Beryllium

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Off the Beaten Track—A Hitchhiker's Guide to Beryllium Chemistry

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This Minireview aims to give an introduction to beryllium chemistry for all less-experienced scientists in this field of research. Up to date information on the toxicity of beryllium and its compounds are reviewed and several basic and necessary guidelines for a safe and proper handling in modern chemical research laboratories are presented. Interesting phenomenological observations are described that are related directly to the uniqueness of this element, which are also put into historical context. Herein we combine the contributions and experiences of many scientist that work passionately in this field. We want to encourage fellow scientists to reconcile the long-standing reservations about beryllium and its compounds and motivate intense research on this spurned element. Who on earth should be able to deal with beryllium and its compounds if not chemists?

1. Don't Panic!

What do you really know about beryllium and its compounds? What do you really know about their toxicity? What do you really know about handling of beryllium and its chemical properties? Have you ever seen beryllium metal or its crystalline compounds? Most chemists only know about beryllium from textbooks, lectures, or diverse internet platforms. But why is there such a neglect of this element that has led to it being disregard by researchers during the last two centuries? Many people would answer that the wall-flower-like existence of beryllium is based on its legendary toxicity and the high risks that are linked to the handling of such compounds. Another answer could be that today it has become very difficult to obtain beryllium or any of its compounds for reasons that will be explained later.

We think that this is an unsatisfying situation that needs to be changed. The fascination of this element and its chemistry has already yielded exciting results that will be summarized herein. We hope that in the future the research on beryllium will be pushed as much as it has been for its neighbors in the periodic table during the last three decades. This element is more than a curiosity that is only noted for the sweetness of its salts, as the "most toxic non-radioactive element",[1,2] or for its well-known use as an X-ray transient window in X-ray tubes.

Luckily, this situation has changed a little during the last two decades, in which several researchers or groups began to investigate this element, such that the number of publications about preparative research on beryllium compounds has greatly increased. But still "*the number of theoretical investigations published on beryllium chemistry is by far larger than the number of experimental studies*", so that "*achieving a thorough understanding of beryllium chemistry through the collection of basic knowledge is still the task of chemists.*"[3]

Herein we try our best to facilitate the entry into beryllium chemistry for our fellow scientists and hope that they will also feel the same pioneering spirit that we feel, when we are doing research on one of the most neglected elements in the periodic table.

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2. A Few Things on the Usage of Be and its Compounds

Beryllium (Figure 1) has a number of properties which make it interesting for a range of applications; it is a material with great strength and low density, making it ideal for use in the aerospace industry, for example in fast rotating gyroscopic compasses and stabilizers. Alternatively, when blended with other metals it gives the alloys special characteristics concerning strength, elasticity, and resistance to corrosion. Beryllium alloys are used in a wide variety of special applications, such as coatings for high-end audio plugs, non-sparking antimagnetic tools, or springs with very-high fatigue limits. Also, it is used as the primary ingredient in the mirrors of space telescopes, such as the James Webb Space Telescope.[4a,b]


Figure 1. A sample of pure beryllium metal under argon in a sealed ampoule. Picture: A. Heddergott.

3. What about the "Toxicity" of Beryllium?

The German Social Accident Insurance (Deutsche Gesetzliche Unfallversicherung, DGUV) reports 21 notices with the suspicion on beryllium-associated occupational diseases were filed in 2013.[5] Hereof three cases were confirmed and recognized as an occupational disease. Furthermore, it is evident from the DGUV statistics for the code of practice 2013 that 13 cases of beryllium-disease and two fatalities occurred in Germany since 2010.[6] During the same time period 39 confirmed new cases and 52 fatalities occurred in relation to the handling of benzene, while for silicosis 4232 cases and 1469 deaths were confirmed. To put these


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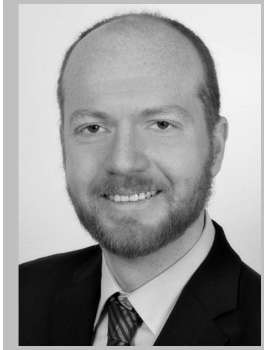
Magnus Buchner, born 1982 in Regensburg (Germany), studied chemistry and obtained his Ph.D. in 2011, under the guidance of Prof. K. Ruhland, at the Technische Universität München. After a postdoctoral stay at the University of York with Prof. R. Perutz and brief stopovers at the Friedrich-Alexander-Universität Erlangen-Nürnberg and the patent department of the Fraunhofer-Gesellschaft he now is a junior research group leader at the Philipps-Universität Marburg focusing on beryllium chemistry.


