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Preparation and Crystal Structures of $Mg(NH_3)_2Cl_2$, $Mg(NH_3)_2Br_2$, and $Mg(NH_3)_2I_2$

A. Leineweber, M. W. Friedriszik, and H. Jacobs[1]

Lehrstuhl für Anorganische Chemie I, Fachbereich Chemie der Universität, D-44221 Dortmund, Germany

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IN MEMORIAM JEAN ROUXEL

Diammine magnesium halides $Mg(NH_3)_2X_2$ with $X=Cl$, Br, I have been prepared from magnesium metal and the corresponding ammonium halide in steel autoclaves at 350°C. $Mg(NH_3)_2Cl_2$ crystallizes in the $Cd(NH_3)_2Cl_2$-structure type: Rietveld X-ray analysis, *Cmmm*, $Z=2$; $a=8.1810(2)$ Å, $b=8.2067(2)$ Å, $c=3.7550(1)$ Å, $R(F^2)_{Bragg}=5.9\%$. The bromide and the iodide are isotypic and crystallize in a new structure type: single crystal X-ray analysis, *Pbam*, $Z=2$; $Mg(NH_3)_2Br_2$: $a=5.944(2)$ Å, $b=11.876(3)$ Å, $c=3.983(1)$ Å, $R_1(F)=0.045$; $Mg(NH_3)_2I_2$: $a=6.285(1)$ Å, $b=12.559(3)$ Å, $c=4.302(1)$ Å, $R_1(F)=0.080$. Both structure types contain chains of edge-sharing octahedra $^1_\infty[MgX_{4/2}(NH_3)_2]$ running along c. These are arranged in different ways relative to one another in the two structure types. © 1999 Academic Press

Key Words: **diammine magnesium halides; ammine salts; structural relationships.**

INTRODUCTION

Systematic temperature-dependent measurements of NH_3 pressure over ammines of magnesium halides $Mg(NH_3)_nX_2$ (for $X = Cl$, Br, and I) were performed by Biltz and Hüttig (1). They showed the existence of ammines with $n \in \{1, 2, 6\}$ for $X = Cl$, Br and $n \in \{2, 6\}$ for $X = I$ and determined the respective absorption isotherms.

According to Olovson (2), the hexaammines $Mg(NH_3)_6X_2$ ($X = Cl$, Br, I) crystallize in an antitype of the K_2PtCl_6-structure (isostructural compounds are known, e.g., for the divalent halides of V–Ni). Single crystal growth and structure analysis of $Mg(NH_3)_6Br_2$ is described in the thesis of one of the authors of this paper (3). The structures of the di- and monoammines are not yet known. Watt and Foerster (4) published a nonindexed X-ray powder pattern of diammine magnesium iodide. We now report a new synthetic route leading to diammine magnesium chloride, bromide, and iodide and to their structures.

PREPARATION AND STRUCTURE DETERMINATION

Magnesium halides and their ammines are hygroscopic and have to be handled under inert conditions. Diammine magnesium halides (Cl, Br, I) were prepared from the reaction of magnesium powder (Ventron, > 99%) and the corresponding ammonium halide (NH_4Cl: > 99.8%, Merck; NH_4Br: > 99%, Aldrich; NH_4I: p.a., Fluka) (molar ratio 1:2) in steel autoclaves ($V = 7$ ml (5) at 350°C for 1–2 weeks. All three reaction products appear well crystalline and are single phase products as determined by X-ray diffraction using a Guinier camera (FR 552, Enraf Nouius, Delft, The Netherlands). It was possible to grow and isolate single crystals of the bromide and iodide, but not of the chloride.

When the reaction between NH_4X and Mg is finished and the autoclave is opened, H_2 escapes. Thus, the temperature is not sufficiently high to allow rapid diffusion of hydrogen through the metal. We estimated the NH_3 partial pressures of the diammines at 350°C by extrapolating the isotherms given by Ref. (1) as 60 bar for the chloride and 17 mbar for the iodide. Because of the small volume of the autoclaves (7 ml) and the large batches (25 to 30 mmol Mg) only decomposition of a small amount of the ammine is required to reach a sufficient counterpressure. Especially for the bromide and the iodide, the material appeared to melt during the reaction, possibly by forming a low melting solution with unreacted NH_4X.

