Reactivity of Ammonium Halides: Action of Ammonium Chloride and Bromide on Iron and Iron(III) Chloride and Bromide

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Abstract. Ammonium chloride and bromide, $(NH_4)Cl$ and $(NH_4)Br$, act on elemental iron producing divalent iron in $[Fe(NH_3)_2]Cl_2$ and $[Fe(NH_3)_2]Br_2$, respectively, as single crystals at temperatures around 450 °C. Iron(III) chloride and bromide, FeCl_3 and FeBr_3, react with $(NH_4)Cl$ and $(NH_4)Br$ producing the erythrosiderites $(NH_4)_2[Fe(NH_3)Cl_5]$ and $(NH_4)_2[Fe(NH_3)Br_5]$, respectively, at fairly low temperatures (350 °C). At higher temperatures, 400 °C, iron(III) in $(NH_4)_2[Fe(NH_3)Cl_5]$ is reduced to iron(II) forming $(NH_4)FeCl_3$ and, further, $[Fe(NH_3)_2]Cl_2$ in an ammonia

atmosphere. The reaction $(NH_4)Br + Fe$ (4:1) leads at 500 °C to the unexpected hitherto unknown $[Fe(NH_3)_6]_3[Fe_8Br_{14}]$, a mixedvalent Fe^{II}/Fe^I compound. Thermal analysis under ammonia and the conditions of DTA/TG and powder X-ray diffractometry shows that, for example, FeCl₂ reacts with ammonia yielding in a strongly exothermic reaction $[Fe(NH_3)_6]Cl_2$ that at higher temperatures produces $[Fe(NH_3)]Cl_2$, FeCl₂ and, finally, Fe₃N.

Keywords: Iron; Halides; Ammonium halides; Reactivity

Reaktivität von Ammoniumhalogeniden. Einwirkung von Ammoniumchlorid und -bromid auf Eisen und Eisen(III)-chlorid bzw. -bromid

Inhaltsübersicht. Ammoniumchlorid und -bromid, $(NH_4)Cl$ und $(NH_4)Br$, wirken auf elementares Eisen unter der Bildung von zweiwertigem Eisen in $[Fe(NH_3)_2]Cl_2$ bzw. $[Fe(NH_3)_2]Br_2$ ein, die in Form von Einkristallen bei etwa 450 °C gebildet werden. Eisen-(III)-chlorid und -bromid, FeCl₃ und FeBr₃, reagieren mit $(NH_4)Cl$ and $(NH_4)Br$ unter Bildung der Erythrosiderite $(NH_4)_2[Fe(NH_3)Cl_5]$ bzw. $(NH_4)_2[Fe(NH_3)Br_5]$ bei niedrigeren Temperaturen (350 °C). Bei höheren Temperaturen, 400 °C, wird Eisen(III) in $(NH_4)_2[Fe(NH_3)Cl_5]$ in Ammoniak-Atmosphäre zu Eisen(II) reduziert unter der Bildung von $(NH_4)FeCl_3$ und weiter

zu [Fe(NH₃)₂]Cl₂ umgesetzt. Bei der Reaktion (NH₄)Br + Fe (4:1) entsteht bei 500 °C völlig unerwartet das bislang unbekannte [Fe(NH₃)₆]₃[Fe₈Br₁₄], eine gemischtvalente Fe^{II}/Fe^I-Verbindung. Thermische Analysen unter Ammoniak unter den Bedingungen der DTA/TG bzw. der Pulver-Röntgen-Diffraktometrie zeigen, daß beispielsweise FeCl₂ zunächst mit Ammoniak in einer stark exothermen Reaktion zu [Fe(NH₃)₆]Cl₂ umgesetzt wird, das dann bei höheren Temperaturen nacheinander [Fe(NH₃)]Cl₂, FeCl₂ und schließlich Fe₃N bildet.

Introduction

Ammonium halides, $(NH_4)X$, may transform oxides or non-noble metals to halides, for example yttria (Y_2O_3) or yttrium into yttrium trichloride (YCl_3) [1]. As intermediates, compounds such as $(NH_4)_3[YCl_6]$, $(NH_4)_2[Sc(NH_3)I_5]$, $[Zn(NH_3)_2]Cl_2$, $[Ga(NH_3)(NH_2)]F_2$ oder $(NH_4)_6[Ta_5-(NH)_4]Cl_{17}$ [2] are observed. Their isolation and characterization may give important information on the reaction pathways leading to their formation.

