



# Cobalt Nitrides

# Synthesis of Metastable $Co_4N$ , $Co_3N$ , $Co_2N$ , and $CoO_{0.74}N_{0.24}$ from a Single Azide Precursor and Intermediates in $CoBr_2$ Ammonolysis

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**Abstract:** Metastable cobalt nitrides  $Co_4N$ ,  $Co_3N$ ,  $Co_2N$ , and cobalt oxide nitride  $CoO_{0.74}N_{0.24}$  were synthesized by ammonolysis of one single metastable azide precursor,  $[Co(NH_3)_5N_3]Cl_2$ , in high purity by controlled variation of the reaction conditions (temperature, duration, gas atmosphere, and flow rate). The alternative route towards cobalt nitrides by ammonolysis of  $CoBr_2$  proceeds via  $[Co(NH_3)_6]Br_2$  and  $Co(NH_3)_2Br_2$  to exclusively yield  $Co_3N$ . For  $Co_3N_{1.1}$  a complex magnetic behavior is observed:

dominating ferromagnetic ordering at low temperatures and a small coercive field of 10 mT.  $Co_2N$  orders antiferromagnetically below 10 K. Electronic structure calculations [DFT, generalized-gradient approximation (GGA)+U] on  $CoO_{0.75}N_{0.25}$  reveal that the experimentally observed rock-salt structure is less stable than the sphalerite-type polymorph by about 30 kJ mol<sup>-1</sup> and possesses an antiferromagnetically ordered ground state.

# Introduction

In the temperature range up to 1200 °C cobalt dissolves only a very small amount of nitrogen (up to  $8.5 \times 10^{-5}$  atom-%).<sup>[1]</sup> First reports about the formation of a metastable cobalt nitride with a proposed composition of Co<sub>3</sub>N<sub>2</sub> were published at the beginning of the 20th century.<sup>[2–4]</sup> Nowadays, the existence of four cobalt nitrides is confirmed, namely Co<sub>4</sub>N,<sup>[5]</sup> Co<sub>3</sub>N,<sup>[4]</sup> Co<sub>2</sub>N,<sup>[4]</sup> and CoN.<sup>[6]</sup>

Co<sub>4</sub>N was first synthesized in 1960 as 30–50 nm thick layers by the nitridation of thin cobalt layers in an ammonia atmosphere between 350 and 450 °C within 1–7 h. Above 570 °C this Co<sub>4</sub>N film decomposes to cubic  $\beta$ -Co.<sup>[5]</sup> Co<sub>4</sub>N crystallizes in the perovskite-type structure of  $\gamma'$ -Fe<sub>4</sub>N with an approximately 5.5 % smaller unit cell parameter.<sup>[7]</sup> At lower temperatures between 200 and 350 °C the formation of Co<sub>3</sub>N and a still not fully characterized hexagonal nitride, Co<sub>x</sub>N, was observed.<sup>[5]</sup> Nowadays, there are various approaches for the controlled synthesis of Co<sub>4</sub>N thin layers.<sup>[8–13]</sup> However, the synthesis of bulk samples of Co<sub>4</sub>N remains challenging. The first reported production of bulk Co<sub>4</sub>N was achieved by an urea-assisted synthesis route in 2013. Ferromagnetic nanoparticles with sizes

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[c] Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany around 22 nm, a saturation magnetization of 123.6 emu g<sup>-1</sup>, and a low coercive field of 7.4  $\times$  10<sup>-3</sup> T were obtained.<sup>[14]</sup> Co<sub>4</sub>N is a powerful catalytic material for hydrodenitrogenation of crude oil,<sup>[15]</sup> decomposition of hydrazine,<sup>[16]</sup> reduction of NO,<sup>[17,18]</sup> and oxidation of CO.<sup>[19]</sup>

Metastable Co<sub>3</sub>N crystallizes in the  $\epsilon$ -Fe<sub>3</sub>N type structure with only a narrow homogeneity range. A stability range from 7.6 to 8.0 wt.-% nitrogen was derived from X-ray diffraction data.<sup>[4]</sup> From caloric measurements a standard formation enthalpy between 4<sup>[20]</sup> and 8 kJ mol<sup>-1[21]</sup> was determined, indicating metastability with respect to decomposition into the elements. Calculations of the thermodynamic properties delivered a consistent value of 5.6 kJ mol<sup>-1,[22]</sup> The traditional synthesis route is based on the thermal decomposition of Co<sub>2</sub>N at about 280 °C. However, this reaction is difficult to control, and often the reaction product is not single-phase.<sup>[4]</sup> In the last years, Co<sub>3</sub>N moved into the focus of research as a potential electrode material in lithium-ion batteries.<sup>[23–25]</sup> Additionally, nitrogen-rich samples Co<sub>3</sub>N<sub>1+x</sub> exhibit a weak antiferromagnetic coupling below 11 K.<sup>[26]</sup>

Co<sub>2</sub>N is an isotype of  $\zeta$ -Fe<sub>2</sub>N with no significant deviation from the ideal 2:1 composition. Different synthesis pathways were reported: (i) ammonolysis of thermally decomposed cobalt(II) oxalate (cf. pyrophoric iron), (ii) ammonolysis of the reduction product of Co<sub>3</sub>O<sub>4</sub> in flowing hydrogen, (iii) ammonolysis of CoBr<sub>2</sub>, and (iv) ammonolysis of CoF<sub>2</sub>•NH<sub>4</sub>F·Co(OH)<sub>2</sub>• 2H<sub>2</sub>O.<sup>[4]</sup> In the first two synthesis approaches, an intermediate formation of cobalt powder containing a large quantity of stacking faults was observed, leading to an enhanced reactivity during the following nitridation with flowing ammonia at approximately 380 °C.<sup>[27,28]</sup> In the ammonolysis of CoBr<sub>2</sub> an intermediate formation of ammoniates was observed;<sup>[4]</sup> however, no

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details on the composition or the structure of those ammoniates are given. Similar to the reaction behavior of FeCl<sub>2</sub>,<sup>[29,30]</sup> at higher temperatures a reformation of a very fine (often amorphous) powder of CoBr<sub>2</sub> occurs, enabling an enhanced formation of Co<sub>2</sub>N.<sup>[4,31]</sup> The direct formation of Co<sub>2</sub>N starting from elemental cobalt seems possible if a low partial pressure of hydrogen is ensured.<sup>[32]</sup> Additionally, a high-pressure–high-temperature synthesis of Co<sub>2</sub>N starting from cobalt and nitrogen was reported at 10 GPa and 1500 °C.<sup>[33]</sup>