An additional route of synthesis was used for diammine magnesium chloride. $MgCl_2$ (Alfa, 99.9%) was reacted with an excess of gaseous NH_3 to form hexaammine magnesium chloride. This was heated with additional $MgCl_2$ in a molar ratio of 1:2 at 200°C in a steel autoclave for 1 week.

Magnesium diammine chloride prepared by either method shows identical Guinier powder diffraction patterns. A

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[1] To whom correspondence should be addressed. Fax +49(0)231/755-3797; E-mail: jacobs@pop.uni-dortmund.de.

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primitive tetragonal unit cell, $a_t = 5.79$ Å and $c_t = 3.76$ Å, can be indexed to all reflections. However, splitting of a few reflections was observed, so a C-centered orthorhombic cell of $a \approx b \approx \sqrt{2}\ a_t$ is more appropriate. Starting with the molar volume of magnesium chloride and ammonia (calculated from other ammines (2)), the number of formula units in the unit cell was estimated to be two. Inspection of these data suggested that $Mg(NH_3)_2Cl_2$ is isotypic with $Cd(NH_3)_2Cl_2$ and $Cd(NH_3)_2Br_2$ (6). The lattice constants a and b of the first cadmium compound are close to each other, those of the second are virtually equal. In Ref. (6) partially twinned crystals were examined. H-sites were not determined.

A powder diffractogram of $Mg(NH_3)_2Cl_2$ prepared by the second route was recorded on a Siemens D500 diffractometer. The sample was covered by Kapton foil ($d \approx 50$ µm, type 200 HN, August Krempel Soehne GmbH & Co., Enzweihingen, Germany).

Rietveld refinement was performed using the GSAS package of programs (7). The structural parameters of $Cd(NH_3)_2Cl_2$ were used as starting values and convergence was readily achieved. However, relatively large errors in reflection intensities occurred, especially at low 2θ values. This suggested a significant contribution of H. With a fixed relative occupancy of 3/4 we succeeded in refining the positions of three H-atoms of an NH_3 molecule in a fourfold split position. The thermal displacement parameter of H was held fixed and was only refined in the last cycles. Technical data for the Rietveld refinement are given in Table 1. The observed and calculated profile and the difference curve are given in Fig. 1. Only a few, very weak reflections cannot be interpreted by the present structure model, or by simple multiples of the unit cell constants given in Table 1 ($2\theta/° = 26.70, 40.38, 42.91, 47.02$). We did not exclude the corresponding regions, as the intensities of these reflections are negligible relative to the overall intensities.

TABLE 1
Technical Data for Data Collection and Rietveld Refinement for $Mg(NH_3)_2Cl_2$

Formula	$Mg(NH_3)_2Cl_2$
Formula weight	129.28 g/mol
Diffractometer, geometry	Siemens D500, Bragg Brentano
Radiation	Cu$K\alpha$ (Graphite secondary monochromator)
Temperature	295 K
2θ range	7–90°
2θ stepwidth	0.01°
Time per step	6 s
Space group	*Cmmm* (No. 65)
Cell parameters	8.1810(2) Å 8.2067(2) Å 3.7550(1) Å
Volume, Z	252.11(1) Å^3, 2
Calculated density	1.703 g/cm^3
Profile parameters	5[a]
Background parameters	4 + 12 fixed background points
Structural parameters	9
Zero point	0.065(8)° (2θ)
No. of reflections	160
wR_P	0.112
$R(F^2)$ ($F^2 \geq \sigma(F^2)$)	0.059

[a] Simpson's rule integration of pseudo-Voigt function with correction for asymmetry (21, 22). No correction for polarization or for preferred orientation was applied.

