(NH3)6Cl2 and Mg0.5Mn0.5(NH3)6Cl2 to determine the activation energy and investigate their NH3 desorption kinetics. Kissinger plots for the three endothermic events with the release of 4, 1 and 1 moles of NH3 are shown in Figure 4a–c. The corresponding activation energies were calculated for each desorption event and are presented in Figure 4d–f. The activation energy of the first four moles of NH3 desorption from Mg0.5Mn0.5(NH3)6Cl2 is 54.8 kJ mol⁻¹, which is approximately in between that of Mg(NH3)6Cl2 (Ea = 60.8 kJ mol⁻¹) and Mn(NH3)6Cl2...
(Eₐ = 43.5 kJ·mol⁻¹). For the second NH₃ desorption step, the activation energy for Mg₀.₅Mn₀.₅(NH₃)₂Cl₂ is 73.2 kJ·mol⁻¹, in between that of Mg(NH₃)₂Cl₂ (Eₐ = 74.8 kJ·mol⁻¹) and Mn(NH₃)₂Cl₂ (Eₐ = 67.7 kJ·mol⁻¹). The final desorption event of Mg₀.₅Mn₀.₅(NH₃)₂Cl₂ has an activation energy of 91.0 kJ·mol⁻¹, as compared to Mg(NH₃)₂Cl₂ (Eₐ = 91.8 kJ·mol⁻¹) and Mn(NH₃)₂Cl₂ (Eₐ = 90.9 kJ·mol⁻¹).

The activation energies for Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ in all three desorption events are significantly lower as compared to monometallic Mg(NH₃)₆Cl₂. Therefore, by obtaining the mixed metal halide ammines, it is possible to tailor the desorption temperature and kinetics of the mixed metal halide ammines compared to the monometallic halide ammines.

3.3. In Situ SR-PXD

The in situ SR-PXD data for Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ in the temperature range RT to 402 °C, with a heating rate of 5 °C·min⁻¹, are shown in Figure 5a, while Figure 5b shows diffraction patterns at selected temperatures for each of the ammoniated compounds observed during heating. Rietveld refinements of the mixed metal hexammines are presented in the supporting material (Figures S1-S5). The in situ SR-PXD data from RT for monometallic Mg(NH₃)₆Cl₂ is shown in the supporting material (Figure S6). SR-PXD data at RT contain Bragg peaks from Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ (97.6(6) wt%) and Mg₀.₅Mn₀.₅(NH₃)₂Cl₂ (2.4(5) wt%). Upon heating, the Bragg peaks corresponding to Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ disappear between 115 and 125 °C, while peaks corresponding to...
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In situ SR-PXD data for Mn(NH₃)₆Cl₂ in the temperature range RT to 406 °C, with a heating rate of 5 °C min⁻¹ confirms the presence of such intermediate phase at 307 °C (Figure S9). However, due to the fast heating rate and, therefore, dominant peaks from Mn(NH₃)Cl₂ and MnCl₂ phases in the diffraction pattern, it was challenging to index it and extract the unit cell parameters for Mn(NH₃)₁.₅Cl₂. The same applies for the diffraction pattern of possible Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ phase at 328 °C from the in situ data for Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ (Figure 5), where the dominant diffraction peaks from Mg₀.₅Mn₀.₅(NH₃)Cl₂ make the indexing challenging. Observation of these intermediate diffraction patterns suggests that the transition of Mn(NH₃)Cl₂ to MnCl₂ and Mg₀.₅Mn₀.₅(NH₃)Cl₂ to Mg₀.₅Mn₀.₅Cl₂, which was described as non-stoichiometric process [42], in our study undergoes by stoichiometric NH₃ releases of δ moles.

