

X-Ray Investigations of Ammines of Alkaline Earth Metal Halides. I. The Structures of $\text{CaCl}_2(\text{NH}_3)_8$, $\text{CaCl}_2(\text{NH}_3)_2$ and the Decomposition Product CaClOH

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The structures of two calcium ammine chlorides and of a decomposition product have been determined and refined by the Rietveld full-profile technique. X-Ray powder diffraction data were obtained with a Guinier-Hägg camera and a computer-based film scanner system.

Symmetries and unit cell parameters are: $\text{CaCl}_2(\text{NH}_3)_8$: *Pnma*, $a=12.1143$, $b=7.3076$ and $c=15.0829$ Å; $\text{CaCl}_2(\text{NH}_3)_2$: *Abm2*, $a=6.0042$, $b=7.8254$ and $c=12.3491$ Å; CaClOH : *P6₃mc*, $a=3.8641$ and $c=9.9044$ Å.

The calcium environment is a distorted $(\text{NH}_3)_6$ triangular prism in the octaammine, and a somewhat irregular $\text{Cl}_4(\text{NH}_3)_2$ octahedron in the diammine. CaClOH is isostructural with CdClOH (EO_3 type).

A serious problem encountered when utilizing solid ammine systems for energy storage is their poor stability upon frequent cycling. This problem has been observed for *e.g.* calcium chloride ammines which, due to their favorable NH_3 vapor pressure characteristics and low cost, are seen as very promising (Refs. 1, 2 and references therein).

In order to gain better understanding of the properties of the ammines of calcium chloride, their formation and decomposition, we initiated an X-ray diffraction study. In this article we are able to present the structures of $\text{CaCl}_2(\text{NH}_3)_8$, $\text{CaCl}_2(\text{NH}_3)_2$ and CaClOH (the last one being a decomposition product of the octaammine). During the course of the investigation it was found that the crystals that could be prepared were too small to allow collection of single-crystal data. Also, the ammonia decomposition pressure and the pro-

pensity of the substances to react with atmospheric moisture prohibit single-crystal experiments. Therefore, the structures reported here were determined, albeit with limited accuracy, from powder data.

The study is being planned to include other new phases of alkaline earth metal ammine halides, *cf.* Table 1. As seen from the table, calcium, strontium and barium salts form octaammines, which is rather uncommon.^{3–5} Noteworthy is also that the decomposition of $\text{CaCl}_2(\text{NH}_3)_8$, $\text{SrCl}_2(\text{NH}_3)_8$ and $\text{BaCl}_2(\text{NH}_3)_8$ does not seem to follow any obvious pattern.

Table 1. Ammines of alkaline earth metal halides. The structures of the ammines in bold type have been found to be cubic, of K_2PtCl_6 type (4).

Salt	Stoichiometry of the ammines (No. of NH_3 molecules)
MgCl_2	6 , 2, 1
MgBr_2	6 , 2, 1
MgI_2	6 , 2
CaCl_2	8, 4 , 2, 1
CaBr_2	8, 6 , 2, 1
CaI_2	8, 6 , 2, 1
SrCl_2	8, 2, ^a 1
SrBr_2	8, 2, 1
SrI_2	8, 6, 2, 1
BaCl_2	8
BaBr_2	8, 4, 2, 1
BaI_2	10, 9, 8, 6, 4, 2

^a *Cf.* Ref. 5.

EXPERIMENTAL

Powder samples of the amines were prepared as follows: Calcium chloride tetrahydrate (Merck, 99.995 %) was dried at 160 °C under vacuum, with a liquid nitrogen trap, for several days prior to use. Each individual sample, after weighing, was transferred to a cylindrical pyrex reaction flask, which was then attached to a pyrex vacuum manifold system by means of glass-to-glass O-ring seals. The reaction flask and parts of the manifold system could be isolated from one another with teflon stopcocks.