Further information on these systems may be obtained through their reaction with reactive gases, most importantly with ammonia (NH_3) , together with *in situ* recording of weight gain or loss and enthalpic effects (i.e., thermogravimetry and thermal analysis) and powder diffraction patterns dependent upon temperature and/or time, respectively.

As part of our ongoing efforts [3], we have now investigated the action of ammonium chloride and bromide, $(NH_4)Cl$ and $(NH_4)Br$, on elemental iron (Fe) and on the iron chlorides and bromides with iron in the highest possible oxidation state +3, FeCl₃ and FeBr₃ [4].

Results and Discussion

The action of ammonium chloride and bromide, $(NH_4)Cl$ and $(NH_4)Br$, respectively, on elemental iron and on iron(III) chloride, FeCl₃, and bromide, FeBr₃, respectively, has been investigated by preparative means in Monel ampoules at temperatures between 350 and 500 °C. The reaction products were analyzed by single crystal and powder X-ray diffraction. Their thermal behaviour under ammonia

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Scheme 1 Reactions in the systems (NH₄)Cl/Fe and (NH₄)Cl/FeCl₃: molar ratios, temperatures and products



Scheme 2 Reactions in the system (NH₄)Br/Fe: molar ratios, temperatures and products

was investigated by thermogravimetry and difference thermal analysis (TG, DTA) and by time- and temperature-resolved X-ray powder diffractometry. Schemes 1 and 2 inform on reaction mixtures and temperatures and the products obtained.

Chlorides. Elemental iron reacts with ammonium chloride in a sealed Monel container at a temperature as high as 450 °C to yield iron(II) diammine dichloride, Fe(NH₃)₂Cl₂.

$$2 (NH_4)Cl + Fe \rightarrow [Fe(NH_3)_2]Cl_2 + H_2$$

This appears to be a key product as it is also obtained from previously produced iron(II) chloride, FeCl₂, with gaseous ammonia. Here at ambient temperature, an exothermic reaction takes place yielding the hexa-ammoniate, [Fe(NH₃)₆]Cl₂, which decomposes under an ammonia pressure of 1 bar to [Fe(NH₃)₂]Cl₂ at 115 °C according to thermal analysis data. Furthermore, iron(III) chloride, FeCl₃, reacts with ammonium chloride at about 350 °C to produce (NH₄)₂[Fe(NH₃)Cl₅], still with iron in the +3 state. At about 400 °C, iron(III) is reduced yielding (NH₄)FeCl₃, probably via an "internal" redox reaction such as:

 $6\,(\mathrm{NH}_4)_2[\mathrm{Fe}(\mathrm{NH}_3)\mathrm{Cl}_5] \rightarrow 6\,(\mathrm{NH}_4)\mathrm{Fe}\mathrm{Cl}_3 + \mathrm{N}_2 + 10\,(\mathrm{NH}_4)\mathrm{Cl} + 2\,\mathrm{HCl}.$

At 450 °C, (NH_4) FeCl₃ reacts with ammonia produced by the decomposition of (NH_4) Cl to yield $[Fe(NH_3)_2]$ Cl₂, viz.

$$(\mathrm{NH}_4)\mathrm{FeCl}_3 + \mathrm{NH}_3 \rightarrow [\mathrm{Fe}(\mathrm{NH}_3)_2]\mathrm{Cl}_2 + \mathrm{HCl}$$

Under ammonia, $Fe(NH_3)_2Cl_2$ is reduced further yielding Fe_3N with iron in the +1 state.

$$3 [Fe(NH_3)_2]Cl_2 \rightarrow Fe_3N + \frac{1}{2}N_2 + 4 (NH_4)Cl + 2 HCl$$

As HCl is often one of the reaction products, these reactions proceed under higher partial pressures of ammonia and at higher temperatures.