For thin layers of CoN, depending on the applied synthesis method, either the rock-salt<sup>[34]</sup> or the sphalerite structure type<sup>[35,36]</sup> was observed. For sphalerite-type CoN the thermal decomposition behavior was investigated: Up to 231 °C CoN is stable but decomposes above this temperature successively via Co<sub>2</sub>N and Co<sub>3</sub>N to eventually be completely converted into  $\alpha$ -Co at 300 °C.<sup>[35]</sup> In the 1960s, different amino–azido complexes of cobalt such as [Co(NH<sub>3</sub>)<sub>6</sub>](N<sub>3</sub>)<sub>3</sub>, [Co(NH<sub>3</sub>)<sub>5</sub>(N<sub>3</sub>)](N<sub>3</sub>)<sub>2</sub>, and [Co(NH<sub>3</sub>)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub>]N<sub>3</sub> were used to synthesize powders of CoN.<sup>[6,37–40]</sup> However, as a result of their high azide content, those precursors tend to undergo an explosive thermal decomposition between 100 and 140 °C depending on the particle size.<sup>[39,40]</sup>

Oxide nitrides of cobalt  $CoO_{1-x}N_x$  were prepared in the form of nanocrystalline particles and thin layers by thermal decomposition of Co(CO)<sub>3</sub>(NO). The thin layers were grown by chemical vapor deposition and showed a strongly reduced electrical resistivity, mainly due to the formation of mixed valence states for Co by substituting N<sup>3-</sup> for O<sup>2-</sup>. X-ray diffraction data showed the formation of  $CoO_{1-x}N_x$  in the sphalerite structure type with  $x \approx 0.4$ , as extracted from the unit cell expansion according to a Vegard's law approximation. Chemical analysis in combination with Rutherford backscattering spectrometry, in contrast, resulted in an average composition of CoO<sub>0.9</sub>N<sub>0.5</sub>. However, a large inhomogeneity was detected in the samples with compositions ranging from CoO<sub>0.78</sub>N<sub>0.12</sub> to CoO<sub>1.3</sub>N<sub>0.67</sub>. Thermogravimetric (TG) measurements revealed thermal stability up to 390 °C.<sup>[41]</sup> DFT calculations on CoO<sub>0.5</sub>N<sub>0.5</sub> delivered an energetic preference of the sphalerite structure type over the rock-salt structure type, in full agreement with the experimental results. The calculated enthalpy indicates a phase transition from the sphalerite to the rock-salt structure type around 30 GPa. From supercell calculations, a preference for the formation of oxygenrich metastable oxide nitrides  $CoO_{1-x}N_x$  and no tendency for anionic ordering was concluded. Additionally, all investigated compositions showed vanishing magnetic moments.<sup>[42]</sup>

Information on ammoniates of CoBr<sub>2</sub> is scarce in literature. The first data about ammoniates of cobalt(II) halides CoX<sub>2</sub> (X = Cl, Br, I) were reported on the tensiometrically monitored decomposition of the respective hexaammoniates [Co(NH<sub>3</sub>)<sub>6</sub>]X<sub>2</sub>. A stepwise decomposition via diammoniate Co(NH<sub>3</sub>)<sub>2</sub>X<sub>2</sub> and monoammoniate Co(NH<sub>3</sub>)X<sub>2</sub> (depending on the halide X) was observed.<sup>[43]</sup> However, crystallographic data were only recorded for [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub><sup>[44]</sup> and Co(NH<sub>3</sub>)Cl<sub>2</sub>.<sup>[45]</sup>

Herein, we present a new and easily controllable synthesis approach for metastable cobalt nitrides  $Co_4N$ ,  $Co_3N$ , and  $Co_2N$  as well as the formation of an oxygen-rich cobalt oxide nitride  $CoO_{0.74}N_{0.24}$  from a single metastable precursor

 $[Co(NH_3)_5N_3]Cl_2$ . Additionally, due to the reduced azide content,  $[Co(NH_3)_5N_3]Cl_2$  was found to be a less explosive alternative precursor compared to  $[Co(NH_3)_6](N_3)_3$ ,  $[Co(NH_3)_5(N_3)](N_3)_2$ , and  $[Co(NH_3)_4(N_3)_2]N_3$ . Furthermore, the intermediates involved in the ammonolysis of CoBr<sub>2</sub> to form Co<sub>3</sub>N were investigated in detail. The resulting reaction products were analyzed by Rietveld refinements of powder X-ray diffraction (PXRD) data, simultaneous thermal analysis in different gas atmospheres, and infrared vibrational spectroscopy. For Co<sub>2</sub>N and Co<sub>3</sub>N a characterization of the magnetic properties was carried out.

Previous calculations on  $CoO_{0.5}N_{0.5}$  indicated the sphalerite crystal structure to be significantly more stable than the rocksalt structure because the latter structure type calls for stronger antibonding Co–Co interactions;<sup>[42]</sup> nonetheless, this very stable structure type is observed for  $CoO_{0.74}N_{0.24}$ . The electronic structure of this composition was therefore re-investigated by means of DFT [generalized-gradient approximation (GGA)+*U*] including both structure types and modeling ground states with diamagnetic, ferromagnetic, and antiferromagnetic spin orderings.

# **Results and Discussion**

## Synthesis and Decomposition of [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub>

Single-phase metastable purple [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> was obtained according to the reported procedure,<sup>[46]</sup> its structure being confirmed by PXRD and chemical analysis. In the following, the term metastability for binary cobalt nitrides is used in the sense that they tend to exothermally decompose to the elements by providing sufficient (thermal) activation energy. The azide precursor exothermally decomposes under liberation of dinitrogen gas. During a differential thermal analysis (DTA)/TG measurement (see Figure 1) in an argon atmosphere, two not fully resolved steps in the TG curve with a total mass loss of 48.2 % are observed above 144 and 233 °C. The mass loss represents approximately the complete release of nitrogen and hydrogen from the sample ( $\Delta m_{\text{exp.}} = -49.4$  %). In the DTA curve three signals are detected, namely an exothermal signal at 155.5 °C (onset) and two endothermal signals at 182.9 °C (onset) and 204.6 °C (onset). We conclude that the exothermal signal at lowest temperature is caused by decomposition of azide anions. Previously, a slow decomposition of [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> was observed above 120 °C and an explosive decomposition at 195 °C after approximately 50 s of annealing.<sup>[46]</sup> For amino-azido complexes of cobalt with higher azide concentrations (see Introduction) explosive decomposition of the azide was detected between 110 and 140 °C.[37-40] In general, the results from our DTA/TG measurement are in accordance with the decomposition behavior of [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> reported in the literature; however, sudden explosive behavior during our DTA/TG measurements was prohibited by a low heating rate. The two endothermal signals observed for the decomposition of  $[Co(NH_3)_5N_3]Cl_2$ can be related to the formation of firstly Co(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and subsequently Co(NH<sub>3</sub>)Cl. In contrast to the reported decomposition of [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>, no clear steps in our TG curve of  $[Co(NH_3)_5N_3]Cl_2$  were observed, but the obtained decomposition temperatures coincide well with the reported values 182 and 230 °C,<sup>[43]</sup> respectively.