The salt was further dried, to eliminate possible water absorption during weighing, by placing the flask in a thermostatted bath at 70 °C and pumping through a liquid nitrogen trap for at least one hour. At this point, the salt was sealed under vacuum and isolated, and ammonia gas (AGA, 99.999 %) was introduced into the remainder of the manifold system.

Knowledge of the pressure-temperature characteristics of the calcium chloride amines, the sample mass and the volumes of all the parts of the glass manifold served to determine the quantity of ammonia, and the procedure, needed to synthesize the desired ammine. The salt was exposed to ammonia at 22 °C and allowed to equilibrate (one week for the diammine, *e.g.*). Pressure during the preparation was measured with a standard mercury manometer. The final stoichiometries of the complexes could be determined with an accuracy better than ± 0.1 mol of NH_3 per mol of complex.

X-Ray powder diffraction samples of the amines were prepared by mixing $\text{CaCl}_2(\text{NH}_3)_n$ preparations, of gross compositions $n = 7.90, 3.93, 2.40$ and 1.10 , with finely powdered silicon ($a = 5.430880 \pm 35$ Å at 25 °C) as internal θ standard.⁶ Minor amounts of the samples were spread out between previously dried pieces of adhesive tape affixed to Guinier camera specimen discs. The whole procedure was

carried out at room temperature in a glove bag flushed with dry ammonia gas at 1 atm pressure. The loaded specimen discs were then stored in ammonia-containing plastic bags in a desiccator, awaiting X-ray exposure.

The $\text{CaCl}_2(\text{NH}_3)_{7.90}$ samples were afterwards left in ambient air for one week and a new set of powder photographs taken. The films showed that complete decomposition had taken place, to NH_4Cl and a new phase, subsequently found to be CaClOH .

The X-ray powder photographs were taken in a subtraction-geometry Guinier-Hägg focusing camera of 80 mm diameter, with strictly monochromatized $\text{CuK}\alpha_1$ radiation ($\lambda = 1.540598$ Å). The atmosphere in the camera housing during the exposures was dry air at room temperature. Single-coated film (CEA Reflex 15) was used in order to avoid superposition of front- and back-layer intensity profiles, and to reduce the background.

All measurements of the films were made by means of an automatic single-beam microdensitometer, recently described by Johansson *et al.*⁷ The slit opening of the collimator was 0.040×2.0 mm, and the corresponding θ step length was $\sim 0.0143^\circ$.

Symmetries and unit cell dimensions of the investigated phases (Table 2) were all found by use of the trial-and-error program TREOR written by one of us (PEW). Three-dimensional Patterson functions were calculated from the integrated intensities, with indices obtained from the most close-lying calculated θ values, thus disregarding the overlaps.

All Ca and Cl positions could be derived from the Patterson functions. However, no definite models for the nitrogen and oxygen coordinations could be ascertained directly from the integrated intensity data. Application of a Rietveld full-profile refinement program for X-ray data⁸ yielded sets of structure factors, from which light atom coordinates could be obtained by standard Fourier techniques.

Table 2. Crystal data.

	$\text{CaCl}_2(\text{NH}_3)_8$	$\text{CaCl}_2(\text{NH}_3)_2$	CaClOH
Space group	<i>Pnma</i> (No. 62)	<i>Abm2</i> (No. 39)	<i>P6₃mc</i> (No. 186)
$a/\text{Å}$ (σ_a)	12.1143 (15)	6.0042 (07)	3.8641 (05)
$b/\text{Å}$ (σ_b)	7.3076 (08)	7.8254 (12)	
$c/\text{Å}$ (σ_c)	15.0829 (22)	12.3491 (16)	9.9044 (21)
Cell fig. of merit	$M_{20} = 26$ $F_{20} = 45$ (0.009, 51)	$M_{20} = 15$ $F_{20} = 17$ (0.013, 96)	$M_{13} = 78$ $F_{13} = 25$ (0.017, 30)
Cell content	$Z = 4$	$Z = 4$	$Z = 2$
$R_F = \frac{\sum \ F_o\ - \ F_c\ }{\sum \ F_o\ }$	21.7 %	17.4 %	13.8 %

RESULTS

Space group symmetries, unit cell parameters, cell contents and reliability indices from the L.S. profile refinements are given in Table 2 for the three

Table 3. $\text{CaCl}_2(\text{NH}_3)_8$ powder diffraction record.