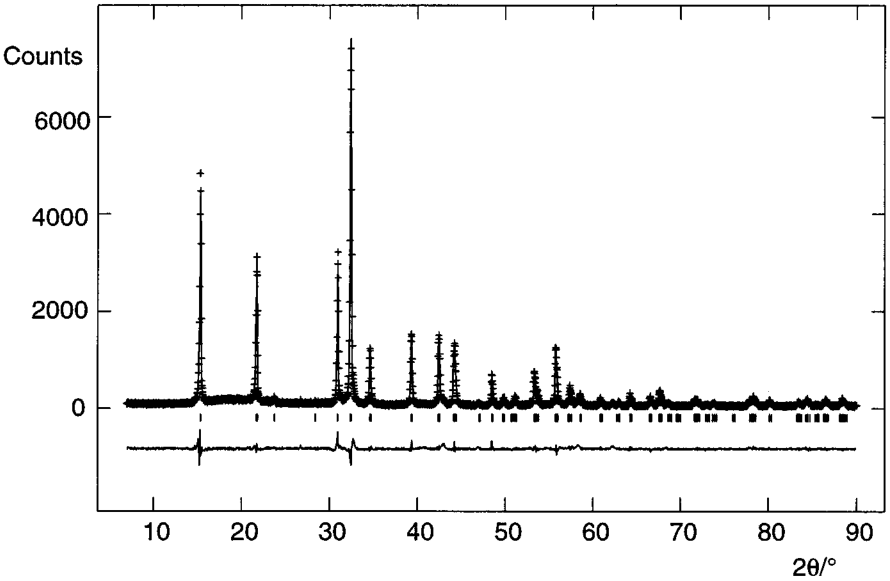

FIG. 1. Observed (+) and calculated (−) X-ray diffractions profiles (top) and difference curve (bottom) for $Mg(NH_3)_2Cl_2$. Markers indicate positions of reflections.

TABLE 2
Positional and Isotropic Thermal Displacement Parameters for $Mg(NH_3)_2Cl_2$

Atom	Wyckoff site	x	y	z	f_{OCC}	U_{ISO} (Å^2)
Mg	2*a*	0	0	0	1	0.0244(9)
Cl	4*h*	0.2133(1)	0	1/2	1	0.0211(5)
N	4*i*	0	0.2595(6)	0	1	0.022(1)
H	16*r*	0.045(4)	0.312(2)	0.158(5)	3/4	0.05(1)

The final positional and thermal displacement parameters are reported in Table 2.

TABLE 3
Technical Data for Single Crystal Measurements for $Mg(NH_3)_2Br_2$ and $Mg(NH_3)_2I_2$[a]

Formula	$Mg(NH_3)_2Br_2$	$Mg(NH_3)_2I_2$
Formula weight (g/mol)	218.20	312.18
Space group type	*Pbam* (No. 55)	*Pbam* (No. 55)
Diffractometer	CAD4	CAD4
Radiation	Mo*Kα*	Mo*Kα*
Cell	5.944(2) Å	6.285(1) Å
	11.876(3) Å	12.559(3) Å
	3.983(1) Å	4.302(1) Å
Volume, *Z*	281.2(1) Å^3, 2	339.6(1) Å^3, 2
Calculated density	2.577 g/cm^3	3.053 g/cm^3
Crystal size	0.15 × 0.15 × 0.15 mm^3	0.25×0.15×0.15 mm^3
Scan	ω/θ	ω/θ
Theta range for data collection	3–35°	4–40°
h, *k*, *l* range	$-9 \le h \le 9$	$0 \le h \le 12$
	$-19 \le k \le 19$	$-25 \le k \le 25$
	$-6 \le l \le 6$	$-8 \le l \le 8$
Number of reflections measured	4459	2920
Number of unique reflections	692	1645
Absorption correction	ψ-scan	ψ-scan
Min rel. transmission	90%	40%
$1/\mu$	0.070 mm	0.108 mm
Extinction coefficient[b]	0.018(1)	0.011(2)
R_{int}	0.066	0.034
$R_1 (F_o \ge 4\sigma(F_o))/R_1$ (all)	0.032/0.045	0.053/0.080
$wR_2 (F_o \ge 2\sigma(F_o^2))/wR_2$ (all)	0.043/0.045	0.116/0.147
Max/min res. density	1.4/ − 1.6 e/Å^3	3.6/–2.7 e/Å^3

[a] Data have been submitted to Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) under Registry Nos. CSD 410352 ($Mg(NH_3)_2Br_2$) and 410353 ($Mg(NH_3)_2I_2$).