Figure 1. Simultaneous DTA (red) and TG (black) measurement of  $[Co(NH_3)_5N_3]Cl_2$  in Ar, heating rate 0.25 K min^{-1}.

#### Synthesis and Characterization of Co<sub>4</sub>N

Metastable Co<sub>4</sub>N can be synthesized from  $[Co(NH_3)_5N_3]Cl_2$  in flowing ammonia only in a small temperature interval between 400 and 450 °C to avoid formation of  $\beta$ -Co. During Rietveld refinements of the collected PXRD data of a sample synthesized at 425 °C within 8 h (see Figure 2 and Table 1) a very small residue of  $\beta$ -Co was discovered. From our experimental results we conclude that the reaction of  $[Co(NH_3)_5N_3]Cl_2$  to Co<sub>4</sub>N is not completed at 400 °C, and decomposition of Co<sub>4</sub>N to  $\beta$ -Co already occurs at 450 °C. This is supported by our experiments: besides Co<sub>4</sub>N significant amounts of  $\beta$ -Co were found even after 12 h at 400 °C, and at 450 °C only small quantities of Co<sub>4</sub>N were observed next to  $\beta$ -Co.



Figure 2. Rietveld refinements of the crystal structure of Co<sub>4</sub>N (Mo- $K_{a1}$  radiation). The measured (red circles), calculated (black line), and difference (observed–calculated, blue line) patterns as well as the Bragg positions of Co<sub>4</sub>N (vertical bars) are shown. The asterisk marks the position of the most intense reflection of  $\beta$ -Co. The most intense superstructure reflection due to primitive Co<sub>4</sub>N as compared to simple *fcc* Co is clearly visible at  $2\Theta = 15.38^{\circ}$ . Cobalt occupies the Wyckoff sites 1*a* and 3*c* [ $B_{iso}$ (Co) = 0.22(2) × 10<sup>4</sup> pm<sup>2</sup>], while nitrogen is located at 1*b* [ $B_{iso}$ (N) = 0.04(4) × 10<sup>4</sup> pm<sup>2</sup>].



Table 1. Unit cell parameters and residual values of Co<sub>4</sub>N, Co<sub>3</sub>N, Co<sub>2</sub>N, and CoO<sub>0.74</sub>N<sub>0.24</sub> as observed from Rietveld refinements (Mo- $K_{\alpha 1}$  radiation).

Parameter	Co <sub>4</sub> N	Co <sub>3</sub> N	Co <sub>2</sub> N	CoO <sub>0.74</sub> N <sub>0.24</sub>
Space group	Pm3m	<i>P</i> 6 <sub>3</sub> 22	Pbcn	Fm3m
<i>a</i> [pm]	374.84(1)	464.35(2)	434.08(4)	425.51(3)
<i>b</i> [pm]			569.68(5)	
<i>c</i> [pm]		435.34(2)	460.41(4)	
V [10 <sup>6</sup> pm <sup>3</sup> ]	52.666(3)	81.292(5)	113.85(2)	77.045(9)
R <sub>p</sub> [%]	7.46	5.18	8.53	7.33
R <sub>wp</sub> [%]	9.51	6.65	11.3	9.25
R <sub>Bragg</sub> [%]	8.53	7.65	10.5	17.0

A stepwise decomposition of cobalt nitrides with higher nitrogen content via Co<sub>4</sub>N to  $\beta$ -Co was reported previously.<sup>[5]</sup> During a DTA/TG measurement of Co<sub>4</sub>N in an argon atmosphere (see Figure S1) we observe the following reaction behavior: Above 613 °C a mass loss of 6.1 % occurs. In parallel, an exothermal signal at 703.8 °C (onset) is observed as anticipated for a metastable compound. The expected mass loss for the decomposition of Co<sub>4</sub>N to  $\beta$ -Co is 5.6 %. Due to the metastable nature of Co<sub>4</sub>N, it is clear that a strongly limited temperature range is suitable for the synthesis of Co<sub>4</sub>N.

#### Synthesis and Characterization of Co<sub>3</sub>N

For the synthesis of  $Co_3N$  three different strategies were studied: (i) ammonolysis of  $[Co(NH_3)_5N_3]Cl_2$  in a pure ammonia atmosphere, (ii) ammonolysis of  $[Co(NH_3)_5N_3]Cl_2$  in a diluted ammonia atmosphere, and (iii) ammonolysis of  $CoBr_2$ .

## Ammonolysis of [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub>

During ammonolysis of  $[Co(NH_3)_5N_3]Cl_2$  at 400 °C in flowing ammonia within 8 h a sample of Co<sub>3</sub>N containing a significant amount of  $\beta$ -Co was obtained. To achieve a single-phase sample of Co<sub>3</sub>N, a change in the gas atmosphere, the temperature program, and a reduction of the amount of precursor was necessary. Single-phase Co<sub>3</sub>N, according to X-ray diffraction, is obtained in a diluted ammonia gas atmosphere (21 vol.-% NH<sub>3</sub> in Ar) by annealing  $[Co(NH_3)_5N_3]Cl_2$  first at 350 °C (5 h) and then at 400 °C (5 h).

#### Ammonolysis of CoBr<sub>2</sub>

In contrast to the pioneering investigations presented by Juza and Sachße,<sup>[4]</sup> during the ammonolysis of CoBr<sub>2</sub> no formation of Co<sub>2</sub>N was observed upon application of a low ammonia gas flow (100 ml min<sup>-1</sup>). Instead, the formation of hexagonal Co<sub>3</sub>N occurs, similar to the ammonolysis of FeCl<sub>2</sub> leading to  $\epsilon$ -Fe<sub>3</sub>N.<sup>[30]</sup> Directly after the contact between ammonia and CoBr<sub>2</sub> a swelling of the starting material is observed, which is accompanied by a color change from green to blue and is caused by the exothermal formation of the hexaammoniate [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub>.<sup>[43,44]</sup> The hexaammoniate can be recovered as a single-phase microcrystalline powder. The results of the Rietveld refinements of the PXRD data are gathered in Figure S2 and Table 2 and are in good agreement with reported data.<sup>[44]</sup>

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The infrared vibrational spectrum can be found in Figure S3, and the respective wavelengths of the vibrational modes are presented in Table 4.

Table 2. Structural data from Rietveld refinements for  $[Co(NH_3)_6]Br_2$  and  $Co(NH_3)_2Br_2$  (Mo- $K_{\alpha 1}$  radiation). In  $[Co(NH_3)_6]Br_2$  cobalt is located at Wyckoff site 4*a*, bromine at 8*c*, nitrogen at 24*e*, and hydrogen at 96*k*. In  $Co(NH_3)_2Br_2$  cobalt is located at 2*a*, bromine at 4*h*, nitrogen at 4*g*, and hydrogen at 8*i*. Parameters fixed during the refinements are marked by \*.