Stephan Schulz studied chemistry at the University of Göttingen and obtained his diploma in 1992 and his Ph.D. in 1994 with Prof. H. Roesky. After a postdoctoral stay at the University of Iowa with Prof. R. F. Jordan he moved to the University of Bonn, finished his habilitation in 2001. He then moved to the University of Köln (2003) and became C3 Professor at the University of Paderborn in 2004. Since 2007, he has been Professor of Inorganic Chemistry at the Universität Duisburg-Essen. His research interest focuses on inorganic and metal organic chemistry as well as the synthesis of nanomaterials.


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Florian Kraus studied chemistry at the universities of Regensburg, Germany, and San Diego, USA (diploma 2003). In 2005 he finished his Ph.D. Thesis with Prof. Dr. Korber and Prof. Dr. B. R. Albert on the reactions of polyphosphides and hydro-closo-borates in liquid NH_3. From 2006 to 2008 he worked as a research assistant with Prof. Dr. Fässler at the TU Munich. Starting his own research on inorganic fluorine chemistry in 2008 and finished his habilitation thesis in 2011. In 2014 he moved to Philipps-Universität Marburg as a full Professor of inorganic chemistry.

number into perspective, 17430 people were exposed to beryllium and its compounds in 2006 in Germany, which correlates to 0.07% developing beryllium disease and 0.0004% beryllium associated deaths.[7] In 2012 564927 people were exposed to asbestos in Germany resulting in 0.75% developing silicosis and 0.26% dying.[8] Even if only the high-exposure-level industries melting, casting, and machining (662 workers in 2011) are considered (1.96% beryllium disease, 0.30% death) the risk is comparable to asbestos.[7] The exposure level in research and development is classified as low.[7] Current medical studies suggest that an allergic reaction is liable for acute and chronic berylliosis (chronic beryllium disease CBD). These studies also indicate that beryllium metal does not show any acute toxic effects, and that the carcinogenicity in humans is not distinctively proven.[6,9–17] The work by Strupp et al., moreover, suggest that beryllium and its compounds should not be classified as "toxic" (requiring the skull and crossbones symbol), unless the toxicity is induced by the anion.[15] However, it should be noted that the work by Strupp and co-workers was funded by the REACH Beryllium Consortium, an industry group led by Materion Brush, a beryllium producer in the United States of America.[14] In fact, the "toxicity" of beryllium and its compounds seems to be somewhere on the borderline of allergic hypersensitivity and autoimmunity.[18] According to the Globally Harmonized System of Classification and Labeling of Chemicals a compound can only be assigned with the hazard symbol "toxic" (skull and crossbones) if certain criteria (Table 1) are met, otherwise the compound shows no acute toxicity and must not show the skull and crossbones. See Table 2 for some LD50 values of Be compounds—some of them carry the "skull and crossbones" warning sign. The "intoxication" may proceed in its "acute" form with high beryllium-doses over a short exposure time and in its "chronic" form with low beryllium-doses over long exposure times. Recent molecular biological studies show that body's response is caused presumably by an autoimmune overreaction. This is indicated through the existence of T-cells, which are sensitized to beryllium species, in berylliosis patients and in cell and animal experiments.[19] This specific immune response is probably triggered by the high affinity of the HLA-DP protein, which is part of the protein/peptide-antigen receptor on the surface of T-cells, towards beryllium compounds.[18,20,21] Mutation studies with HLA-DP imply binding to only a few distinctive amino acid side-chains[22,23] or only one specific glutamic acid in the protein.[11]