[b] Correction factor for F_C: $[1 + 0.001 \cdot x \cdot F_C^2 \cdot \lambda^3/\sin(2\theta)]^{-1/4}$.

TABLE 4
Positional and Isotropic Thermal Displacement Parameters of $Mg(NH_3)_2Br_2$ and $Mg(NH_3)_2I_2$

Atom	Wyckoff site	x	y	z	f_{OCC}	U_{eq}, U_{ISO} (Å^2)
			$Mg(NH_3)_2Br_2$			
Mg	2*a*	0	0	0	1	0.0196(7)[a]
Br	4*h*	0.27904(7)	0.38672(2)	1/2	1	0.0227(2)[a]
N	4*g*	0.2542(5)	0.1250(2)	0	1	0.025(2)[a]
H(1)	8*i*	0.383(8)	0.109(2)	0.09(2)	3/4	0.07(1)
H(2)	8*i*	0.223(6)	0.185(2)	0.11(2)	3/4	0.10(2)
			$Mg(NH_3)_2I_2$			
Mg	2*a*	0	0	0	1	0.031(1)[a]
I	4*h*	0.26842(6)	0.38127(3)	1/2	1	0.0276(2)[a]
N	4*g*	0.2394(7)	0.1188(4)	0	1	0.031(2)[a]

[a] $U_{eq} = 1/3\ [\mathrm{Trace}(U_{ij})]$.

Stronger reflections of the powder patterns of our $Mg(NH_3)_2I_2$ samples were also observed by Watt and Foerster (4) (no indexing was given in Ref. 4). However, we find additional weak reflections. Our patterns of the bromide and the iodide were completely indexed—including the weak reflections—with a primitive tetragonal unit cell ($a_t = 11.93$ Å, $c_t = 3.99$ Å for the bromide, $a_t = 12.53$ Å, $c_t = 4.30$ Å for the iodide). Single crystals of both the bromide and iodide were isolated from the reaction products and tested by precession photography. These indicated orthorhombic ($a \approx a_t/2$, $b \approx a_t$, $c = c_t$) rather than tetragonal symmetry. Data collection was performed on a CAD4-diffractometer (Enraf-Nonius, Delft, NL) using Mo*Kα*-radiation.

The structures were solved in the space group *Pbam* for both compounds. Halogen atoms were located from Patterson maps (SHELXS-86, 8). Structure refinement was performed with SHELXL-93 (9). Mg and N sites were obtained from difference Fourier maps. For the diammine bromide, H sites were found, leading to a similar model as

TABLE 5
Components of the U_{ij} Tensors[a] of the Non-H Sites in $Mg(NH_3)_2Br_2$ and $Mg(NH_3)_2I_2$

Atom	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)
		$Mg(NH_3)_2Br_2$		
Mg	0.0189(7)	0.0195(5)	0.0207(9)	− 0.0038(5)
Br	0.0234(2)	0.0248(1)	0.0199(2)	− 0.0040(1)
N	0.023(2)	0.026(1)	0.026(2)	− 0.003(1)
		$Mg(NH_3)_2I_2$		
Mg	0.025(1)	0.036(1)	0.033(1)	− 0.0104(9)
I	0.0264(2)	0.0304(2)	0.0261(2)	− 0.00373(9)
N	0.029(2)	0.029(2)	0.036(3)	− 0.010(1)

[a] The anisotropic thermal displacement factor exponent takes the form $-2\pi^2\ [h^2\ a^{*2}\ U_{11} + \cdots + 2hka{}^*b^*\ U_{12}]$, with $U_{13} = U_{23} = 0$ for the positions 2*a*, 4*h*, and 4*g* of space group *Pbam.*