<i>h k l</i>	$2\theta_o/\text{deg}$	$2\theta_c/\text{deg}$	$d_o/\text{\AA}$	$10^3 I_o/I_{\text{max}}$
0 1 1	13.429	13.453	6.5883	338
1 0 2	13.808	13.821	6.4080	366
2 0 0	14.607	14.612	6.0595	150
1 1 1	15.308	15.318	5.7834	209
1 1 2	18.399	18.409	4.8181	505
2 1 0	19.007	19.015	4.6655	401
2 1 1	19.901	19.912	4.4577	923
0 1 3	21.431	21.435	4.1429	307
1 1 3	22.667	22.669	3.9197	533
3 0 1	22.780	22.779	3.9006	213
0 2 0	24.331	24.340	3.6553	171
3 0 2	24.974	24.993	3.5626	185
3 1 1	25.860	25.870	3.4425	136
4 0 1	30.069	30.071	2.9695	380
2 1 4		30.462		
1 0 5	30.519	30.514	2.9268	206
3 1 3		30.901		
2 2 2	30.930	30.918	2.8888	185
1 2 3	31.119	31.121	2.8717	948
4 0 2	31.819	31.815	2.8101	150
2 0 5	33.148	33.150	2.7004	882
3 2 1	33.577	33.579	2.6668	526
2 2 3	33.718	33.714	2.6560	331
1 2 4	34.977	34.959	2.5633	171
3 2 2	35.167	35.168	2.5499	1000
2 1 5	35.409	35.411	2.5330	174
2 2 4	37.318	37.316	2.4077	230
0 3 1		37.365		
1 3 2		39.552		
5 1 1	39.601	39.610	2.2740	206
2 3 1	40.329	40.320	2.2346	125
1 3 3	41.832	41.844	2.1577	136
5 1 3	43.227	43.225	2.0912	122
0 1 7		43.766		
3 3 1	43.778	43.779	2.0662	143
1 2 6	44.352	44.338	2.0408	460
5 0 4		44.408		
4 2 4	45.720	45.712	1.9828	143
3 2 6	49.415	49.417	1.8429	125
0 4 0		49.875		
0 1 8	49.903	49.915	1.8260	237
3 3 4		49.927		
5 2 4		51.282		
6 0 4	51.291	51.286	1.7798	157
3 0 8		53.604		
4 1 7	53.633	53.645	1.7075	157

Table 4. $\text{CaCl}_2(\text{NH}_3)_8$ position parameters in space group *Pnma*.

Atom	Site	<i>x</i>	(σ_x)	<i>y</i>	(σ_y)	<i>z</i>	(σ_z)
Ca	4(c)	0.746	(2)	1/4		0.133	(1)
C11	4(c)	0.144	(3)	1/4		0.034	(2)
C12	4(c)	0.047	(3)	1/4		0.681	(2)
N1	8(d)	0.147	(4)	0.493	(6)	0.457	(4)
N2	8(d)	0.434	(4)	0.049	(6)	0.362	(3)
N3	8(d)	0.204	(4)	0.015	(6)	0.250	(3)
N4	8(d)	0.191	(4)	0.016	(6)	0.638	(3)

phases that could be positively identified from the X-ray data obtained in this investigation. The resulting R_F values would be rather high for a single-crystal refinement; obtained in a powder investigation, in which severe overlap of lines regularly occurs, even with single phase samples, and in which the substances furthermore decompose continuously during the exposure, they may be taken to indicate that the structures are essentially correct. The refined position parameters are rather imprecise, though, especially for the light atoms, as can be seen from the following Tables.