![Figure 5](image_url)  
*Figure 5. (a) In situ SR-PXD of Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ measured from RT to 402 °C with a heating rate of 5 °C min⁻¹ and λ = 0.82646 Å and (b) SR-PXD data at specific temperatures.*

The NH₃ desorption temperatures are decreased significantly for Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ as compared to monometallic Mg(NH₃)₆Cl₂ (Figure S8), confirming the results from TGA-DSC analysis. The first NH₃ desorption step of 4NH₃ moles and transformation from Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ to Mg₀.₅Mn₀.₅(NH₃)₂Cl₂ (T = 125 °C) is 20 °C lower than observed for Mg(NH₃)₆Cl₂ (T = 146 °C). All NH₃ is desorbed from Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ at T = 337 °C, significantly lower than reported for Mg(NH₃)₂Cl₂ (T = 375 °C) [15]. The first desorption step of Mg(NH₃)₆Cl₂ at 146 °C is similar to the temperature reported in the literature (T = 142 °C) [15].

Rietveld refinements of the hexa-, di-, monoammine and chloride are shown in Figure 6, and Table 2 summarizes their structural information.
with each Mg

in the structure, resulting in a marked di
the monoammine phase (see Figure 6c), indicating the presence of structural disorder or stacking faults.

Figure 6. Rietveld refinements of the SR-PXD data for (a) Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$ at RT (R$_{wp}$ = 1.48%), (b) Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ at 214 °C (R$_{wp}$ = 3.17%), (c) Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ at 280 °C (R$_{wp}$ = 5.02%), and (d) Mg$_{0.5}$Mn$_{0.5}$Cl$_2$ at 402 °C (R$_{wp}$ = 3.19%); showing the experimental (black circles), calculated (solid green line) and the difference plot (solid black line). The vertical ticks mark the Bragg peak positions for the corresponding compounds.

Rietveld refinement of Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$ at RT is performed using the structural model of Mg(NH$_3$)$_6$Cl$_2$ (Figure 6a). Two phases are present in the sample, which are identified as Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$ and Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ with the refined phase fractions to 97.6(6) wt% and 2.4(5) wt%, respectively, which might be resulted from partial NH$_3$ release at RT. Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$ crystallizes in a cubic unit cell, $a = 0.82646$ Å. In (a) vertical ticks mark Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$ (97.6(6) wt%, black) and Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ (2.4(5) wt%, red).

Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ was refined using the Mg(NH$_3$)$_2$Cl$_2$ structure as a starting point. Figure 6b shows the Rietveld refinement of the fully desorbed Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ at 214 °C. For the diammine Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ (2.4(5) wt%, red).

The monoammine Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_2$Cl$_2$ is isostuctural to Ni(NH$_3$)$_2$Cl$_2$, which crystallizes in a monoclinic unit cell with space group $I2/m$ [44] where each Cl atom is shared by three Mg$_{0.5}$Mn$_{0.5}$ atoms in edge-sharing double octahedral chains. Both broad and narrow diffraction peaks are observed for the monoammine phase (see Figure 6c), indicating the presence of structural disorder or stacking faults in the structure, resulting in a marked difference between the experimental and calculated patterns.