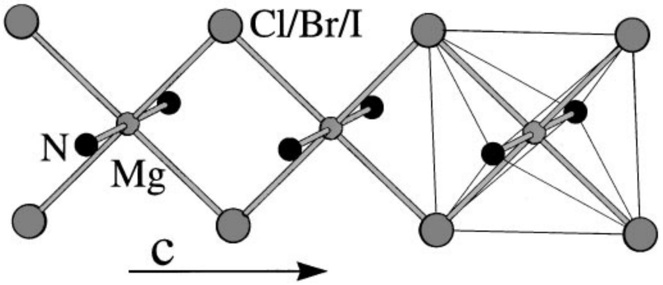

FIG. 2. $^{1}_{\infty}[MgX_{4/2}(NH_3)_2]$-chains (H omitted) of edge-sharing octahedra as main constituents of $Mg(NH_3)_2X_2$ (X = Cl, Br, I).

for the diammine chloride. Now two different H sites are required, each with a fixed relative occupancy of 3/4. The reliability parameters significantly improved after the H atoms were introduced. However, for the iodide, similar H sites resulting from the difference Fourier maps do not give sensible N–H distances, and their refinement does not significantly improve the reliability factors. Hence, H sites are neglected for the iodide. Further maxima are located close to the I atoms. Technical data for the data collection and the refinement are given in Table 3, positional and U_{iso}/U_{eq}-parameters in Table 4, and the components of the U_{ij} tensors in Table 5.

STRUCTURE DESCRIPTION AND DISCUSSION

The structures of $Mg(NH_3)_2Cl_2$ and of $Mg(NH_3)_2X_2$ (X = Br, I) both contain chains of edge-sharing octahedra $^{1}_{\infty}[MgX_{4/2}(NH_3)_2]$ (Fig. 2) running along **c**. These are arranged in different ways relative to one another (Figs. 3 and 4). The structure of $Mg(NH_3)_2Cl_2$ belongs to the previously described $Cd(NH_3)_2Cl_2$-type (6). The structure of the bromide and iodide can be regarded as a new structure type, which we will refer to as the $Mg(NH_3)_2Br_2$ type.

Monoclinic variants of the $Cd(NH_3)_2Cl_2$ type are known for $M(H_2O)_2X_2$ (M = Mn, Fe, Co, Ni: X = Cl, Br) (10–12) and α-$Cu(NH_3)_2Br_2$ (13). The distortions originate with hydrogen bonding of ordered water molecules to the halide ions and to Jahn–Teller distortions of the coordination octahedra around Cu^{2+}. Similar arrangements of the octahedral chains are found in other compounds such as $[OsCl_2Cl_{4/2}]$ (14), β-$Cd[UO_2O_{4/2}]$ (15) (both *Cmmm*), and $Na_2[MnCl_2Cl_{4/2}]$ (16) (*Pbam*).

In both diammine structure types, halogen and N atoms form an approximate CsCl-like arrangement (see Table 6). Two such CsCl units have an Mg atom in common in a square of X atoms. Hence, one $Mg(NH_3)_2$ unit is placed in two such units. Figures 3 and 4 show the arrangement of these "double cells" in the (001) planes of both structures.