Only the $\text{CaCl}_2(\text{NH}_3)_{7.90}$ and $\text{CaCl}_2(\text{NH}_3)_{2.40}$ samples gave adequate data for structure determinations. The $\text{CaCl}_2(\text{NH}_3)_{3.93}$ preparation consisted almost exclusively of decomposition products, and $\text{CaCl}_2(\text{NH}_3)_{1.10}$ yielded much the same pattern as $\text{CaCl}_2(\text{NH}_3)_{2.40}$, but with poorer definition. Further attempts are being made to obtain satisfactory X-ray intensity data for the tetra- and mono-ammines. These structures will be the subject of a forthcoming report.

Table 5. Interatomic distances (\AA) in $\text{CaCl}_2(\text{NH}_3)_8$.

Ca - N1	2.54	
Ca - N2	2.72	
Ca - N3	2.52	
C11 - N1	3.36	
C11 - N2	3.33	3.51
C11 - N3	3.20	3.76
C11 - N4	3.21	
C12 - N1	3.64	
C12 - N2	3.51	
C12 - N3	3.73	3.75
C12 - N4	2.52	
N4 - N1	2.79	
N4 - N3	2.13	

CA CL2 (NH3) 8

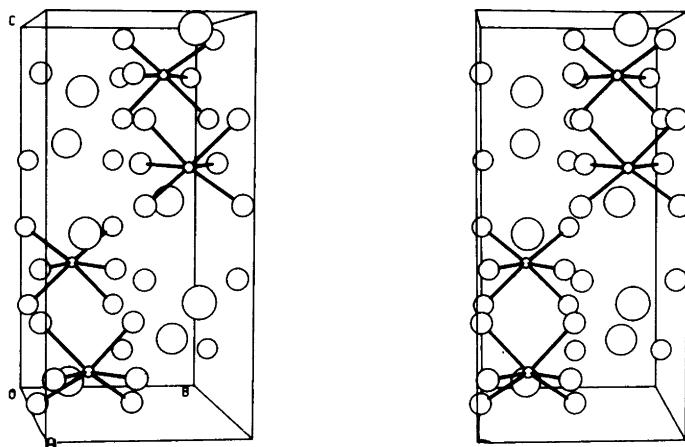


Fig. 1. Stereo view of the $\text{CaCl}_2(\text{NH}_3)_8$ structure. Small circles = Ca, medium circles = N and large circles = Cl. The bonding in the $\text{Ca}(\text{NH}_3)_6$ coordination prisms is indicated.

$\text{CaCl}_2(\text{NH}_3)_8$. Data yielded by the $\text{CaCl}_2\text{-(NH}_3\text{)}_{7.90}$ samples within 12 h from the time of preparation proved them to be nearly single-phase, with some admixture of decomposition products (*vide infra*). The crystal structure model obtained has $\text{CaCl}_2(\text{NH}_3)_8$ stoichiometry.

Fig. 1 depicts the structure, which consists of calcium ions in two planes ($y=1/4$ and $3/4$), surrounded by distorted triangular coordination prisms of NH_3 molecules (N1–N3) situated at $y \approx 0$ and $y \approx 0.5$. Against each of the 9 prism edges there rests

a chloride ion. The seventh and eighth ammonia molecules (N4) connect the chloride ions in pairs (C11 and C12, one situated at $y=1/4$, the other at $y=3/4$). These ammonias may also be thought of as serving to concatenate the $(\text{NH}_3)_6$ prisms in the c direction by hydrogen bonding. The nitrogen–nitrogen distance accuracy is too poor, however, to allow this statement to be definite.

Powder data for the phase are given in Table 3, structural parameters in Table 4, and interatomic distances in Table 5.