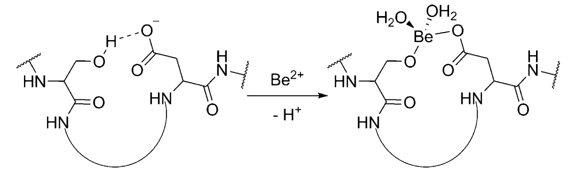
Table 1: LD_{50} threshold values for the GHS health hazard symbol "toxic" (skull and crossbones).[24]

Exposure route	LD_{50} (rat)
oral	$\leq 300\ \mathrm{mg\,kg^{-1}}$ bodyweight
dermal	$\leq 1000\ \mathrm{mg\,kg^{-1}}$ bodyweight
gases	≤ 2500 ppm
vapors	$\leq 10\ \mathrm{mg\,l^{-1}}$
dusts & mists	$\leq 1\ \mathrm{mg\,l^{-1}}$

Table 2: LD_{50} values for several compounds. Water of crystallization neglected in the formulas.

Compound	LD_{50} oral (species)
Be	Not available
$Be(OAc)_2$	Not available
$BeBr_2$	Not available
$BeCl_2$	$86\ \mathrm{mg\,kg^{-1}}$ (rat)
BeF_2	$98\ \mathrm{mg\,kg^{-1}}$ (rat)
$Be(NO_3)_2$	Not available
BeO	Not available
$BeSO_4$	$82\ \mathrm{mg\,kg^{-1}}$ (rat)
KCN	$5\ \mathrm{mg\,kg^{-1}}$ (rat)
NaN_3	$27\ \mathrm{mg\,kg^{-1}}$ (rat)
$Hg(NO_3)_2$	$26\ \mathrm{mg\,kg^{-1}}$ (rat)

It is suggested in the literature that the preferred complexation of Be^{2+} in proteins occurs through the displacement of protons in "strong hydrogen bonds" between acidic and alcoholic amino acid side-chains, as shown in Scheme 1.[2,25,26] These strong hydrogen bonds were identified through their distinct downfield NMR shift in the range of δ = 10–22 ppm.[25] However, the substitution of the twofold coordinated proton by a tetrahedral coordinated Be^{2+} ion would cause a massive decrease of the bond angle to about 109°. The bond angle in hydrogen bonds tends to be as linear as possible, and almost never below 120°. This would lead to strong changes in the conformation of the protein. It is questionable if a Be^{2+} species would acidify a proton of a hydroxy group enough to liberate it and to our knowledge this has not been shown.



Scheme 1. Proposed mechanism of interaction for beryllium with proteins.[10,25,26]

Biochemical investigations additionally show that proteins may be loaded with several beryllium cations.[25,27] While the coordination of multiple beryllium ions to a protein might be relevant for acute berylliosis, this is impracticable for the understanding of chronic berylliosis. This is because minimal amounts of beryllium ($2\ \mu\mathrm{g\,m^{-3}}$) and its compounds in the lung can already act highly "toxic" while the solubility of beryllium compounds in the lung is very low under physiological conditions.[3,28] It should be noted that for a compound to reach the alveoli in the lung, the water solubility must be low, otherwise it will already be absorbed in the upper respiratory tract. Particle size is also an issue. Therefore only a very low beryllium concentration is expected in the cells. Hence the long and unpredictable period of latency of beryllium associated diseases (latency times of up to 30 years are reported, a maximum of the illness rate is observed after three years)[29] rather suggests a specific interaction in the HLA-DP-T-cell receptor-complex. The chronic berylliosis as a lung-disease presumably has to be assessed similarly to silicosis, asbestosis and, even more to sarcoidosis. In sarcoidosis, the body encapsulates foreign matter with scarring of the lung tissue, which is then basically incapable of oxygen uptake and carbon dioxide release. The similarities of berylliosis and sarcoidosis, of which the cause is still unknown, has to be emphasized.[15a]

