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In-situ Study of the Solid-Gas Reaction of $BiCl_3$ to BiOCl via the Intermediate Hydrate $BiCl_3 \cdot H_2O$

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Dedicated to Professor Rüdiger Kniep on the occasion of his 65th birthday

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At ambient conditions the hydrolysis of $BiCl_3$ to BiOCl proceeds via the intermediate hydrate $BiCl_3 \cdot H_2O$ as has been revealed by time dependent in-situ X-ray powder diffraction as well as time and temperature controlled TG-MS experiments. Below 50 °C the topochemical formation of the hydrate can be reversed by reducing the H_2O vapour pressure. Above this temperature the hydrate is unstable and the mechanism of the hydrolysis changes. $BiCl_3 \cdot H_2O$ crystallizes in the monoclinic space group $C2/m$ with lattice parameters a = 1114.25(1) pm, b = 876.82(1) pm, c = 584.20(1) pm, and β = 106.64(1)°.

Introduction

Since more than a century the precipitation of a basic bismuth salt from an aqueous solution of $BiCl_3$ serve as a prime example of an inorganic hydrolysis reaction.[1] In contrast to the nitrates of bismuth, which comprises complex intermediate hydrates,[2] the hydrolysis of $BiCl_3$ was regarded to be of "very high simplicity".[3] On the other hand, the existence of $BiCl_3$ hydrates was discussed[4] and a nuclear quadrupole resonance study of a commercially available sample of "$BiCl_3 \cdot H_2O$" was published.[5] However, the proof of existence, the chemical composition and the crystal structure of the hydrate are still missing.

The starting material $BiCl_3$[6] and the hydrolysis product BiOCl[7] are widely used materials, for example in organometallic catalyzed reactions,[8] cosmetic industry,[9] pharmaceutical industry,[10] and battery applications.[11] For these applications it is of fundament interest to understand the reaction processes involved including the "simple" hydrolysis reaction. In order to shed light on this long-standing problem, we performed in-situ X-ray powder diffraction experiments, monitoring the reaction of $BiCl_3$ with humid air at room temperature. These investigations were complimented with temperature-dependent TG-MS measurements in humid and in dry inert gas atmosphere.

Results and Discussion

According to time-dependent X-ray powder diffraction data, $BiCl_3$ reacts at ambient conditions with air moisture to give intermediate $BiCl_3 \cdot H_2O$, which subsequently decomposes to BiOCl. The pattern could be indexed on the basis of a *C*-centered monoclinic lattice, and the structure was solved using simulated annealing methods.[12] $BiCl_3 \cdot H_2O$ has a layered crystal structure with stacking direction [001] (Figure 1). The primary coordination of the Bi^{III} cation by three chloride ions in a distance of about 249 pm resembles the "molecular" structure of $BiCl_3$ (average Bi–Cl 250 pm). The bond length to the oxygen atom of the water molecule is 247 pm, i.e. only 15 pm longer than the Bi–O distance in BiOCl. Three remote chloride ions, which are 306 pm (2×) and 327 pm apart, complete the sevenfold coordination.

There is a topological relation between the crystal structures of $BiCl_3$ and $BiCl_3 \cdot H_2O$. For visualization, the comparison is restricted to the Bi cations (Figure 2), which in both cases form inclined primitive lattice complexes. The monoclinic angle β = 106.6° of $BiCl_3 \cdot H_2O$ is also found as ε = 106.7° in the cation skeleton of $BiCl_3$. The uptake of water increases the volume by 26.5×10^6 pm^3 per formula unit $BiCl_3$.

Although the positions of the hydrogen atoms were not determined, the O···Cl distances (> 324 pm) allow speculations about hydrogen bonds. The majority and also the

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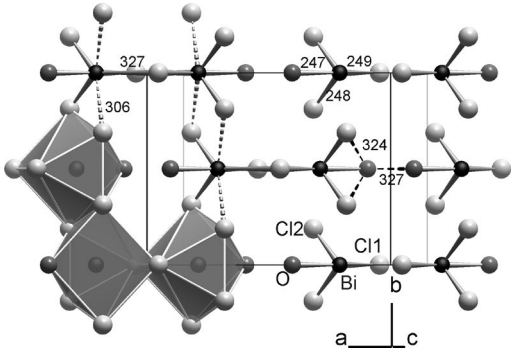


Figure 1. Layer in the monoclinic crystal structure of $BiCl_3{\cdot}H_2O$. Interatomic distances are given in pm.