CA CL2 (NH3) 2

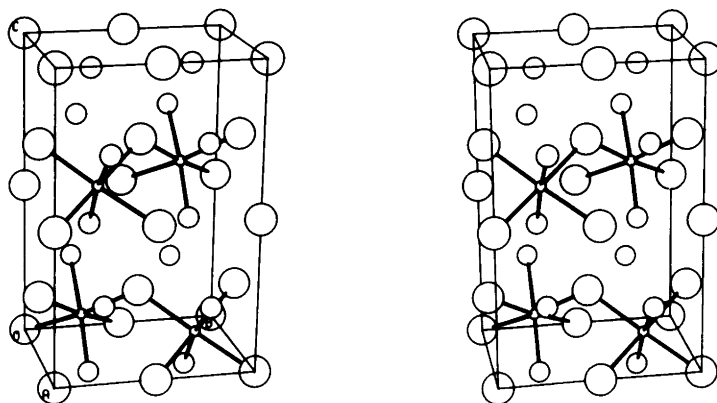


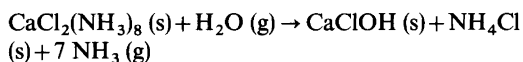
Fig. 2. Stereo view of the $\text{CaCl}_2(\text{NH}_3)_2$ structure. Small circles = Ca, medium circles = N and large circles = Cl. The bonding in the $\text{CaCl}_4(\text{NH}_3)_2$ coordination octahedra is indicated.

Table 6. CaClOH powder diffraction record.

<i>h k l</i>	$2\theta_o/\text{deg}$	$2\theta_c/\text{deg}$	$d_o/\text{\AA}$	$10^3 I_o/I_{\text{max}}$
0 0 2	17.962	17.897	4.9344	127
1 0 0	26.661	26.616	3.3409	82
1 0 1	28.152	28.124	3.1672	558
1 0 2	32.277	32.260	2.7713	259
0 0 4	36.247	36.250	2.4763	116
1 0 3	38.257	38.265	2.3507	1000
1 1 0	46.995	46.993	1.9320	388
1 1 2	50.663	50.677	1.8004	64
0 0 6	55.646	55.633	1.6504	87
2 0 1		55.666		
1 1 4	60.770	60.756	1.5229	142
2 0 3	62.132	62.145	1.4928	180
1 0 6	62.706	62.708	1.4805	60
2 1 1	75.754	75.753	1.2546	97

CaClOH. When powder photographs were taken again of the octaammine Guinier samples, after they had been stored for one week in ambient air, they were found to contain NH_4Cl and a new phase of hexagonal symmetry. This phase proved to be isomorphous with CdClOH , of EO_3 structure type.⁹ Powder data, structural parameters and interatomic distances are given in Tables 6, 7 and 8, respectively.

What happens to the octaammine in air may be described by:



Refinement of the $\text{CaClOH}/\text{NH}_4\text{Cl}$ molar ratio in the sample, performed by means of the two-phase profile refinement program⁸ confirmed the stoichiometry of the proposed reaction equation.

Table 7. CaClOH position parameters in space group $P6_3mc$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	(σ_z)
Ca	2(b)	1/3	2/3	0.680	(1)
Cl	2(b)	1/3	2/3	0	
O	2(a)	0	0	0.237	(3)

Table 8. Interatomic distances (\AA) in CaClOH.

Ca—Cl	2.85	3.17
Ca—O	2.30	
Cl—O	3.24	3.43

Table 9. $\text{CaCl}_2(\text{NH}_3)_2$ powder diffraction record.