The Rietveld refinement of the fully desorbed Mg$_{0.5}$Mn$_{0.5}$Cl$_2$ at 402 °C is shown in Figure 6d. Mg$_{0.5}$Mn$_{0.5}$Cl$_2$ structure, space group $R-3m$, is formed by the octahedra of Cl atoms with central Mg$_{0.5}$Mn$_{0.5}$ atoms sharing half of their edges, and thus resulting in layers of Mg$_{0.5}$Mn$_{0.5}$Cl$_2$.
was calculated. For Mg with the lower and higher Mn contents (Mg
MnCl₂), which corresponds to a pressure drop of only ∆P = 0.33 bar and the final pressures at the end of absorption were 2.21 and 2.22 bar for MgCl₂ and Mg₀.₅Mn₀.₅Cl₂, respectively. MnCl₂ only absorbed 5.5 moles of NH₃, which corresponds to a pressure drop of only ∆P = 0.29 bar reaching a final pressure p = 2.23 bar. This indicated that not all the MnCl₂ powder had reacted with NH₃, despite the still relatively high value of the final pressure of absorption. Indeed, due to the large volume expansion of the metal chloride during ammonia absorption, some clogging may occur and prevent ammonia from reaching all the salt crystals [16]. On the other, it cannot be excluded that that the absorption reaction stops because the equilibrium pressure for Mn(NH₃)₂Cl₂ at RT is higher than the final pressure reached during absorption (p = 2.23 bar). A more detailed thermodynamic study using pressure-composition-isotherms is needed to clarify this in detail. MgCl₂ absorbed 6 moles of NH₃ in less than 1000 s, while Mg₀.₅Mn₀.₅Cl₂ absorbed 6 moles of NH₃ in 6000 s. Similarly, the NH₃ absorption rate for the pristine halides are very different: Four moles of NH₃ is absorbed in MgCl₂ in about 200 s, while it took about 800 s to absorb the similar amount of NH₃ in MnCl₂. The rate of absorption for Mg₀.₅Mn₀.₅Cl₂ is similar to that of MnCl₂, indicating that Mn plays a predominant role for governing the kinetics of the hexamine formation.

The NH₃ desorption processes during cycling were carried out upon heating with a constant heating rate of 2 °C-min⁻¹ from RT to 350 °C under an initial NH₃ pressure of 1 bar, see Figure 8. The moles of desorbed NH₃ were calculated using Equation (1) and the pressure increase, ∆P = 0.32 bar, due to NH₃ release. The three desorption steps of NH₃ were observed as a pressure increase and ∆n was calculated. For Mg₀.₅Mn₀.₅(NH₃)₂Cl₂, the first 4 moles of NH₃ starts desorbing at around 100 °C and are fully released at 166 °C. The resulting Mg₀.₅Mn₀.₅(NH₃)₂Cl₂ desorbs one mole of NH₃ in the temperature range from 240 °C to 260 °C, forming Mg₀.₅Mn₀.₅(NH₃)Cl₂. The final NH₃ desorption step occurs above 300 °C. However, the transformation from monoammine to fully desorbed mixed metal chloride, Mg₀.₅Mn₀.₅Cl₂, does not proceed via a single step as for the previous desorption. Instead it undergoes through two discrete steps, consistent with the observations of a different crystalline phase in the in situ SR-PXD experiments.

### 3.4. NH₃ Cycling and Kinetics

Studies of the NH₃ sorption kinetics and cyclability of the pristine and mixed metal halides with the lower and higher Mn contents (Mg₀.₉Mn₀.₁Cl₂ and Mg₀.₅Mn₀.₅Cl₂) were performed using a Sieverts apparatus. The results from the desorption cycles performed on Mg₀.₉Mn₀.₁(NH₃)₆Cl₂ are presented in the supporting information (Figure S10). The fifth NH₃ absorption process (after four cycles) of pristine MgCl₂, MnCl₂ and Mg₀.₅Mn₀.₅Cl₂ are presented in Figure 7. For absorption, the applied NH₃ gas pressure was ~2.5 bar and the processes were conducted at RT. The moles of absorbed NH₃ were calculated (see Equation (1)), where ∆n is calculated from the pressure drop, ∆P, occurring during NH₃ absorption. The observed pressure drop was ∆P = 0.33 bar and the final pressures at the end of absorption were 2.21 and 2.22 bar for MgCl₂ and Mg₀.₅Mn₀.₅Cl₂, respectively.