Bromides. In close analogy to the Fe/(NH₄)Cl system, (NH₄)Br acts on elemental iron at 350 °C irrespective of the molar ratio of 1:1 or 1:2 (Fe : (NH₄)Br) to yield (NH₄)₂[Fe(NH₃)Br₅] with iron in the +3 state. At higher temperatures (450 °C), [Fe(NH₃)₂]Br₂ is produced. (NH₄)FeBr₃ could not be detected which does not mean that it would not play a role in the reaction pathways. At even higher temperatures, 500 °C, and with a higher content of (NH₄)Br in the reaction mixture (Fe : (NH₄)Br = 1:4), a novel, hitherto unknown mixed-valent compound, [Fe(NH₃)₆]₃[Fe₈Br₁₄], appears with divalent iron in the hexammine complex and monovalent (!) iron in the octameric anion [Fe₈Br₁₄]⁶⁻. Its formation may be formulated as follows:

 $18 (NH_4)Br + 11 Fe \rightarrow [Fe(NH_3)_6]_3[Fe_8Br_{14}] + 4 HBr + 7 H_2$

Another possibility would be that $[Fe(NH_3)_2]Br_2$ formed at 450 °C undergoes an "internal" redox reaction such as:

$$\begin{array}{l} 33 \; [Fe(NH_3)_2] Br_2 \rightarrow 3 \; [Fe(NH_3)_6]_3 [Fe_8 Br_{14}] \, + \, 4 \; N_2 \, + \, 4 \; (NH_4) Br \\ & + \; 20 \; HBr. \end{array}$$

This would, in conclusion, mean that $(NH_4)_2[Fe(NH_3)Br_5]$ first produced from iron and ammonium bromide at 350 °C undergoes an internal redox reaction at 450 °C yielding $[Fe(NH_3)_2]Br_2$, which reacts further, at 500 °C, yielding $[Fe(NH_3)_6]_3[Fe_8Br_{14}]$. Under ammonia, $[Fe(NH_3)_2]Br_2$ is stable up to 375 °C after which further reduction takes place forming Fe₃N with all iron monovalent as is the case in the analogous system $[Fe(NH_3)_2]Cl_2 \rightarrow Fe_3N$.

Crystal Structures

At the obviously lowest possible reaction temperatures (350 °C), the erythrosiderites $(NH_4)_2[Fe(NH_3)Cl_5]$ and $(NH_4)_2[Fe(NH_3)Br_5]$ are obtained, the first one as single crystals. This structure, first determined for the mineral erythrosiderite, K₂[Fe(H₂O)Cl₅] [5], may be derived from the basic K₂[PtCl₆] type of stucture, all well known from textbooks [6]. Tables 1 and 2 contain the crystallographic details for $(NH_4)_2[Fe(NH_3)Cl_5]$; Fe³⁺-Cl⁻ distances are be-