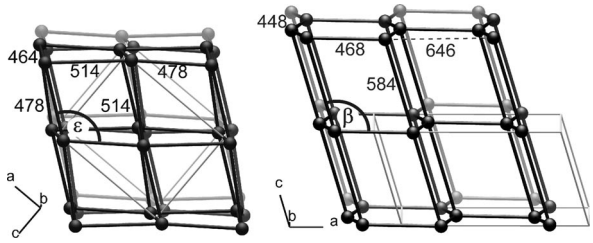


Figure 2. Lattice complexes of Bi cations in $BiCl_3$ and $BiCl_3{\cdot}H_2O$ (right) demonstrating the topological relation. The indicated angles are $\varepsilon = 106.7°$ and $\beta = 106.6°$; distances are given in pm.

shortest of the possible hydrogen bridges reach out for Cl2, which makes it quite probable that these atoms are eliminated as HCl during the reaction to BiOCl. The remaining almost linear fragment Cl1–Bi–O can be identified in the crystal structure of BiOCl, however, a topological relation between the structures of $BiCl_3{\cdot}H_2O$ and BiOCl is not obvious.

The kinetics of the two consecutive heterogeneous solid-gas reactions at room temperature were investigated by quantitative analysis of the time-dependent powder diffraction patterns (Figure 3). Within the time interval necessary for the recording of the diffractogram, $BiCl_3$ reacts with humid air immediately when exposed to it. According to the Johnson–Mehl–Avrami equation[13] the induction period is about 8 min and the half life time of the reaction is about 45 min. The distinctly slower decomposition of $BiCl_3{\cdot}H_2O$ into BiOCl is completed 99% after 622 min.

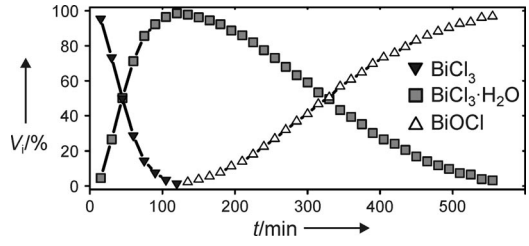


Figure 3. Change of volume fractions V_i of $BiCl_3$, $BiCl_3{\cdot}H_2O$ and BiOCl during the hydrolysis at room temperature according to in-situ X-ray powder diffraction.

Thermogravimetric (TG) investigations with simultaneous analysis of the gas atmosphere by means of mass spectrometry (MS) were conducted at 27, 40, 50, and 60 °C (Figure 4). Due to the denser sample in this experimental setup the reaction rate is about two orders of magnitude slower than in the X-ray diffraction experiment. The mass gain of 4.6 wt.-% at 27 °C resp. 3.8 wt.-% at 40 °C during the purging with a stream of $Ar/H_2O_{(g)}$ clearly evidence the formation of the intermediate hydrate (calcd.: 5.7 wt.-%). The following linear mass loss monitors the decomposition to BiOCl (calcd.: 82.6 wt.-%). Especially the second reaction accelerates when the temperature is increased from 27 °C to 40 °C. However, at 50 °C and above, the reaction mechanism seems to change. Right from the start a depletion of mass down to a plateau close to the expected mass of BiOCl occurs. X-ray diffraction data of the product confirm the formation of BiOCl.

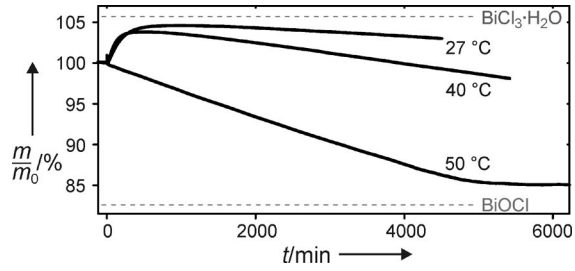


Figure 4. Time-dependent mass change during the exposure of $BiCl_3$ to humid argon gas at different temperatures. The theoretical wt.-% values of $BiCl_3{\cdot}H_2O$ and BiOCl are indicated as dashed grey lines.

Stopping the reaction at 27 °C at the maximum weight gain yields a three phase sample with $BiCl_3{\cdot}H_2O$ as main component. A portion of this sample was heated with 10°/min in dry (!) argon up to 500 °C (Figure 5). A step in TG with onset at about 50 °C and a simultaneous increasing ion current at $m/z = 18$ (H_2O^+) unambiguously evidence the decomposition of the hydrate since none of the impurities have gravimetrical transitions in this range. At about 250 °C sublimation of $BiCl_3$ starts, which is experimentally indicated by a substantial mass loss and the occurrence of several $BiCl_x^+$ ($x = 1, 2, 3$) species in the MS.