It is assumed that only 1–5% of the general population have a predisposition for chronic berylliosis.[30] The definite diagnosis of the chronic form requires a discrimination from sarcoidosis, which is a clinically similar granulomatose lung disease of also still unknown origin. An important criterion for the differentiation of berylliosis and sarcoidosis is the proof of an exposure to Be and its compounds.[31] It was estimated that concentrations above 0.02 $\mu g\,m^{-3}$ are required for the formation of chronic beryllium disease.[30–33] It was deduced from the available medical literature that beryllium and its compounds should be treated as carcinogenic.[32] Inhalation studies have been carried out using two animal species and showed a significant increase of the lung cancer rate.[30] However, some committees of experts consider the studies on occupationally exposed human individuals as not sufficient to prove the carcinogenicity in humans.[33]

However since the biochemical mechanisms which cause beryllium associated diseases are still unknown, special (safety) precautions should to be taken when handling beryllium, (see Section 6).

4. What are the Legal and Medicinal Requirements when Working with Beryllium and Its Compounds?

We will outline the situation for Germany and briefly for the USA, UK, and Russia, for other countries the information may be obtainable from the national health institutions. Employees are only allowed to work with Be and its compounds after they have seen the company physician if the workplace exposure limit of the respective Be compound may be exceeded.[34a–c] Then, visits to the company physician are to be offered to the employees on a regular basis. Also, as beryllium and its compounds are regarded as a human carcinogen, category 1B, (in Germany the Technische Regeln für Gefahrstoffe TRGS 410 must be followed which states more necessities in detail).[35] However, as Be and its compounds are treated as a human carcinogen, there is no workplace exposure limit in operation![29] This renders the introductory sentences erroneous. A workplace exposure limit of 0.060 $\mu g\,m^{-3}$ has been proposed recently for Germany.[36] It should be noted that the tobacco of one cigarette may contain up to 0.74 μg of Be, the smoke up to 0.074 μg per cigarette.[37] Thus, if you happen to be a smoker, or you have passive smokers in your laboratories, modern chemical analytics will always detect beryllium in the air—also in areas no one ever worked with it. In the USA the OSHA recommends lowering the eight-hour beryllium exposure limit from 2.0 $\mu g\,m^{-3}$ to 0.2 $\mu g\,m^{-3}$.[38] The current threshold limit values (TLV) for the USA are available here (https://www.osha.gov/dts/chemicalsampling/data/CH_220600.html). Furthermore the requirements of the Title 10, *Code of Federal Regulations*, "Energy", Chapter 3, "Department of Energy", Part 850, "Chronic Beryllium Disease Prevention Program"[39] and Title 29, *Code of Federal Regulations*, "Labor", Chapter 17, "Occupational Safety and Health Administration, Department of Labor", Part 1910, "Occupational Safety and Health Standards"[40–42] need to be met in the USA.[43] In the United Kingdom the "*Control of Substances Hazardous to Health*" (COSHH) regulations[44] and in Russia the GOST 12.1 995-76 apply.[45,46] The exposure limits in these countries as well as in most countries of the European Union are between 2 and 0.2 $\mu g\,m^{-3}$.[7]

Therefore, as currently no German rules seem to fit properly when working with Be and its compounds, we recommend a close collaboration with the company physician. He/she is fully aware of this situation and will also follow the future changes to guide us chemists. Examples of work with Be and its compounds, where "high exposures" may be present, are available in the literature.[29] One needs to estimate this for the company physician. Chemical work is not seen as a work were high exposure is possible, at least not on the lab scale (remember that safety rules are primarily made to protect workers in industries that work with large amounts of material). Additionally, the rules also state working conditions, were no exposure is to be expected—and working in closed apparatus (as chemists do most of the time)—is among them. Sampling, however, will almost always require that the closed conditions cannot be maintained. What we recommend for these cases may be read below.