Parameter	$[Co(NH_3)_6]Br_2$	Co(NH <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub>
Space group	Fm3m	Pbam
<i>a</i> [pm]	1039.2(1)	587.36(9)
<i>b</i> [pm]		1173.7(2)
<i>c</i> [pm]		392.58(5)
V [10 <sup>6</sup> pm <sup>3</sup> ]	1122.3(2)	270.64(7)
B <sub>iso</sub> (Co) [10 <sup>4</sup> pm <sup>2</sup> ]	2.0(2)	4.6(3)
x(Br)		0.261(9)
y(Br)		0.3900(4)
$B_{\rm iso}({\rm Br}) \ [10^4 \ {\rm pm}^2]$	2.9(2)	1.3(2)
<i>x</i> (N)	0.340(6)	0.309(4)
<i>y</i> (N)		0.124(3)
$B_{\rm iso}({\rm N}) \ [10^4 \ {\rm pm}^2]$	0.5*	0.8(8)
<i>x</i> [H(1)]	0.077(3)	0.38(1)
<i>y</i> [H(1)]		0.11*
<i>z</i> [H(1)]	0.265(3)	$0.14^* = z[H(2)]$
B <sub>iso</sub> [H(1)] [10 <sup>4</sup> pm <sup>2</sup> ]	0.5*	$8(1) = B_{iso}[H(2)]$
<i>x</i> [H(2)]		0.23*
<i>y</i> [H(2)]		0.18*
<i>P</i> (H)	0.75*	0.75*
R <sub>p</sub> [%]	2.21	2.59
R <sub>wp</sub> [%]	2.79	3.30
R <sub>Bragg</sub> [%]	8.36	12.1

To investigate the thermal decomposition behavior of [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> a DTA/TG/evolved gas analysis (EGA) measurement in a helium atmosphere up to 900 °C was carried out (see Figure S4), (Table 3). Three steps are observed in the TG curve. In the first step above 78 °C a mass loss of 16.2 % is detected. This is related to the loss of four molecules of NH<sub>3</sub> per formula unit. However, for the release of four molecules of NH<sub>3</sub> a mass loss of 21.2 % is expected. Deviations to lower measured values in such experiments are well known for the similar hexaammoniates [Mn(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub><sup>[49]</sup> and [Fe(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub><sup>[29,30]</sup> due to their low decomposition temperatures and thus partial ammonia loss during sample preparation. The loss of four molecules of NH<sub>3</sub> results in the formation of diammoniate Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>, which crystallizes isotypically to Fe(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>.<sup>[29]</sup> Above 168.5 °C a second mass loss of 12.6 % occurs; this is related to the loss of the residual two NH<sub>3</sub> molecules per formula unit and the reformation of CoBr<sub>2</sub>. Above 635 °C the evaporation of CoBr<sub>2</sub> starts. For the first two steps only signals for m/z = 15 (NH<sup>+</sup>), 16 (NH<sub>2</sub><sup>+</sup>), and 17 (NH<sub>3</sub><sup>+</sup>) are observed in the mass spectra. In perfect accordance with the observation for FeCl<sub>2</sub>,<sup>[30]</sup> for CoBr<sub>2</sub> the evapo-

Table 3. DTA/TG/EGA measurement of  $[{\rm Co}({\rm NH}_3)_6]{\rm Br}_2$  in He. The respective onset temperatures are given.

	TG			FGA	
T [°C]	$\Delta m_{\rm obs.}$ [%]	$\Delta m_{\mathrm{exp.}}$ [%]	Compound	m/z	
78	-16.2	-21.23	Co(NH <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub>	15, 16, 17	
168.5	-12.6	-10.61	CoBr <sub>2</sub>	15, 16, 17	
635	-62.6	n/s	evaporation	n/s	

ration temperature is decreased by about 30 K by the treatment of CoBr<sub>2</sub> with NH<sub>3</sub> compared to that of pristine CoBr<sub>2</sub>,<sup>[50]</sup> indicating an increasing reactivity during the formation of Co<sub>3</sub>N in the ammonolysis reaction.

The diammoniate  $Co(NH_3)_2Br_2$  is synthesized in a controlled way by the reaction of  $CoBr_2$  in flowing ammonia at 160 °C and cooling under dynamic vacuum. The resulting powder is singlephase according to Rietveld refinements (see Table 2 and Figure 3) and IR vibrational spectroscopy (see Table 4 and Figure S3).



Figure 3. Rietveld refinements of the crystal structure of  $Co(NH_3)_2Br_2$  (Mo- $K_{\alpha 1}$  radiation). The measured (red circles), calculated (black line), and difference (observed–calculated, blue line) patterns as well as the Bragg positions of  $Co(NH_3)_2Br_2$  (vertical bars) are shown.

Table 4. Wave numbers  $\tilde{\nu}$  [cm<sup>-1</sup>] of the NH<sub>3</sub> vibrational modes from IR spectroscopy of [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> and Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> compared to reference values are marked by #.<sup>[51,52]</sup>

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Vibrational mode	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Br <sub>2</sub>	$[Co(NH_3)_6]Br_2^{\#}$	$Co(NH_3)_2Br_2$	Ni(NH <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub> <sup>#</sup>
$v_{as}$ (N–H)	3341	3343	3310	3347
$\nu_{s}$ (N–H)	3250	3230	3233	3264
$2\delta_{\rm as}$ (HNH)	3191	3156	3147	3171
$\delta_{as}$ (HNH)	1596	1600	1590	1615
$\delta_{\sf s}$ (HNH)			1406	1405
$\delta_{\sf s}$ (HNH)			n/s	1258
$\delta_{\rm s}$ (HNH)	1170	1172	1244	1247
$\varrho$ (NH <sub>3</sub> )	643	645	642	674
<i>ϱ</i> (NH₃)			591	607
$\varrho$ (NH <sub>3</sub> )			420	442