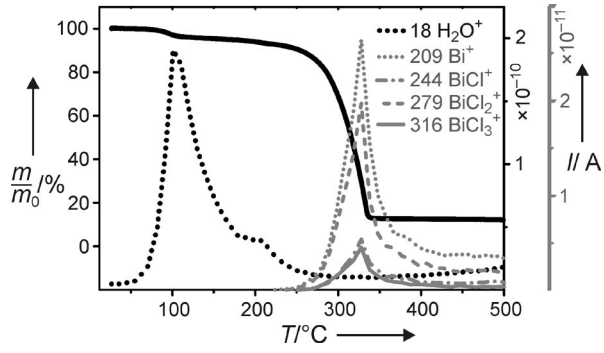
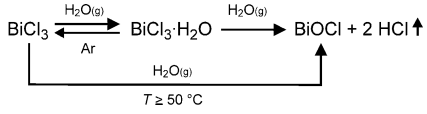


Figure 5. TG-MS measurement of $BiCl_3{\cdot}H_2O$ in dry argon atmosphere. The dehydratisation starts at about 50 °C, the sublimation of $BiCl_3$ at about 250 °C.

Switching of the gas atmosphere from $Ar/H_2O_{(g)}$ to dry argon at the maximum of mass increase at 27 °C, i.e. decreasing the partial pressure of water in the atmosphere, the reversed reaction from $BiCl_3 \cdot H_2O$ to $BiCl_3$ is observed. At this temperature the heterogeneous hydrate formation of $BiCl_3$ is reversible and, with respect to the crystal structures, almost certainly topochemical.

Conclusions

Experimental results support the following reaction scheme for the hydrolysis of $BiCl_3$: below 50 °C, the topochemical reaction of solid $BiCl_3$ with $H_2O_{(g)}$ yields the monohydrate $BiCl_3 \cdot H_2O$ (see also Scheme 1). Under constant conditions, the subsequent slow and irreversible decomposition of the hydrate leads to the final products BiOCl and HCl. Alternatively, the reduction of the partial pressure of water results in the back transformation of $BiCl_3 \cdot H_2O$ to $BiCl_3$. At 50 °C and above no intermediate hydrate is formed and BiOCl is obtained directly. These findings should be kept in mind evaluating catalytic activities, battery applications and pharmaceutical usage of $BiCl_3$ when traces of water are present.



Scheme 1. Reaction of $BiCl_3$ with $H_2O_{(g)}$.

Experimental Section

General: $BiCl_3$ (Alpha Aesar, 99.99%) was purified by sublimation. In an argon-filled glove box [MBraun, $c(H_2O)$ and $c(O_2) < 1$ ppm] the powdered samples were placed on a mylar foil covered with vaseline. Another foil was used to cover the sample. X-ray powder diffraction data were collected in time intervals of 15 min using a Huber Guinier G670 diffractometer (Cu-$K_{\alpha 1}$ radiation, λ = 154.06 pm, $3° \leq 2\theta \leq 100°$) at 20 °C in atmosphere (humidity about 65%). The structure was solved and refined with the aid of the FullProf package.[12] According to Rietveld refinements the structure crystallizes monoclinic in the space group *C*2/*m*, no. 12, a = 1114.25(1) pm, b = 876.82(1) pm, c = 584.20(1) pm, β = 106.64(1)°, Z = 4. Bi on 4*i*: 0.2088(2), 0, –0.0081(4), U_{iso} = 173(6) pm^2; Cl1 on 4*i*: 0.090(1), 0, 0.294(2), U_{iso} = 850(50) pm^2; Cl2 on 8*j*: 0.3547(7), 0.1879(8), 0.245(1), U_{iso} = 670(40) pm^2; O on 4*i*: 0.3710(3), 0, –0.222(8), U_{iso} = 2400(200) pm^2. The positions of the H atoms could not be determined. For the modeling of the diffraction pattern Voigt functions for the reflection profiles and 26 points with adjustable intensities for the background were used. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421319.

TG-MS measurements were performed with a NETZSCH STA409C Skimmer apparatus situated in an argon-filled glove box. The sample was spread on a flat corundum sample holder (d = 15 mm). The water partial pressure was achieved by piping argon through a cartridge filled with moistened charcoal. For the qualitative analysis of the products of the TG-MS measurements the X-ray diffraction measurements were performed as described above, but only the first 15 min were taken as representative.

Supporting Information (see also the footnote on the first page of this article): Plots of the Rietveld refinements of the X-ray powder diffraction data.

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