The German Federal Institution for Occupational Health and Safety (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin, BAuA) demands in their technical rules for hazardous materials (Technische Regeln für Gefahrstoffe, TRGS) that records of exposition amounts and durations have to be made when working with carcinogenic substances (rule TRGS 410).[34] Beryllium and its compounds fall in this category, especially since respiratory protection and gloves are advised. However, no records need to be kept if the work is conducted in closed and sealed apparatus and only quantities are used which are "laboratory common" according to rule TRGS 526.[29] Even though the first criterion is not met when the closed conditions are compromised for sampling, the quantities are small and exposition times short. Therefore record keeping is never mandatory for research work on beryllium and its compounds according to TRGS 410.[35]

As can be inferred from the paragraphs above, acute berylliosis, or an acute "intoxication" is an extremely unlikely event for the chemist. Table 2 shows the LD_{50} values of some compounds for comparison.[30–33]

For the acute oral toxicity in humans no data are available. In animal experiments, Be compounds of low solubility proved to be less toxic than soluble Be compounds. The LD_{50} values of soluble Be compounds, based on the Be content, is in between 10–20 $mg\,kg^{-1}$ (1.1–2.2 $mmol\,kg^{-1}$; rat), showing their high toxicity. However, no details of the symptoms and the target organs of the intoxication could be inferred.[30–33] Also, the statement that Be is the most toxic non-radioactive element, does clearly not withstand a close inspection. The toxicity of Be compounds may thus be best compared with the toxicity of soluble compounds of mercury or arsenic—and chemists have dealt with them successfully for several hundred years. It should also be noted that chemical warfare agents are at least one order of magnitude more toxic than KCN, and these agents have been synthesized on large scale, so for several decades handling of extremely toxic compounds has not proved difficult for chemists and chemical engineers.

5. How do I Obtain Beryllium and Its Compounds?

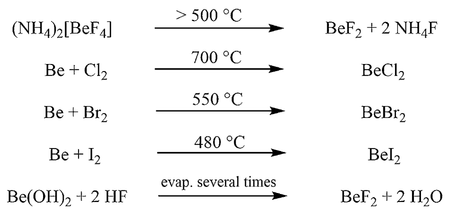
Besides the safety concerns based on the toxicological or allergenic potential of beryllium and its compounds discussed above, the access to the pure element is limited mainly due to its use in nuclear power or warfare applications as a neutron reflector. The trade of beryllium metal is strictly regulated by national and international nuclear agencies and therefore the number of suppliers for research facilities is very limited.[4]

"*The current status of the beryllium industry is unclear because of beryllium uses in nuclear weapons and the secret nature of this business.*"—Beryllium Chemistry and Processing by Kenneth A. Walsh.[4]

There are very few suppliers for the industrial use, of which Materion (USA) is the largest, followed by NGK (JPN), the second largest supplier, which produces beryllium alloys and more. The Ulba Metallurgical Plant in Kazakhstan is a supplier of Be metal and its alloys.[4]

To our knowledge, it is not possible to obtain beryllium metal commercially in Germany. During contact with several well-established suppliers (SigmaAldrich, Alfa Aesar, abcr, Chempur, Strem, smart-elements) we were invariably told that the amount of paperwork related to safety regulations and other additional bureaucracy was too high related to the number of customers. As far as we know, it is only possible to obtain $BeCl_2$ (25 g for 2445 €—Sigma Aldrich 16.6.2015), $BeSO_4 \cdot 4H_2O$ and BeO in Germany. Nonetheless, suppliers might be available in other regions (http://www.goodfellow.com/).