| Chemical Formula | Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ | Mg₀.₅Mn₀.₅(NH₃)₂Cl₂ | Mg₀.₅Mn₀.₅(NH₃)Cl₂ | Mg₀.₅Mn₀.₅Cl₂ |
|------------------|---------------------|---------------------|---------------------|----------------|
| T (°C)           | RT                  | 214                 | 280                 | 402            |
| Crystal system   | Cubic               | Orthorhombic        | Monoclinic          | Trigonal *     |
| Space group      | Fm-3m               | Cmmm                | 12/m                | K-3m           |
| a (Å)            | 10.22037(8)         | 8.258(5)            | 15.575(1)           | 3.69494(3) Å  |
| b (Å)            | -                   | 8.290(4)            | 3.756(1)            | -              |
| c (Å)            | -                   | 3.812(2)            | 14.453(1)           | 17.8698(4)     |
| β (°)            | -                   | -                   | 106.55(3)           | -              |
| V (Å³)           | 1067.58(3)          | 261.0(2)            | 810.6(9)            | 211.28(6)      |
| Z                | 4                   | 2                   | 8                   | 3              |

* Hexagonal parameters are used in this work.
This indicates that physical behavior to be similar to that of Mn(NH₃)₆Cl₂. In our study, we observe two separate steps, and from the number of desorbed NH₃ moles calculated from ΔP in Sieverts studies, δ seems to be equal to 0.5. Furthermore, the NH₃ desorption studies of Mg₀.₉Mn₀.₁(NH₃)₆Cl₂ (Figure S10) suggest that this phenomenon does not occur in Mg₁₋ₓMnₓ(NH₃)₆Cl₂ with low Mn content, as the last decomposition step occurs as a single event. This indicates that sufficiently high amount of Mn in Mg₁₋ₓMnₓ(NH₃)₆Cl₂ results in a change in the physical behavior to be similar to that of Mn(NH₃)₆Cl₂.

These results suggest that by changing the relative Mg:Mn ratio in Mg₁₋ₓMnₓ(NH₃)₆Cl₂ the NH₃ sorption properties can be tuned and optimized. For instance, substituting Mg in Mn(NH₃)₆Cl₂ increases its stability, avoiding NH₃ desorption at RT. Furthermore, due to the low weight of Mg, the gravimetric capacity increases, with increasing Mg content. Finally, increasing the relative content of magnesium can be beneficial if cost reduction is desirable.

A thorough investigation of the NH₃ desorption reaction enthalpies is planned for further thermodynamic studies of the Mg₁₋ₓMnₓ(NH₃)₆Cl₂ hexammines by applying pressure composition isotherm (PCI) studies.

Figure 7. NH₃ absorption processes of Mg(NH₃)₆Cl₂ (blue), Mg₀.₅Mn₀.₅(NH₃)₆Cl₂ (yellow) and Mn(NH₃)₆Cl₂ (purple).

Figure 8. A series of NH₃ desorption from Mg₀.₅Mn₀.₅(NH₃)₆Cl₂. The four cycles confirm the stability and cyclability of the mixed metal halide after several ab/desorption cycles.

For some hexammines, M(NH₃)₆Cl₂ (M = Mg, Ni), the desorption consists of three events [13]. In contrast, Mn(NH₃)₆Cl₂ was reported to undergo non-stoichiometric NH₃ release in the last desorption step [13,42]. In our study, we observe two separate steps, and from the number of desorbed NH₃ moles calculated from ΔP in Sieverts studies, δ seems to be equal to 0.5. Furthermore, the NH₃ desorption studies of Mg₀.₉Mn₀.₁(NH₃)₆Cl₂ (Figure S10) suggest that this phenomenon does not occur in Mg₁₋ₓMnₓ(NH₃)₆Cl₂ with low Mn content, as the last decomposition step occurs as a single event. This indicates that sufficiently high amount of Mn in Mg₁₋ₓMnₓ(NH₃)₆Cl₂ results in a change in the physical behavior to be similar to that of Mn(NH₃)₆Cl₂.

These results suggest that by changing the relative Mg:Mn ratio in Mg₁₋ₓMnₓ(NH₃)₆Cl₂ the NH₃ sorption properties can be tuned and optimized. For instance, substituting Mg in Mn(NH₃)₆Cl₂ increases its stability, avoiding NH₃ desorption at RT. Furthermore, due to the low weight of Mg, the gravimetric capacity increases, with increasing Mg content. Finally, increasing the relative content of magnesium can be beneficial if cost reduction is desirable.