	[Fe(NH ₃) ₂]Cl ₂	[Fe(NH ₃) ₂]Br ₂	(NH ₄)FeCl ₃	[Fe(NH ₃) ₆] ₃ [Fe ₈ Br ₁₄]	(NH ₄) ₂ [Fe(NH ₃)Cl ₅]
Lattice constants / pm	a = 804.2(4) b = 799.8(5) c = 373.8(2)	a = 1187.2(4) b = 592.1(1) a = 399.11(8)	a = 698.4(2) c = 599.6(2)	a = 1069.4(1) c = 2133.5(5)	a = 1372.7(2) b = 993.4(2) c = 706.1(1)
Cell volume / pm ³ Z	$240.45 \cdot 10^{6}$	$280.53 \cdot 10^{6}$	253.22 2	$2440.01 \cdot 10^{6}$	c = 700.1(1) 962.8·10 ⁶ 4
Space group Diffractometer Radiation Monochromator Temperature	Cmmm (Nr.65) Stoe IPDS II	Pbam (Nr. 55) Stoe IPDS I	P6 ₃ /mmc (Nr.194) Stoe IPDS I MoK _a . $\lambda = 71.07$ pm Graphite 20 °C	I 4/mmm (Nr. 139) Stoe IPDS I	Pnma (Nr.62) Stoe IPDS
Scan mode	$\varphi = 0^{\circ}, \omega: 2^{\circ}$ steps, 90 frames $\varphi = 90^{\circ}, \omega: 2^{\circ}$ steps, 87 frames	2°, steps, 125 frames	2° steps, 125 frames	2° steps, 100 frames	2° steps, 100 frames
Measured range / °	$3.8 < 2\theta < 70.6$	$3.8 < 2\theta < 56.3$	$3.8 < 2\theta < 56.3$	$3.8 < 2\theta < 56.3$	$3.8 < 2\theta < 56.3$
F(000)	160.0	219.9	176.0	1911.4	571.9
Absorption correction	numerical	numerical	numerical	numerical	numerical
$\mu/ \text{ mm}^{-1}$	3.90	16.77	4.19	14.34	2.89
Measured reflections	3405	3156	2236	11618	8606
Unique reflections	154	374	127	744	1242
R _{int}	0.1699	0.1661	0.0555	0.1209	0.1216
Structure solution and SHELXS-97 and SHELX				7 [7]	
Scattering factors		Internationa	al Tables for Crystallogram	hy Vol C	
Parameters	12	17	9	41	49
R ₁	0.0497 for 124 Fo > 4σ (Fo); 0.0581 for all data	0.590 for 281 Fo > 4σ (Fo); 0.591 0.0795 for all data	0.0298 for 111 Fo > 4σ (Fo) 0.0371 for all data	0.0459 for 457 Fo > 4σ (Fo) 0.085 for all data	0.0449 for 644 Fo > 4σ (Fo) 0.1131 for all data
wR_{2} (all data)	0.1629	0 1543	0 1025	0.1252	0.0970
Goodness of fit CSD	1.038 412907	0.987 412906	1.033 412904	0.984 412650	1.009 412905

Table 1 Crystallographic data and their determination for $[Fe(NH_3)_2]Cl_2$, $[Fe(NH_3)_2]Br_2$, NH_4FeCl_3 , $[Fe(NH_3)_6]_3[Fe_8Br_{14}]$, and $(NH_4)_2[Fe(NH_3)Cl_5]$

Table 2 Atomic positions and equivalent temperature factors in pm^2 for $(NH_4)_2[Fe(NH_3)Cl_5]$

Atom	Site	х	У	Z	U _{eq}
Fe	4c	0.38389(9)	0.25	0.1895(2)	228(3)
Cl1	4c	0.2522(2)	0.25	0.3983(3)	272(5)
Cl2	8d	0.3951(1)	0.0108(1)	0.1763(2)	317(4)
Cl3	4c	0.4939(2)	0.25	0.4531(3)	337(5)
Cl4	4c	0.2769(2)	0.25	0.9280(3)	349(6)
N1	4c	0.5033(5)	0.25	0.999(10)	220(10)
N2	8d	0.1420(3)	0.5007(5)	0.1588(7)	350(10)

tween 233 and 240 pm, the Fe^{3+} -N(H₃) distance is 212 pm. The $[Fe(NH_3)Cl_5]^{2-}$ octahedra are all equal and, of course, distorted but with Cl⁻-Fe³⁺-Cl⁻ angles close to 90° and the Cl⁻-Fe³⁺-N(H₃) angle almost 180°. Fig. 1 gives an impression of the crystal structure of $(NH_4)_2[Fe(NH_3)Cl_5]$.

(NH₄)FeCl₃ crystallizes with the hexagonal CsNiCl₃/ BaNiO₃ type of structure (Tables 1 and 3). Previously space group P6₃mc was addressed to (NH₄)FeCl₃ [8]; we find no reason for a deviation from space group P6₃/mmc. In the crystal structure of (NH₄)FeCl₃, [FeCl₆] octahedra share common faces forming columns that run parallel to [001]. Fe²⁺-Cl⁻ distances are all equal, 244.8(1) pm, Cl-Fe-Cl angles are 86.42(4) and 93.58(4)°, respectively.