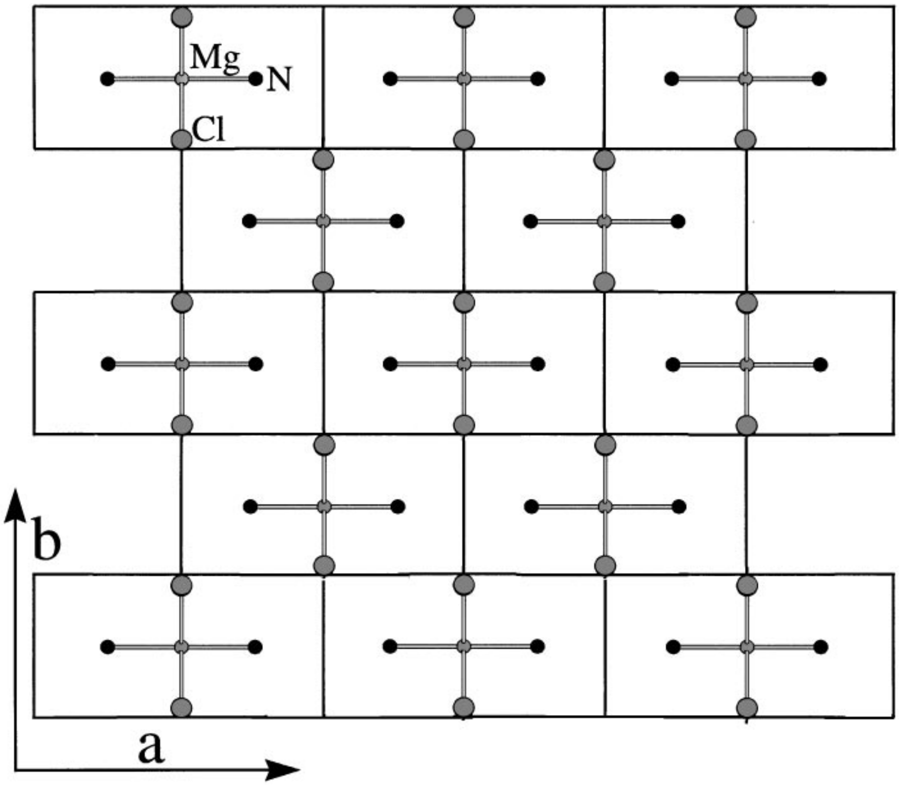

FIG. 3. Structure of $Mg(NH_3)_2Cl_2$, view along (001): A "brick"-like arrangement of "double CsCl units" is indicated by rectangles; for the CsCl units, the corners are Cl and the centers N atoms.

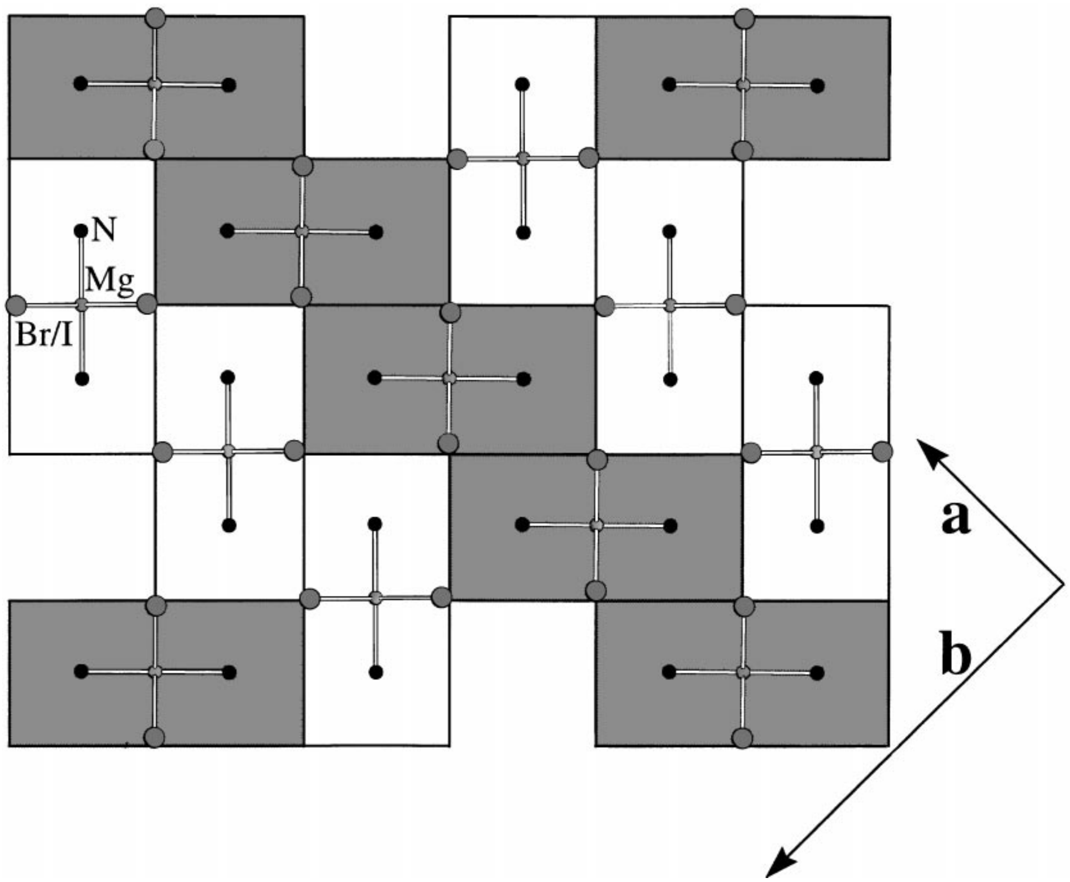

FIG. 4. Structure of $Mg(NH_3)_2Br_2$ (and $Mg(NH_3)_2I_2$), view along (001): "herringbone" pattern of the same units as in $Mg(NH_3)_2Cl_2$; all rectangles are equivalent; shading is done to clarify the pattern.