Since BeO and $BeSO_4 \cdot 4H_2O$ are not the best starting compounds for organometallic or coordination chemistry and the price for anhydrous $BeCl_2$ is relatively high, there is the need to find other ways to obtain the desired reagents. The best way to start is from beryllium metal, which can be converted into BeX_2 (X = Cl, Br, I; Scheme 2) by treating the metal with elemental halides at elevated temperatures, however it is best not to prepare the fluoride like this as elemental fluorine is too reactive.[47] But where to get beryllium metal from, when there are almost no suppliers? The easiest way is to ask around your faculty for old samples of beryllium, which can sometimes be found in storage, untouched for a long time. One would not think this to be a proper source, but nevertheless in many cases it can help to get an early start and most of the people asked are happy and sometimes almost relieved to give you what you desire. As to be expected the supply is most often very limited. Anyway, just give it a try. Another more mechanical way to procure beryllium is to break old X-ray tubes that a crystallographer might be willing to give you. We provide a detailed description of how to break a high-vacuum X-ray tube and the safe extraction of the beryllium windows in the Supporting Information. You can also try to contact one of the above mentioned companies and hope for a positive reply. Once you have access to elemental beryllium you can start the synthesis of the desired starting materials, which mostly are the above-mentioned halides. In most cases it is necessary to purify the obtained halides by fractional sublimation to remove impurities, such as Fe^{III}.[47] For detailed descriptions please read Section 6 as well as the Supporting Information. Once you have obtained these starting materials you are well prepared for the start of your own beryllium focused research.



$$(NH_4)_2[BeF_4] \xrightarrow{>500\ ^\circ C} BeF_2 + 2\,NH_4F$$
$$Be + Cl_2 \xrightarrow{700\ ^\circ C} BeCl_2$$
$$Be + Br_2 \xrightarrow{550\ ^\circ C} BeBr_2$$
$$Be + I_2 \xrightarrow{480\ ^\circ C} BeI_2$$
$$Be(OH)_2 + 2\,HF \xrightarrow{\text{evap. several times}} BeF_2 + 2\,H_2O$$

Scheme 2. Conditions for the synthesis of beryllium halides.[4]

6. How do I Handle Beryllium and Its Compounds?

In general there are two aspects that need to be considered when working with beryllium and its compounds. One is related to safety advice that helps you to avoid any contact with the compounds and the other is knowledge about the special preparative handling of these compounds, which is used in modern advanced inorganic chemistry.

The main aspect when working with beryllium is to strictly avoid any incorporation or contact in general with beryllium-containing materials. For the laboratory chemist the only form of potential incorporation may be inhalation. Ingestion may only occur on purpose. A toxicological potential is based on direct contact. If contact can be avoided, a compound is as dangerous (or not dangerous) as any other material! Also, concentration and exposure time play a role as already noted by Paracelsus in 1538.[135]

Thus one should stick to the rules that are recommended for working with compounds of unknown toxicological potential, which everyone ought to know from routine health and safety briefings, and every chemist has received this training during his/her studies. Additionally, we suggest the following procedures:

6.1. Technical Safety Procedures and Demands on Infrastructure

There are some basic demands on the safety infrastructure, such as a well-ventilated fumehood, in which all work has to be performed to make sure that contact with beryllium containing dust is avoided. Modern laboratories easily fit into that standard, so nothing special concerning the fumehood has to be considered, in most cases. Otherwise they would not have an operating permit. It should be noted that a certified and annually inspected fumehood guarantees that dangerous compounds are not released under normal working conditions. Remember that an accident is not a normal working condition so the fumehood may not protect you then. In general any reaction or handling of volatile or dust-raising compounds should be performed under inert-gas atmosphere, as any contact with the compounds must be avoided and any contact with moisture is to be limited owing to the highly hygroscopic nature of beryllium halides. We recommend the use of standard Schlenk-line techniques in combination with the use of a glovebox. Please note that properly performed work on a Schlenk line is always more anhydrous than the work performed inside a glovebox (compare the surface areas, and the box cannot be flame dried). An overview of typical glassware, fumehoods and gloveboxes can be found in the Supporting Information. Unfortunately, in most cases researchers have to share their laboratory and gloveboxes with others, so special care has to be taken for the safety of others when working on beryllium chemistry. Make sure that everyone that is working with you is given a special safety advice that focuses on the toxicological potential of beryllium and the required safety procedures (see Section 6.2). Make sure that everyone else in your lab/group is aware of the potential dangers that are related to working with beryllium. You should not share any glassware or other laboratory equipment with others to avoid any contamination (decontamination is substance dependent, but for Be and its compounds dilute HCl can usually to be recommended). Nevertheless, sometimes you have to share glassware. So make sure that this glassware is clean. Always keep all beryllium containing vessels, waste or other personal equipment, for example, permanent gloves, in the fumehood or in a ventilated cupboard, but do not store or handle anything on the bench. Make sure that your lab coat is not stored together with your colleagues' lab coats and do not take anything that contains beryllium out of the lab without the use of a second containment for safe transport. We suggest the use of metal buckets with a lockable cap for the transport of for example, Schlenk flasks, NMR tubes, or vessels to the glovebox or the NMR machine.