 $Fe(NH_3)_2Cl_2$ crystallizes with the Cd(NH₃)₂Cl₂ type of structure [9] with [Fe-*trans*-(NH₃)₂Cl₄] octahedra sharing opposite edges forming infinite chains that run parallel to [001] which is in accord with the formulation



Fig. 1 Perspective view of the crystal structure of $(NH_4)_2[Fe(NH_3)X_5]$ (X = Cl,Br), the erythrosiderite type of structure

Table 3 Atomic positions and equivalent temperature factors in $\rm pm^2$ for (NH_4)FeCl_3

atom	site	х	У	Z	U _{eq}
Fe	2a	0	0	0	228(6)
Cl	6h	0.8400(1)	0.1600(1)	0.25	336(6)
Ν	2c	0.667	0.333	0.75	470(31)

[Fe(NH₃)_{2/1}Cl_{4/2}]. Therefore, Fe^{2+} - Fe^{2+} distances of 373.8(2) pm occur. Fe^{2+} - Cl^- distances are 254.0(2) pm and



Fig. 2 A representation of the chain of edge-sharing $[Fe(NH_3)_2-Hal_{4/2}]$ octahedra and perspective views of the crystal structures of $[Fe(NH_3)_2]Cl_2$ (left) and $[Fe(NH_3)_2]Br_2$ (right), representatives of the structure types of $[Cd(NH_3)_2]Cl_2$ and $[Mg(NH_3)_2]Br_2$

Table 4 Atomic positions and equivalent temperature factors in $\rm pm^2$ for $[Fe(NH_3)_2]Cl_2$

atom	site	х	У	Z	U_{eq}
Fe	2b	0.5	0	0	286(9)
Cl	4j	0.5	0.2151(2)	0.5	320(10)
N	4g	0.242(1)	0	0	333(21)

Table 5 Atomic positions and equivalent temperature factors in pm^2 for $[Fe(NH_3)_2]Br_2$

atom	site	х	у	Z	U_{eq}
Fe	2c	0	0.5	0	312(8)
Br	4h	0.1129(1)	0.2791(2)	0.5	317(5)
Ν	4g	0.8736(9)	0.243(2)	0	330(26)

 Fe^{2+} -N(H₃) distances are 207.6(9) pm. For crystallographic details see Tables 1 and 4, for a representation of the crystal structure Fig. 2. This compound has been well investigated previously, see ref. [10].

Fe(NH₃)₂Br₂ crystallizes with the $[Mg(NH_3)_2]Br_2$ type of structure [11], equally with edge-sharing [Fe-*trans*-(NH₃)₂Br₄] octahedra (Tables 1 and 5). Fe²⁺-Br⁻ and Fe²⁺-NH₃ distances are, of course, longer than in the chloride analogue, 273.7(1) and 214 pm, respectively. The Fe²⁺-Fe²⁺ distances are also longer, 399.11(8) pm. The difference between both structures lies in the arrangement of the chains relative to each other. These are arranged in the fashion of a tetragonal packing of rods in [Fe(NH₃)₂]Br₂, see Fig. 2.

 $[Fe(NH_3)_6]_3[Fe_8Br_{14}]$ exhibits a crystal structure hitherto unobserved (Tables 1 and 6). This compound is mixed-valent and contains Fe²⁺ in an octahedral surrounding of NH₃ ligands with Fe²⁺-N(H₃) distances ranging from 215 to

Table 6 Atomic positions and equivalent temperature factors in pm^2 for[Fe(NH₃)₆]₃[Fe₈Br₁₄]

atom	site	x	у	Z	U _{eq}
Fe1	16m	0.1411(1)	0.1411(1)	0.0702(1)	578(7)
Fe2	4d	0	0.5	0.25	226(7)
Fe3	2b	0.5	0.5	0	219(10)
Br1	4e	0	0	0.1364(1)	404(7)
Br2	8i	0.2739(2)	0	0	414(5)
Br3	16m	0.26903(8)	0.26903(8)	0.13465(6)	422(4)
N1	8g	0	0.5	0.1476(7)	473(40)
N2	8j	0.5	0.704(1)	0	483(42)
N3	4e	0.5	0.5	0.899(1)	472(58)
N4	16n	0	0.297(1)	0.2474(5)	437(27)



Fig. 3 Perspective view of the crystal structure of $[Fe(NH_3)_6]_3[Fe_8Br_{14}]$ and of the octameric anion $[Fe_8Br_{14}]^{6-}$ therein