In the $Cd(NH_3)_2Cl_2$-type structure of $Mg(NH_3)_2Cl_2$, they are arranged in parallel rows along (010) shifted by $\mathbf{b}/2$ relative to each other, like bricks, whereas they form a herringbone pattern in the $Mg(NH_3)_2Br_2$-type structure. The arrangements of these "double-cell" $2a' \times a'$ rectangles form two different regular 2D tilings (17) of pseudotetragonal dimensions (Figs. 3 and 4).

A median c/a ratio of the CsCl subcells is defined by $(c/a)_{\mathrm{CsCl}} = 2c/(a \cdot b)^{1/2}$ for both structure types. This is a measure of the distortion of the pseudo-CsCl cells along the octahedral chains $^{1}_{\infty}[MgX_{4/2}(NH_3)_2]$. The values of $(c/a)_{\mathrm{CsCl}}$ are the following: $X = \mathrm{Cl}$, 0.917; $X = \mathrm{Br}$, 0.948; $X = \mathrm{I}$, 0.968. The pseudotetragonal structures become closer to pseudocubic with increasing size of the halide ion.

TABLE 6
Important Distances and Angles in the Compounds

Distances/angles	$Mg(NH_3)_2Cl_2$	$Mg(NH_3)_2Br_2$	$Mg(NH_3)_2I_2$
$4 \times$ Mg–X (Å)	2.563(1)	2.739(1)	2.995(1)
$2 \times$ Mg–N (Å)	2.130(5)	2.118(3)	2.119(4)
N–H(1) (Å)	0.82(2)	0.87(6)	—
N–H(2) (Å)		0.85(5)	
Bridging X–Mg–X	85.8(3)°	86.70(2)°	88.18(2)°

It is well known from hexaammine metal(II) halides $M(NH_3)_6X_2$ of the K_2PtCl_6 antitype that the NH_3 molecules show rotational disorder above a critical temperature that depends on the constituting ions but is somewhat below 200 K (18). In the high temperature phase, the C_{4v}-site symmetry of N is incompatible with the molecular C_{3v} symmetry of the NH_3 molecule. In accordance with the site symmetry and dynamics of the NH_3 molecules, one observes a four-fold split position with a relative occupancy of 3/4 by H (19, 20). These lie approximately on the line X...N. One should expect a similar situation for diammine metal(II) halides. The H atoms of the NH_3 molecules are directed toward an approximate square of four X atoms, a situation similar to that in the hexaammines. Because of the C_{2v} site symmetry of the N atoms in the $Cd(NH_3)_2Cl_2$ structure, an ordered arrangement of H is not possible without reduction of the symmetry. Although the site symmetry of N (C_s) in the $Mg(NH_3)_2Br_2$ type would allow an ordered arrangement of NH_3 molecules, we find a situation quite similar to that seen in $Mg(NH_3)_2Cl_2$, although two crystallographically different split positions for the H atoms are required. In both the chloride and the bromide the split H atoms are approximately directed to the X-atoms.

It should be emphasized that the approximate CsCl arrangement of N and X in these compounds limits the contribution of the "heavy atoms" to the structure factors to certain reflections. For some of these, the relative contribution of H is high, so the H positions can be determined by X-ray data with relatively high significance.

Nevertheless, the results referring the H sites of the chloride and bromide are only preliminary. From X-ray diffraction one cannot be sure whether weak superstructure reflections were not detected, whether the structure is of lower symmetry without superstructure reflections, or whether is, in fact, disordered at room temperature. Therefore, neutron diffraction experiments are in progress to clarify this situation and to detect possible phase transitions at low temperatures.

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