6.2. Organizational Safety Procedures

Employees, lab neighbors, and visitors to the lab must be informed of the potential and assumed hazards of Be chemistry. We also recommend to clearly label all lab doors leading to a beryllium working area in a manner that people cannot enter the lab without removing the warning sign, that is, place the warning signs over the door handles. The warning signs for a beryllium working area should contain the official (for the European Union) symbols (Figure 2).

Figure 2. Warning signs (for the European Union).

6.3. Personal Safety Procedures

When working with beryllium compounds a breathing mask should always be worn that is able to filter out small dust particles to prevent any inhalation. Dust particle filters come in three different categories, from FFP-1 to FFP-3, the FFP-3 filtering even the finest particles down to 0.6 μm. (For a detailed introduction into breathing protection and the requirements of the DGUV, see their publication BGR/GUV-R 190.[48]) We recommend the use of only FFP3 filter masks (e.g. from 3M) for all routine work. For the handling of beryllium in combination with elemental halogens a combined gas and particle filter mask (ABEK2P3/A2B2E2K2-P3) may be used—but would you use a gas mask when working with the halogens? Probably not, since you have a proper fume hood. So, we recommend again "only" a FFP-3 particle filter mask. In the case of work with volatile organometallic Be compounds or complexes that do not immediately hydrolyze upon air contact, filter masks with active carbon filters are to be preferred (ABEK-P3, for example, the MSA Advantage 400). It must be mentioned that using filter masks or gas masks may require to see the company physician before the work with them can be started. (See the DGUV publication BGI/GUV-I 504-26.[49]) For skin protection any standard gloves such as latex- or nitrile-based products can be used if solvents are involved. A lab coat and safety goggles must anyways be worn.

6.4. Disposal of Beryllium Wastes

When you work with beryllium you will always get residues and other leftovers that have to be disposed of safely. For standard laboratory waste, such as old tissues, gloves, or filters, we recommend the use of an exclusive storage vessel for beryllium-containing waste side by side with the standard vessels that are used for other laboratory waste. These vessel can be disposed of as regular toxic solid laboratory waste. Usually there is no special disposal for Be-wastes necessary, ask your local waste disposer for advice. In this way you are sure that there is no chance of cross-contamination with the waste produced by other co-workers. This is the best way to protect your colleagues in daily laboratory routine. The disposal of beryllium compounds should be done in solution to avoid the formation of dust or exposure to it. In general we use cold water for halides (very exothermic reaction) and common organic solvents for organometallic or coordination compounds of beryllium. To avoid the release of beryllium-containing aerosols we suggest to use large flasks (the volume of the flask should be ten times greater than the volume of the solution with the reactive species, for example, 100 mL Schlenk-tube with 10 mL of solution) and external cooling. If there should be a release of aerosol you can also use hair-spray or glue-spray to bind the aerosol. For extremely reactive residues, such as Be-dialkyles or compounds with Be-hydrides, we recommend mild decomposition by reacting these residues with a solution of 5% *t*BuOH in toluene under inert atmosphere in a Schlenk vessel.[50] Be aware of H_2 evolution and prevent the release of aerosols. The resulting solutions can be disposed of as toxic inorganic liquid waste.

Most chemists use KOH/isopropanol base baths to clean their glassware. As an additional safety feature you should make sure that you do not share a base bath with other colleagues but use one exclusively for your beryllium-residues containing glassware.