219 pm and Fe¹⁺ in tetrahedral surrounding with Fe¹⁺-Br⁻ distances of 237.4(2) and 255.7(2) (2x) and 255.8(3) pm. Eight of these tetrahedra are connected such that an octanuclear anion [Fe₈Br₁₄]⁶⁻ occurs were the Fe¹⁺ ions occupy the corners of an almost undistorted cube, six bromide ions reside as μ_4 ligands above the faces of the cube and eight additional bromide ions are terminal, in accord with the formulation [Fe₈(μ_4 -Br₆)(μ_1 -Br₈)]⁶⁻. These anions (Fig. 3) are isolated from each other as are the cations [Fe(NH₃)₆]²⁺. A tetragonal body-centered crystal structure occurs with the anions residing at the corners and in the center of the unit cell and with the cations centering the (001) faces and residing on the (011) faces and on the [001] edge, as is illustrated in Fig. 3. The octameric anion is also known from (Et₄N)₂[Fe₈S₆I₈](CH₂Cl₂)₂ [12].

Thermal Behaviour

The reaction of the iron(II) and iron(III) chlorides and bromides, respectively, with ammonia was investigated by powder temperature/time resolved X-ray diffractometry and by simultaneous DTA/TG analysis.

Fig. 4 gives, for example, the DTA and TG curves of the reaction of $FeCl_2$ with ammonia. At room temperature, a



Fig. 4 Thermogravimetry (TG) and difference thermal analysis (DTA) diagrams of the reaction of iron(II) chloride with ammonia

spontaneous exothermic reaction takes place with the formation of $[Fe(NH_3)_6]Cl_2$. With increasing temperature und an atmosphere of about 1 bar of NH₃, this is gradually decomposed to $[Fe(NH_3)_2]Cl_2$ at 115 °C which loses further ammonia at 290 °C with the binary FeCl₂ formed at 360 °C (there is one further step at about 350 °C which could be attributed to "FeCl₂(NH₃)" which could not be characterized further). Iron(II) chloride then reacts with ammonia yielding the nitride Fe₃N.

The same experiment, $FeCl_2 + NH_3(gas)$, was carried out in the X-ray powder diffractometer (Fig. 5). There $[Fe(NH_3)_6]Cl_2$ is also produced spontaneously and crystalline at ambient temperature. Interestingly, $Fe(NH_3)_2Cl_2$ is only formed at 225 °C, at a much higher temperature than in the DTA/TG experiment which may be due to a somewhat higher ammonia pressure. At about 350 °C, Fe₃N is produced. FeCl₂ can not be observed, most certainly because the successive reactions $[Fe(NH_3)_2]Cl_2 \rightarrow FeCl_2 \rightarrow Fe_3N$ are too fast to be observed in the slow equilibrium controlled X-ray experiment.

Similar reactions take place when iron(III) chloride is reacted with ammonia: First [Fe(NH₃)₆]Cl₃ is produced spontaneously. At about 325 °C [Fe(NH₃)₂]Cl₂ is observed, formed by reduction of iron(III) to iron(II) and release of ammonia. Of course, the so produced [Fe(NH₃)₂]Cl₂ reacts at 350 °C yielding Fe₃N.

Iron(II) bromide, FeBr₂, also reacts with ammonia forming [Fe(NH₃)₆]Br₂ which decomposes to Fe(NH₃)₂Br₂ at 225 °C in the X-ray diffraction experiment under ammonia. This first crystallizes with the [Cd(NH₃)₂]Cl₂ type of structure and transforms to the [Mg(NH₃)₂]Br₂ type at 375 °C. Note that the latter structure was observed from single crystals that were obtained by the action of (NH₄)Br on elemental iron. [Fe(NH₃)₂]Br₂ is finally transformed to Fe₃N at 400 °C.

Experimental Details

Iron and ammonium chloride, $(NH_4)Cl$, were purchased from Merck (reinst), $(NH_4)Br$ as p.a., sublimed quality from Acros Organics, New Jersey, USA. Ammonia was 6.0 grade from Linde (Hannover). All other chemicals used were of the highest possible purity.