The reaction behavior changes significantly if the gas atmosphere is changed to ammonia. A DSC/TG experiment on  $[Co(NH_3)_6]Br_2$  (see Figure S5) was carried out in 21 vol.-% NH<sub>3</sub> in Ar up to 445 °C. After 3 h the reaction mixture was cooled to ambient temperature. A PXRD pattern recorded afterwards shows the formation of single-phase Co<sub>3</sub>N (see Figure 4 and Table 5). In general, the same decomposition sequence is observed for  $[Co(NH_3)_6]Br_2$  in an inert atmosphere as well as for  $[Fe(NH_3)_6]Cl_2$ .<sup>[30]</sup> Due to the higher ammonia partial pressure in





the differential scanning calorimetry (DSC)/TG experiment compared to that in the DTA/TG/EGA experiment, the respective decomposition temperatures are shifted to higher values. The TG curve shows two steps above 160 °C with a mass loss of 20.6 and 58.5 % above 243 °C. The first step is related to the release of four molecules of NH<sub>3</sub> per formula unit from [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> with formation of Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>. The latter step is caused by the decomposition of Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> and the starting formation of Co<sub>3</sub>N accompanied by a release of ammonium bromide. For the reaction of [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> to Co<sub>3</sub>N a mass loss of 80.2 % is expected, compared to the experimental 79.1 %. In the DSC curve two endothermal signals at 178.9 °C (onset) and 268.4 °C (onset) are obtained. In contrast to the reported tensiometric decomposition measurements on [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub><sup>[43]</sup> and the thermal decomposition of [Fe(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub><sup>[30]</sup> and  $Cu(NH_3)_2F_2$ ,<sup>[53]</sup> we observed no formation of a monoammoniate; however, for [Fe(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> also no formation of a monoammoniate was found.<sup>[29]</sup> A synthesis of Co<sub>3</sub>N starting from Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> is equally possible.



Figure 4. Rietveld refinements of the crystal structure of Co<sub>3</sub>N (Mo- $K_{\alpha 1}$  radiation). The measured (red circles), calculated (black line), and difference (observed – calculated, blue line) patterns as well as the Bragg positions of Co<sub>3</sub>N (vertical bars) are shown.

Table 5. Structural data from Rietveld refinements of the crystal structures of Co<sub>3</sub>N and Co<sub>2</sub>N (Mo- $K_{\alpha 1}$  radiation). In Co<sub>3</sub>N cobalt is located at Wyckoff site 6g and nitrogen at 2c, and in Co<sub>2</sub>N cobalt is at 2b and nitrogen at 8d and 4c. Parameters fixed during the refinements are marked by \*.

Parameter	Co <sub>3</sub> N	Co <sub>2</sub> N	
x(Co)	0.336(1)	0.253(2)	
y(Co)		0.1326(7)	
z(Co)		0.0746(3)	
B <sub>iso</sub> (Co) [10 <sup>4</sup> pm <sup>2</sup> ]	0.37(2)	0.29(5)	
<i>y</i> (N)		0.340(6)	
$B_{\rm iso}[N(1)] [10^4 \text{ pm}^2]$	$0.5^* = B_{iso}[N(2)]$	0.3(6)	
<i>P</i> [N(1)]	1.00*	1.00(6)	
<i>P</i> [N(2)]	0.031*		

# Thermal Behavior of Co<sub>3</sub>N

The thermal decomposition of  $Co_3N$  in an argon atmosphere (see Figure S6) with a mass loss of 8.5 % (expected 7.3 % for

complete nitrogen loss) starts above 419 °C, which is 60 K lower than the decomposition temperature for  $\varepsilon$ -Fe<sub>3</sub>N<sub>1.37(2)</sub>.<sup>[54]</sup> In general, a decrease in stability with an increasing number of 3d electrons is observed for 3d transition metal nitrides.<sup>[22]</sup> The observed mass loss indicates the presence of a nitrogen-rich Co<sub>3</sub>N<sub>1+x</sub> ( $x \approx 0.1$ ). Additionally, in the DTA curve an exothermal signal is observed at 593.5 °C (onset), revealing the metastable nature of Co<sub>3</sub>N. Co<sub>3</sub>N shows only limited stability towards oxidation in a DTA/TG experiment in synthetic air. The formation of Co<sub>3</sub>O<sub>4</sub> starts slowly above 163 °C (onset) an exothermal signal is detected in the DTA curve.

## Magnetic Characterization of Co<sub>3</sub>N

The variation of the magnetic susceptibility of Co<sub>3</sub>N with temperature indicates two major anomalies: a pronounced maximum at T = 27 K and a broad shoulder in the vicinity of  $T \approx$ 65 K (see Figure 5). To identify the nature of these transitions we have performed magnetization measurements at T = 5 K and T = 40 K (see Figure 6). By collecting a hysteresis loop at



Figure 5. Temperature dependence of (a) the magnetic susceptibility and (b) the reciprocal susceptibility of  $Co_3N$ . The solid lines are the fits of the data to a Curie–Weiss relation.



Figure 6. (a) Field-dependent magnetization of  $Co_3N$  at T = 5 K and T = 40 K. (b) Low-field magnetization curves.



5 K, a ferromagnetic behavior with a coercive field of  $H_c \approx 0.01$  T was observed (see inset in Figure 6). At 40 K a weak ferromagnetic component with a coercive field of  $H_c \approx 0.0015$  T superimposed to the paramagnetic phase was still evident.

This behavior suggests the presence of at least two contributions in the sample: a ferromagnetic and a paramagnetic one. Indeed, at low temperatures, a paramagnetic tail is visible due to a small fraction of unpaired Co spins. These arise most probably from a very small fraction of elemental Co impurity not detectable by PXRD and behave as localized free spins. This produces a magnetic susceptibility following a Curie-Weiss law. A fit of the data below 14 K results in a Curie-Weiss temperature  $\Theta = -2.6$  K and an effective magnetic moment  $\mu_{eff} = 1.2 \mu_{B}$ . The effective magnetic moment of Co is clearly reduced as compared to the spin-only values typically observed for low-spin (LS) or high-spin (HS) states of Co:  $\mu_{eff}(Co^{2+},LS) = 3.87 \mu_{B}$  $\mu_{eff}(Co^{2+},HS) = 1.87 \ \mu_{B}, \ \mu_{eff}(Co^{3+},LS) = 0 \ \mu_{B}, \ \mu_{eff}(Co^{3+},HS) = 4.9 \ \mu_{B},$  $\mu_{\text{eff}}(\text{Co}^{4+},\text{LS}) = 1.73 \ \mu_{\text{B}}, \ \mu_{\text{eff}}(\text{Co}^{4+},\text{HS}) = 5.82 \ \mu_{\text{B}}.$  The reported magnetic behavior of  $Co_3N_{1+x}$  in the literature is enigmatic. For a sample identified as hexagonal Co<sub>3</sub>N<sub>1+x</sub> by PXRD, primarily a paramagnetic to antiferromagnetic transition below 11 K was reported. However, the results of chemical analysis delivered a composition of Co<sub>3</sub>N<sub>1.55</sub>,<sup>[26]</sup> which is more reasonable to be described as  $Co_2N_{1.03}$ . This behavior strongly differs from our observations and from the presented magnetic behavior of mixtures of Co4+vN and Co3N1+x. [55] Nevertheless, the results presented previously<sup>[26]</sup> fit our observation on Co<sub>2</sub>N (see below) exactly. Magnetization measurements were performed on different mixtures of Co<sub>4+v</sub>N and Co<sub>3</sub>N<sub>1+x</sub>.<sup>[55]</sup> From the DFT calculations, an energetic preference of a ferromagnetic ordering compared to a paramagnetic configuration was confirmed. Similarities in the behavior of the saturation magnetization of  $Co_3N_{1+x}^{[55]}$  and  $\epsilon$ -Fe<sub>3</sub>N<sub>1+x</sub> were observed.<sup>[57]</sup> With increasing nitrogen content, represented by an increase in the phase fraction of  $Co_3N_{1+x}$  compared to that of  $Co_{4+y}N_1$ , a decrease in the observed saturation magnetization was observed.<sup>[55]</sup> For  $\epsilon$ - $Fe_3N_{1+x}$  a decrease in the Curie temperature  $T_c$  and consequently a reduction of the saturation magnetization was observed with increasing nitrogen content. When x approaches 0.5, paramagnetic behavior down to 4 K was observed.<sup>[57]</sup>