<i>h k l</i>	$2\theta_o/\text{deg}$	$2\theta_c/\text{deg}$	$d_o/\text{\AA}$	$10^3 I_o/I_{\text{max}}$
0 0 2	14.384	14.333	6.1516	465
1 1 1	19.995	19.962	4.4370	311
1 0 2	20.645	20.617	4.2987	181
1 0 3	26.275	26.228	3.3891	19
1 1 3	28.653	28.638	3.1130	150
0 0 4	28.915	28.897	3.0854	54
2 0 0	29.727	29.735	3.0029	92
1 2 2	30.863	30.858	2.8950	1000
1 0 4	32.603	32.587	2.7443	169
2 0 2	33.159	33.155	2.6996	34
2 0 3		37.033		
0 2 4	37.064	37.063	2.4236	161
2 2 0	37.727	37.739	2.3825	184
1 3 1	38.311	38.290	2.3475	33
1 2 4	40.082	40.088	2.2478	12
2 2 2	40.559	40.564	2.2225	226
1 1 5	41.125	41.135	2.1932	39
2 0 4	41.942	41.942	2.1523	250
1 3 3	43.742	43.728	2.0678	32
0 4 0	46.400	46.375	1.9554	127
3 0 2	47.763	47.732	1.9027	22
0 4 2	48.827	48.791	1.8637	28
0 2 6	50.053	50.033	1.8209	129
3 2 0		51.229		
1 4 2	51.266	51.253	1.7806	33
3 1 3	52.064	52.098	1.7552	12
1 2 6	52.473	52.452	1.7425	47
3 2 2	53.489	53.481	1.7117	121
2 0 6	53.989	53.972	1.6970	42
3 0 4	54.614	54.604	1.6791	12
1 4 4	57.805	57.825	1.5938	15
3 3 1	58.571	58.565	1.5747	10
3 2 4	59.929	59.887	1.5423	14
4 0 0	61.755	61.751	1.5010	44
1 0 8	62.018	62.027	1.4952	31
4 0 2	63.767	63.757	1.4584	10
0 2 9	73.029	73.013	1.2946	17
1 4 7	73.958	73.996	1.2806	32
1 6 0	74.343	74.370	1.2749	43
2 2 9	80.737	80.765	1.1893	15
5 1 0	80.900	80.929	1.1873	11

Table 10. $\text{CaCl}_2(\text{NH}_3)_2$ position parameters in space group $Abm2$.

Atom	Site	<i>x</i>	(σ_x)	<i>y</i>	<i>z</i>	(σ_z)
Ca	4(c)	0.275	(3)	1/4	0.095	(3)
Cl1	4(a)	0		0	0	
Cl2	4(b)	1/2		0	0.205	(1)
N1	4(c)	0.494	(9)	1/4	0.440	(3)
N2	4(c)	-0.073	(17)	1/4	0.239	(9)

Table 11. Interatomic distances (Å) in $\text{CaCl}_2(\text{NH}_3)_2$.

Ca—Cl1	2.82	
Ca—Cl2	2.74	
Ca—N1	2.37	
Ca—N2	2.74	
Cl1—Cl1	3.91	
Cl2—Cl2	3.91	
Cl1—Cl2	3.93	
Cl1—N1	3.63	
Cl1—N2	3.57	3.79
Cl2—N1	3.49	
Cl2—N2	3.25	

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$\text{CaCl}_2(\text{NH}_3)_2$. The powder specimen of $\text{CaCl}_2(\text{NH}_3)_{2.40}$ was almost monophasic, judged from its diffraction record. After removal of some weak high-angle lines, the rest of the pattern could be indexed on the basis of an orthorhombic cell.

The structure model, of $\text{CaCl}_2(\text{NH}_3)_2$ stoichiometry, is depicted in Fig. 2. It may be described in terms of calcium ions in two planes ($y=1/4$ and $y=3/4$), forming a staggered arrangement, surrounded by almost perfect squares of chloride ions in the (102) planes, at $y=0$ and $y=1/2$. Two ammonia molecules, at $y=1/4$ (or $3/4$) complete a somewhat distorted octahedral coordination about Ca. Some of the distortion may be attributable to hydrogen bonding among the NH_3 molecules in the (010) plane.

Tables 9, 10 and 11 list powder data, structural parameters and interatomic distances for the diammine complex.

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