A thorough investigation of the NH₃ desorption reaction enthalpies is planned for further thermodynamic studies of the Mg₁₋ₓMnₓ(NH₃)₆Cl₂ hexammines by applying pressure composition isotherm (PCI) studies.
4. Conclusions

A series of novel mixed metal halide ammines, Mg$_{1-x}$Mn$_x$(NH$_3$)$_6$Cl$_2$, with a usable ammonia capacity in the temperature range 20–350 °C were synthesized and characterized. The crystal structures of the different ammine phases are identified and investigated by in situ SR-PXD. All Mg$_{1-x}$Mn$_x$(NH$_3$)$_6$Cl$_2$ solid solutions crystallize in a cubic unit cell with space group symmetry Fm-3m and unit cell parameters intermediate that of the two monometallic materials, Mg(NH$_3$)$_6$Cl$_2$ and Mn(NH$_3$)$_6$Cl$_2$. DSC analysis reveal a decrease in the onset temperature for NH$_3$ desorption for the solid solutions as compared to the monometallic Mg(NH$_3$)$_6$Cl$_2$. Activation energies for each desorption step are calculated and show the possibility of tailoring the activation energies for the NH$_3$ release in mixed metal chloride hexammines. The lower activation energies for NH$_3$ desorption in Mn(NH$_3$)$_6$Cl$_2$ resulted in a lowering of the activation energies for the solid solution Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$. Finally, NH$_3$ reversibility measurements reveal that the solid solution has a high stability, thus making them promising candidates for solid-state NH$_3$ storage systems.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/13/11/2746/s1, Table S1: Structural parameters for the MgCl$_2$, MnCl$_2$ and Mg$_{1-x}$Mn$_x$Cl$_2$ (x = 0.025, 0.05, 0.1, 0.3 and 0.5) solid solutions obtained for this study, Figure S1: Rietveld refinement of SR-PXD data of Mg(NH$_3$)$_6$Cl$_2$ at RT, Figure S2: Rietveld refinement of SR-PXD data of Mg$_{0.5}$Mn$_{0.5}$(NH$_3$)$_6$Cl$_2$ at RT, Figure S3: Rietveld refinement of SR-PXD data of Mg$_{0.7}$Mn$_{0.3}$(NH$_3$)$_6$Cl$_2$ at RT, Figure S4: Rietveld refinement of SR-PXD data of Mn(NH$_3$)$_6$Cl$_2$ at RT, Figure S5: Rietveld refinement of SR-PXD data of Mn(NH$_3$)$_6$Cl$_2$ at RT, Figure S6: DSC measurements performed on Mg(NH$_3$)$_6$Cl$_2$, Mn(NH$_3$)$_6$Cl$_2$ and Mg$_{1-x}$Mn$_x$(NH$_3$)$_6$Cl$_2$. Table S2: The NH$_3$ desorption onset temperatures of Mg(NH$_3$)$_6$Cl$_2$, Mn(NH$_3$)$_6$Cl$_2$ and Mg$_{1-x}$Mn$_x$(NH$_3$)$_6$Cl$_2$. Table S3: The gravimetric NH$_3$ capacities of the monometallic and mixed cation hexammines investigated in this study, Figure S7: SR-PXD patterns of Mg$_{1-x}$Mn$_x$Cl$_2$ after one cycle of NH$_3$ absorption and desorption. Figure S8: In-situ SR-PXD of Mg(NH$_3$)$_6$Cl$_2$ measured from RT to 227 °C, Figure S9: In-situ SR-PXD of Mn(NH$_3$)$_6$Cl$_2$ measured from RT to 406 °C, Figure S10: NH$_3$ desorption upon cycling of Mg$_{0.8}$Mn$_{0.2}$(NH$_3$)$_6$Cl$_2$.

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