The amount of unpaired spins has been estimated from the experimental value of the Curie constant *C* according to Equation (1):

$$C = \frac{\mu_B^2}{3k_B} Ng^2 S(S+1)$$
(1)

where  $k_{\rm B}$  represents the Boltzmann constant, *N* the number of magnetic spins per unit volume, *g* the Landé *g*-factor (*g* = 2 was taken for the free spins),  $\mu_{\rm B}$  the Bohr magneton, and *S* the spin quantum number. Since the spin state of Co was not obvious, we only estimate the approximate range of the paramagnetic impurity fraction to be in the order of  $10^{22}$  mol<sup>-1</sup>.

The inverse susceptibility of  $Co_3N$  is shown in the inset of Figure 5. A significant deviation from the Curie–Weiss law can be observed at temperatures below approximately 250 K; the



curve is only linear in the small temperature range from 250 to 300 K. A fitting of the data according to a Curie-Weiss law in this temperature range results in a Curie-Weiss temperature of  $\Theta$  = -853 K and an effective magnetic moment  $\mu_{eff}$  = 4.9  $\mu_{Br}$ which is close to the spin-only value for Co<sup>3+</sup>(HS). It is interesting to note that some cobaltates such as La<sub>2-x</sub>Sr<sub>x</sub>CoO<sub>4</sub> show a similar deviation from Curie-Weiss behavior.<sup>[56]</sup> An increase of susceptibility in this material at high temperatures was attributed to a thermally induced spin-state transition of Co<sup>3+</sup>. This scenario might be also applied to Co<sub>3</sub>N, but bulk magnetic measurements cannot address this question. It is worth to note that a similar magnetic behavior was already observed between 200 and 300 K for the Co<sub>3</sub>N<sub>1.55</sub> sample mentioned before, which follows a Curie-Weiss law only in this temperature interval. A large negative Curie–Weiss temperature of  $\Theta$  = –500 K and an effective magnetic moment equal to  $3 \pm 0.3 \ \mu_B$  were observed.<sup>[26]</sup> To clarify the nature of the spin states of Co ions, other methods like X-ray absorption spectroscopy or neutron scattering have to be utilized. However, the present sample is still inhomogeneous, comprising at least two phases. This result underlines the necessity of further experiments to verify the ground state of Co<sub>3</sub>N.

## Synthesis and Characterization of Co<sub>2</sub>N

In contrast to the results of the pioneering work by Juza and Sachße,<sup>[4]</sup> synthesis of Co<sub>2</sub>N from elemental cobalt as well as from Co<sub>3</sub>O<sub>4</sub> was unsuccessful during our studies. A successful pathway to Co<sub>2</sub>N is found by ammonolysis of [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> at 450 °C (12 h) followed by annealing in ammonia at 350 °C (18 h). According to the reported synthesis conditions for Co<sub>4</sub>N and Co<sub>3</sub>N, it seems reasonable to assume the following reaction sequence: In the first nitridation step at 450 °C Co<sub>4</sub>N is produced possibly in a mixture with Co<sub>3</sub>N. Those reaction products are completely nitridated to Co<sub>2</sub>N in the second step at lower temperature (see Figure 7 and Table 2).



Figure 7. Rietveld refinements of the crystal structure of  $Co_2N$  (Mo- $K_{\alpha 1}$  radiation). The measured (red circles), calculated (black line), and difference (observed–calculated, blue line) patterns as well as the Bragg positions of  $Co_2N$  (vertical bars) are shown.





Under the conditions of a DTA/TG measurement in argon (see Figure S7), Co<sub>2</sub>N exhibits a mass loss of 8.5 % above 344 °C. An exothermal signal at 429.6 °C (onset) reveals the metastable nature of Co<sub>2</sub>N. The expected mass loss for the decomposition of Co<sub>2</sub>N to  $\beta$ -Co is 10.7 %. The large difference between measured and expected mass loss is due to the presence of about 20 %  $\beta$ -Co in the particular investigated sample. In general, a decreasing thermal stability with increasing nitrogen content is observed for the investigated metastable cobalt nitrides.

## Magnetic Characterization of Co<sub>2</sub>N

In the magnetization curve of Co<sub>2</sub>N (single-phase according to PXRD) antiferromagnetic behavior was observed. The maximum, which equals the Néel temperature, was obtained at  $T_{\rm N} = 10$  K (see Figure 8) and perfectly fits the data previously reported for Co<sub>3</sub>N<sub>1.55</sub> (= Co<sub>2</sub>N<sub>1.03</sub>).<sup>[26]</sup> However, the mass susceptibility we obtained at T = 295 K ( $\chi = 148 \times 10^{-6}$  emu g<sup>-1</sup>) deviates significantly from the values reported earlier ( $\chi = 23 \pm 8 \times 10^{-6}$  emu g<sup>-1</sup>).<sup>[26]</sup> The collection of the field-dependent magnetization curves at T = 5 K and T = 100 K reveal the presence of a small fraction of a ferromagnetic impurity, not detectable by PXRD, with a very small coercive field. This can be related to the presence of either Co or Co<sub>4</sub>N. Additionally, the presence of a small fraction of unpaired Co spins, as observed before in the case of Co<sub>3</sub>N, cannot be ruled out.



Figure 8. Temperature-dependent magnetic susceptibility of  $\mathrm{Co_2N}$  at H=0.05 T.