Iron trichloride, FeCl₃, was produced from the elements. Reduction with hydrogen gas at 320-340 °C yields iron dichloride, FeCl₂. For anhydrous FeBr₂, iron was dissolved in conc. hydrobromic acid solution under anaerobic conditions (argon stream) and the solvent was removed at 100 °C under vaccum.

Ampoules made of tubing of the Monel alloy (Cu32Ni68, DIN 2.4360) were used as reaction containers. The educt mixtures were filled within an argon dry box (M. Braun, Garching) in ampoules that had been sealed at one end using an helium arc welder. These were then crimped, transferred to the arc welder and sealed at the second end. The Monel ampoules were then jacketed with silica ampoules under a slight vacuum. They were then heated in tubular



Fig. 5 The same reaction as recorded in Fig. 4 now in the Bühler chamber of a X-ray powder diffractometer with θ - θ geometry

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furnaces at chosen temperatures or featuring temperature programs and, after cooling, opened in the argon dry box.

Single crystals were selected under a microspcope equipped with polarisator/analysator in an argon dry box, and mounted in thinwalled glass capillaries. The crystals were checked for their quality on an image plate diffractometer IPDS (I and II, Stoe & Cie., Darmstadt), and intensity data sets were collected afterwards using the same diffractometer. For details see Table 1. Further details may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (FAX: (+49)7247-808-666, email: crysdata@fiz-karlsruhe.de) referring to the CSD number, the authors and the journal citation.

The reaction products were also checked for their purity and their phase content making use of a Huber Guinier diffracometer; small powder samples were therefore filled in thin-walled glass capillaries in the argon dry box immediately after opening the reaction containers. For reactions under ammonia the Stoe θ - θ diffracometer equipped with a so-called Bühler camera (HDK 2.4) was used.

Thermal analysis (thermogravimetry, TG, and difference thermal analysis, DTA) was carried out with a Mettler TA 1 where reactions under an ammonia gas flow at a pressure of approximately 1 bar of ammonia were possible.

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References

- G. Meyer, T. Staffel, S. Dötsch, Th. Schleid, *Inorg. Chem.* 1985, 24, 3504; G. Meyer, *Inorg. Synth.* 1989, 25, 146.
- [2] M. Simon, G. Meyer, Z. Kristallogr. 1996, 211, 327; M. Roos, G. Meyer, Z. Anorg. Allg. Chem. 1999, 625, 1839; C.H. Mac-Gillavry, J.M. Bijvoet, Z. Kristallogr. 1936, 94A, 231; T. Yamaguchi, O. Lindqvist, Acta Chem. Scand. 1981, 35, 727; M. Simon, G. Meyer, J. Chem. Soc., Chem. Comm. 1993, 460; M. Simon, G. Meyer, Eur. J. Solid State Inorg. Chem. 1997, 34, 73.
- [3] G. Meyer, Adv. Synth. React. Solids 1994, 2, 1.
- [4] S. Bremm, Dissertation, Univ. zu Köln, 2002.
- [5] A. Bellanca, Ric. Sci. Ricost. 1947, 17, 1360.
- [6] U. Müller, Anorganische Strukturchemie, B.G. Teubner, Stuttgart (1991); Inorganic Structural Chemistry, Wiley, Chichester (1993).
- [7] G. M. Sheldrick, Programs for the solution and refinement of crystal structures, Göttingen, 1997.
- [8] M. Amit, A. Zodkevitz, J. Makovsky, Israel J. Chem. 1970, 8, 737.
- [9] C. H. MacGillavry, J. M. Bijvoet, Z. Kristallogr. 1936, 94, 231.
- [10] R. Eßmann, G. Kreiner, A. Niemann, D. Rechenbach, A. Schmieding, T. Sichla, U. Zachwieja, H. Jacobs, Z. Anorg. Allg. Chem. 1996, 621, 1161.
- [11] A. Leineweber, H. Jacobs, P. Fischer, G. Böttger, J. Solid State Chem. 2001, 156, 487.
- [12] S. Pohl, W. Saak, Angew. Chem. 1984, 96, 886; Angew. Chem. Int. Edit. Engl. 1984, 23, 907.