

# Structure Determination of $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Ni}(\text{NH}_3)_2\text{Br}_2$ by Powder Diffraction using Synchrotron Radiation

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Ammines of simple salts  $M(\text{NH}_3)_nX_m$  are of interest for several reasons: They can serve as model systems for a stepwise solvation of salts as a function of the solvation number  $n$ . Furthermore, there is a fundamental interest in the rotational dynamics of the  $\text{NH}_3$  molecules fixed by coordinative bonds to metal centres. Often this is accompanied by order-disorder transformations (e.g. in hexaammine metal(II) halides [1]).

Ammines of low  $\text{NH}_3$  content are not well studied. Only few crystal structures are known. This is mostly due to difficulties in preparing well crystalline samples and especially single crystals. In many cases only the solvation numbers  $n$  are known from the absorption isotherms [2].

We studied the ammines of nickel chloride, bromide and iodide. The hexaammines are well known [3]. Furthermore, we determined the structures of the diammine halides [4]. However, the structures of the monoammine metal(II) chloride and bromide are unknown. We prepared the materials by reacting the corresponding nickel(II) halide and the diammine nickel(II) halide (molar ratio 1:1) in a steel autoclave at 300°C. The compounds are dark yellow and are very sensitive to moisture.

Both materials show similar, complicated diffraction patterns indicating isotypic structures and the presence of a small amount of the corresponding diammine. A hexagonal unit cell suggested in [5] for  $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$  does not explain the diffraction patterns recorded by us.

Due to severe overlap of reflections we recorded highly resolved powder patterns on the diffractometer B2 using synchrotron radiation. We applied the Debye-Scherrer technique for  $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$  and transmission technique for  $\text{Ni}(\text{NH}_3)_2\text{Br}_2$ . The patterns were indexed with a body centred monoclinic unit cell ( $a/\text{\AA} = 14,90$  (15,58),  $b/\text{\AA} = 3,56$  (3,74),  $c/\text{\AA} = 13,92$  (14,42)  $\text{\AA}$ ,  $\beta/^\circ = 106,3$  (105,9)). The diffractogram for the bromide is shown in Figure 1. The final structural model was successfully derived from geometrical considerations. It has  $I2/m$  symmetry (standard setting:  $C2/m$ ) and consists of two crystallographically distinct octahedral double chains  $\infty [\text{NiX}_{3/3}X_{2/2}(\text{NH}_3)]$  ( $X = \text{Cl}, \text{Br}$ ) (Figure 2) which run along the  $b$ -axis. There are two nickel, four halogen and two nitrogen sites. Although, one might imagine a higher symmetry, the coordination spheres around the  $\text{NH}_3$  groups are essentially different. Therefore, the octahedral double chains cannot be equivalent by symmetry.

We refined the crystal structures using the GSAS package of programs. H atoms were introduced to calculated positions assuming rotational disorder. For the bromide the reflection (020) (see Figure 1 at  $2\theta = 48^\circ$ ) is observed far too strong. This may indicate preferred orientation. However, a convincing model explaining the discrepancies was not found.

One can interpret the stepwise solvation starting from the pure halide ( $\text{CdCl}_2$  type structure) and leading finally to the hexaammine by a successive fragmentation of the edge sharing octahedral layers  $\text{NiX}_{6/3}$  by  $\text{NH}_3$ : In the monoammine double chains  $\infty [\text{NiX}_{3/3}X_{2/2}(\text{NH}_3)]$  result whereas one finds single octahedral chains  $\infty [\text{NiX}_{4/2}(\text{NH}_3)_2]$  in the diammines [4]. The fragmentation is complete in the hexaammines, where isolated units  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  are present.

The crystal structures of  $\text{Ni}(\text{NH}_3)_2X_2$  ( $X = \text{Cl}, \text{Br}$ ) are similar to that of  $\text{Cd}(\text{H}_2\text{O})\text{Cl}_2$  [7], only the relative arrangement of the octahedral double chains is different.

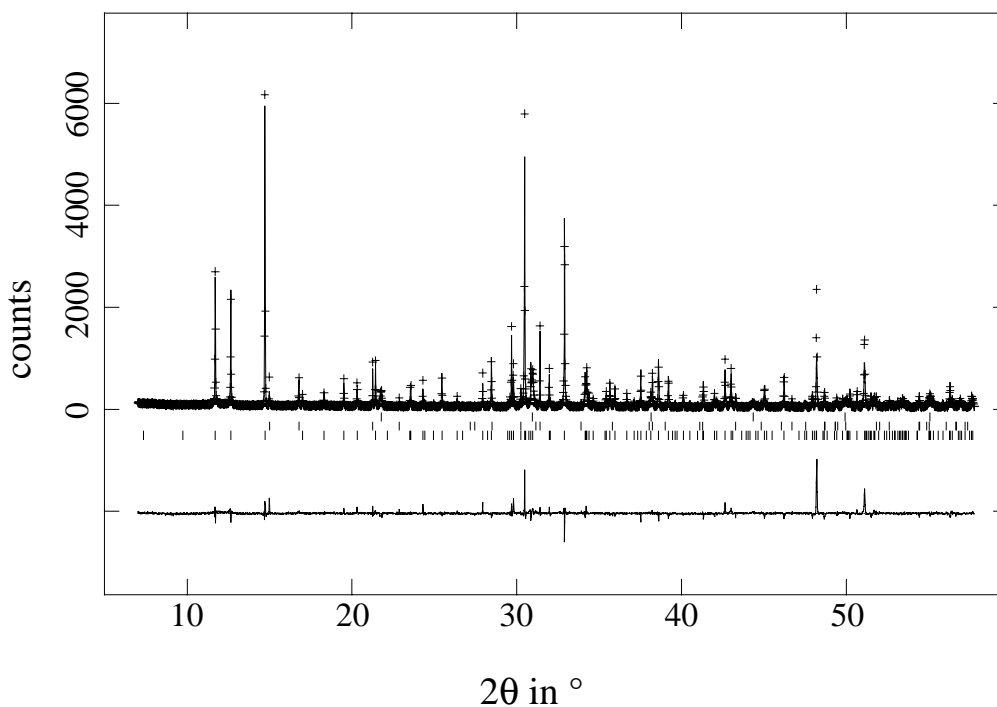


Figure 1: Powder diffraction pattern of  $\text{Ni}(\text{NH}_3)\text{Br}_2$ . ( $\lambda = 1.5289 \text{ \AA}$ ). Reflection markers from top to bottom:  $\text{NH}_4\text{Br}$  (formed probably due to partial hydrolysis during the measurement),  $\alpha\text{-Ni}(\text{NH}_3)_2\text{Br}_2$ ,  $\text{Ni}(\text{NH}_3)\text{Br}_2$

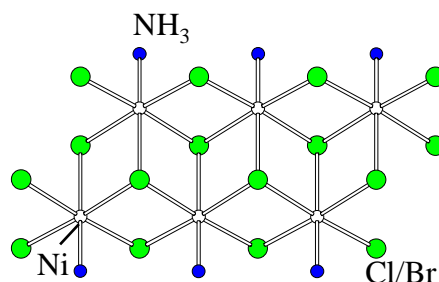


Figure 2: Octahedral double chains  $\infty [\text{NiX}_{3/3}\text{X}_{2/2}(\text{NH}_3)]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) as present in  $\text{Ni}(\text{NH}_3)\text{Cl}_2$  and  $\text{Ni}(\text{NH}_3)\text{Br}_2$ . The octahedra are connected via common edges.

## References

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