## Synthesis and Characterization of CoO<sub>1-x</sub>N<sub>x</sub>

During experiments aiming for the synthesis of CoN from  $[Co(NH_3)_5N_3]Cl_2$  a cobalt oxide nitride was obtained by thermal decomposition of the precursor at 400 °C under dynamic vacuum. From chemical analysis, a composition of  $CoO_{0.74 \pm 0.03}N_{0.24 \pm 0.11}$  was determined. Rietveld refinements of the collected PXRD data revealed the presence of a rock-salt structure type cobalt oxide nitride (see Figure 9) in contrast to earlier experimental results<sup>[41]</sup> and theoretical predictions.<sup>[42]</sup> The refined isotropic displacement parameters are  $B_{iso}(Co) = 0.59(7) \times 10^4 \text{ pm}^2$  and  $B_{iso}(O) = B_{iso}(N) = 0.8(2) \times 10^4 \text{ pm}^2$ . The

oxygen-rich composition detected by chemical analysis is supported by the evaluation of the diffraction data, since the measured unit cell parameter of the oxide nitride  $[a(\text{CoO}_{1-x}\text{N}_x) = 425.51(3) \text{ pm}]$  is much closer to the value of rock-salt type CoO  $[a(\text{CoO}) = 425.18(2) \text{ pm}]^{[47]}$  than to that of CoN [a(CoN) = 427.86 pm].<sup>[48]</sup> Additionally, according to electronic structure calculations, the largest stabilization of  $\text{CoO}_{1-x}\text{N}_x$  was observed for  $x \approx 0.2$ ,<sup>[42]</sup> and experimentally an oxide nitride with rock-salt structure type with a very similar composition of  $\text{CoO}_{0.71}\text{N}_{0.27}$  was reported previously to form during the ammonolysis of  $\text{Co}_3\text{O}_4$  at 390 °C.<sup>[4]</sup>



Figure 9. Rietveld refinements of the crystal structure of  $CoO_{0.74}N_{0.24}$  (Mo- $K_{\alpha 1}$  radiation). The measured (red circles), calculated (black line), and difference (observed–calculated, blue line) patterns as well as the Bragg positions of  $CoO_{0.74}N_{0.24}$  (vertical bars) are shown. The composition was fixed during the refinements to the value observed by chemical analysis. The inset shows the simulated intensities of  $CoO_{0.74}N_{0.24}$  in sphalerite (red) and rock-salt (black) structure type.

New DFT calculations were performed with the explicitly correlated GGA+U method to shed some light on the supposed discrepancy between experimental observation (rock-salt type) and previous calculations (sphalerite type suggested). Because the rock-salt and sphalerite unit cells both contain four formula units, this allows for an easy theoretical modeling of the experimental composition CoO<sub>0.75</sub>N<sub>0.25</sub>. After relaxation, the cell parameters of the optimized structures were varied by scaling them, and the resulting energy versus volume data were fitted to the Birch-Murnaghan equation of state (Figure 10). As expected, the most stable polymorph is the sphalerite structure (blue), independent of the magnetic state; among them, however, the antiferromagnetic ordering (AFM) is lowest, slightly higher in energy is the ferromagnetic (FM) ordering, and then the diamagnetic one comes far above. In contrast, the rock-salt structure (red) is always higher in energy but with the same order of the magnetic states: AFM, then FM (somewhat unstable), then diamagnetic. As a result, the AFM rock-salt polymorph is less stable than the AFM sphalerite type by more than 30 kJ mol<sup>-1</sup>. Therefore, the previous calculations are fully corroborated. It is also worth mentioning that the experimental cell volume (dashed line) of 19.26 Å<sup>3</sup> per formula unit agrees





perfectly with the calculated AFM-ordered rock-salt structure. Regarding the perfect coincidence, there is good reason to assert that the experimentally found structure is a metastable and antiferromagnetically ordered polymorph of  $CoO_{0.75}N_{0.25}$ .



Figure 10. Density functional energy versus volume phase diagram of  $CoO_{0.75}N_{0.25}$ . The rock-salt [NaCl] (in red) and the sphalerite [ZnS] polymorphs (in blue) are each represented by nonmagnetic, ferromagnetic (FM), and antiferromagnetic (AFM) spin orderings. The experimental volume of 19.26 Å<sup>3</sup> per formula unit has been indicated by a dashed black line and matches the calculated volume for [NaCl] AFM-type  $CoO_{0.75}N_{0.25}$ .

# Conclusions

A new approach for the synthesis of metastable cobalt nitrides Co<sub>4</sub>N, Co<sub>3</sub>N, and Co<sub>2</sub>N starting from a single metastable azide precursor [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> was established. The respective nitrides can be obtained in a controlled way by varying the temperature program and/or the gas atmosphere. The metastable nature of the cobalt nitrides was confirmed by the detection of an exothermal decomposition during DTA measurements in Ar. Measurements of the magnetic properties of our Co<sub>3</sub>N<sub>11</sub> revealed a clear difference from the magnetic behavior previously observed on a sample with higher nitrogen content ( $Co_3N_{1.55}$ ). For  $Co_3N_{1.1}$  a ferromagnetic behavior with a small coercive field superimposed to a paramagnetic impurity phase was observed. Former DFT calculations presented in the literature reveal an energetic preference of a ferromagnetic ordering for Co<sub>3</sub>N<sub>1+x</sub> over a paramagnetic assembly. For Co<sub>3</sub>N<sub>1.55</sub> an antiferromagnetic behavior was observed experimentally below 11 K in the literature. However, this resembles exactly the magnetic behavior we have obtained for Co<sub>2</sub>N. Regarding the fact that  $Co_3N_{1.55}$  can also be described as  $Co_2N_{1.03}$  this observation becomes plausible.

Additionally, the decomposition of the precursor in vacuo allows access to a rock-salt type cobalt oxide nitride with a composition of  $CoO_{0.74}N_{0.24}$ . DFT calculations revealed that this oxide nitride is a metastable polymorph with an antiferromagnetic ordering. Despite the fact that the likewise AFM sphalerite polymorph is preferred by more than 30 kJ mol<sup>-1</sup>, the rock-salt polymorph forms under experimental conditions, possibly because of smaller activation barriers for crystallization.

An alternative synthesis of Co<sub>3</sub>N starts from CoBr<sub>2</sub> as precursor. In the first step, at temperatures lower than 200 °C, the blue hexaammoniate [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> forms in ammonia. With increasing temperature the formation of the diammonate Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> occurs prior to a conversion to Co<sub>3</sub>N at 450 °C.

# **Experimental Section**

# Syntheses

All manipulations of starting materials and samples were carried out in an argon-filled glove box [MBraun,  $p(O_2) < 0.1$  ppm].

Metastable Co<sub>4</sub>N was synthesized from metastable [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> within 8 h at 425 °C in a controlled ammonia (>99.999 %, Linde) flow of 60 mL min<sup>-1</sup>.

Metastable Co<sub>3</sub>N was synthesized from two different precursors, namely [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> and CoBr<sub>2</sub> (97 %, Alfa Aesar). [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]-Cl<sub>2</sub> was heated in a gas atmosphere consisting of 21 vol.-% NH<sub>3</sub> in argon with a heating rate of 2 K min<sup>-1</sup> to 350 °C. After 5 h, the temperature was increased to 400 °C with 2 K min<sup>-1</sup>. Cooling to ambient conditions was done after 5 h at 400 °C. Starting from green CoBr<sub>2</sub> at ambient temperature in an ammonia gas flow of 150 mL min<sup>-1</sup>, within 2 h the blue hexaammoniate [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> is formed. Heating [Co(NH<sub>3</sub>)<sub>6</sub>]Br<sub>2</sub> at 160 °C in flowing ammonia results in the formation of the diammoniate Co(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> within 2 h. Cooling was carried out under dynamic vacuum ( $p_{min} \approx 2 \times 10^{-3}$  mbar). Single-phase Co<sub>3</sub>N was synthesized by heating CoBr<sub>2</sub> in an ammonia gas flow of 150 mL min<sup>-1</sup> at 445 °C for 5 h.

Metastable Co<sub>2</sub>N was obtained by ammonolysis of  $[Co(NH_3)_5N_3]Cl_2$  at 450 °C for 12 h in a gas flow of 60 mL min<sup>-1</sup> NH<sub>3</sub>. Afterwards, the reaction mixture was cooled to 350 °C, and the nitridation was continued for additional 18 h.

The thermal decomposition of metastable [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> at 400 °C for 24 h under dynamic vacuum ( $p_{min} \approx 2 \times 10^{-2}$  mbar) resulted in the formation of CoO<sub>0.74 ± 0.03</sub>N<sub>0.24 ± 0.11</sub>.

[Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]Cl<sub>2</sub> was synthesized as described earlier.<sup>[46]</sup> CoCl<sub>2</sub>•6H<sub>2</sub>O (reinst, Merck) was dissolved in a small quantity of deionized water. To this solution was added a second solution consisting of NaN<sub>3</sub> (>99 %, Merck), NH<sub>4</sub>Cl (suprapur, Merck), and NH<sub>3</sub> (aq., 25 wt.-%, chem. pure, Merck) under vigorous stirring at 60 °C. After 2 h, the reaction mixture was cooled with ice water to ensure complete precipitation. The precipitate was collected and washed three times with diluted hydrochloric acid and ethanol (100 %). For recrystallization the precipitate was dissolved in deionized water and afterwards precipitated by the careful addition of concentrated hydrochloric acid. The collected precipitate was washed with ethanol and dried at 50 °C for 4 d. The detected weight fractions of nitrogen and hydrogen by chemical analysis were  $w(N) = 43.6 \pm 0.2$  wt.-% and  $w(H) = 5.89 \pm 0.05$  wt.-%. The expected values are  $w_{exp.}(N) = 43.55$  wt.-%

**Thermal Analysis:** Thermal analysis experiments in ammonia/ argon mixtures were carried out with a Netzsch STA449C thermal analyzer equipped with a corrosive gas kit. The DTA/TG/EGA measurement was performed with a Netzsch thermal analyzer STA409CD with a skimmer coupling and a Quadstar 422 (Pfeiffer Vacuum) mass spectrometer in a helium atmosphere (>99.999 %, AirLiquide). Further DTA/TG measurements in an argon atmosphere (>99.999 %, AirLiquide) were carried out with Netzsch thermal analyzers STA409 and STA449C. Before the start of the respective measurements the sample chamber was flushed at least three times with inert gas. All TG measurements were corrected for buoyancy effects.



**Powder Diffraction and Rietveld Refinements:** PXRD patterns of the reaction products were recorded with a STOE STADI P equipped with a Mythen1K micro-strip detector in transmission geometry with Mo- $K_{\alpha 1}$  radiation ( $\lambda = 70.93$  pm).

Rietveld refinements<sup>[58,59]</sup> of the crystal structures on PXRD data were carried out with use of the FULLPROF 2.k<sup>[60]</sup> program and pseudo-Voigt functions to describe the reflection profile. Additionally, the following parameters were allowed to vary: The zero point of the 2 $\Theta$  scale, one scale factor per phase, three reflections widths (Caglioti formula. *U*, *V*, and *W*), two asymmetry parameters, one mixing ( $\eta$ ) parameter and its angle-dispersive correction ( $\chi$ ), the unit cell parameters, the atomic site parameters, and the isotropic thermal displacement parameters ( $B_{iso}$ ). The background was treated either by a polynomial or by interpolation between chosen background points with refinable heights. The structural models used for the Rietveld refinements of Co<sub>4</sub>N,<sup>[14]</sup> Co<sub>3</sub>N,<sup>[54]</sup> Co<sub>2</sub>N,<sup>[54]</sup> and CoO<sub>0,74</sub>N<sub>0,24</sub><sup>[47,48]</sup> are based on the indicated references.

**Chemical Analysis:** Quantitative analysis of the hydrogen and nitrogen contents of  $[Co(NH_3)_5N_3]Cl_2$  was carried out by the hot gas extraction method with a LECO TC300/EF300. Quantitative analysis of the oxygen and nitrogen contents of the cobalt oxide nitride was carried out by the hot gas extraction method with a LECO ONH836.

**Infrared Vibrational Spectroscopy:** For collection of the vibrational spectra of  $[Co(NH_3)_6]Br_2$  and  $Co(NH_3)_2Br_2$  a Thermo Electron Scientific Instruments FTIR Nicolet iS5 in ATR mode installed inside a glove box was used.

**Magnetization Measurements:** The samples were sealed under an argon atmosphere into a polycarbonate capsule, which was glued into a small polyvinylchloride tube. Magnetization measurements were performed with a SQUID magnetometer (Quantum Design) for  $Co_2N$  and a MPMS7 magnetometer (Quantum Design) for  $Co_3N$  in the temperature range of 2–300 K and magnetic fields up to 6 T.

Electronic Structure Calculations: The unexpected rock-salt structure type of cobalt oxide nitride as well as its sphalerite counterpart were investigated with periodic DFT as implemented in the Vienna ab initio simulation package (VASP).<sup>[61]</sup> Projector-augmented waves (PAW)<sup>[62]</sup> were used, and the contributions of exchange and correlation were treated within the GGA as described by Perdew, Burke, and Ernzerhof.<sup>[63,64]</sup> To minimize the self-interaction error, the GGA+U method according to Dudarev et al.[65] was used. An effective U of 3.3  $eV^{[66,67]}$  was used as it has previously shown to provide good results for CoO. An energy-cutoff of 500 eV and an adapted k-point sampling ensured well-converged structures. During the optimization process the atomic positions and the lattice parameters were allowed to relax until the convergence criterion of 10<sup>-6</sup> eV was reached. The cell parameters of the optimized structures were then scaled from 94 to 104 %, and the resulting energy versus volume data were fitted to the Birch-Murnaghan equation of state.[68]

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