6.5. Working in a Glovebox

We recommend wearing additional gloves (L or XL sized latex or nitrile gloves) inside the glovebox on top of the original gloves to prevent contamination through small overlooked holes. Also, the second pair of gloves helps in the prevention of spreading contamination as they can be disposed afterwards. Again cross-contamination with co-workers' glassware in a shared glovebox must be avoided by all means. For disposal of waste that accumulates in the glovebox we use a vessel that is stored inside the glovebox and can be disposed of in a second containment once it is full. To avoid contamination through dust which might be adsorbed or electrostatically bound on the outer walls of your glassware or plastic vessels we suggest to wipe the outside with a wet tissue or submerge the closed vessels under water, directly after removal from the glove box.

Besides safety aspects we also present experience from our daily work in the lab that includes planning of reactions, preparation; and handling of beryllium compounds.

6.6. Handling of Beryllium Compounds

Many chemists work with air- or moisture-sensitive compounds and are thus used to working under inert-gas atmosphere. For a successful synthesis of unknown beryllium compounds, you have to keep in mind, that beryllium compounds are often more reactive and sensitive to air/moisture than similar compounds of, for example, magnesium or aluminum. Every preparative working chemist has their own personal style of so called "standard Schlenk-technique", but through our experience over the last few years we have some suggestions that might help you to get to the desired compound. We have experienced that some beryllium compounds need "special" treatment.

First of all, one has to make sure that the solvents used are sufficiently dry, meaning that the remaining water content after drying should be below 0.1 ppm (Karl–Fischer titration), as beryllium compounds often are very strong electrophiles and chemically very hard acids according to the Pearson concept. The choice of your solvent depends on the reaction you have in mind. As far as we can say, organometallic or coordination compounds of beryllium can tolerate many solvents, such as hydrocarbons (heptane, hexane, pentane etc.), aromatic hydrocarbons (benzene, toluene), coordinating solvents (pyridine, thf, diethyl ether, 2-methoxy-2-methylpropane, acetonitrile, benzonitrile), or polar solvents (CH_2Cl_2, 1,2-difluorobenzene, fluorobenzene, benzotrifluoride), and of course liquid ammonia. So, depending on the coordination mode and number at the beryllium cation, the compounds tend to be stable in solution. As a rough rule of thumb the lower the coordination number of the beryllium cation and the "softer" the ligands, the less the compound tolerates solvents. Typical side reactions can be halide abstractions or ether cleavage. In case of coordinating solvents it can be problematic (difficult or impossible) to remove the solvent molecules from the beryllium cation.

Beryllium compounds are also sensitive towards certain types of grease (mostly based on polysiloxanes). We highly recommend the use of J-Young type threaded stopcocks or at least the use of female joint stopcocks to avoid any contamination with grease. The grease of choice for the work with beryllium compounds can be PTFE-based pastes. In the Supporting Information there is a collection of flasks and set-ups that we use for our synthesis. Note that a skilled chemist always favors the work with Schlenk techniques over working in a glovebox, as working in a glovebox means high risk of contamination with other compounds that might be present in the glovebox atmosphere. A provocative phase says, "the glovebox atmosphere contains argon (and every other compound with vapor pressure)". Please note that in a glovebox there should be no carbohydrates—such as paper wipes, paper labels, or pencils. Any compound hygroscopic enough will force the water out of such things. Predrying paper in an oven does not help.

Before starting a reaction you will have to exclude the presence of water that might be still adsorbed on the surface of the glassware. We always store our glassware in a heated cabinet, that is kept at 130–160 °C, for a minimum of four hours.[51] Then we connect the flasks to a Schlenk line and heat them with the help of a gas burner (Bunsen or Teclu type) under vacuum until the flame of the burner turns yellowish-orange, that is, you start to see the sodium flame. At this point the glassware is hot enough and is then allowed to cool to room temperature (still under vacuum). This procedure can be repeated several times, we recommend a minimum of three. Please also note that using a heat gun (maximum temperature only ca. 650 °C) is in most cases not sufficient to establish "anhydrous" conditions—this depends on the sensitivity of your compounds towards moisture. However, using a Bunsen or Teclu burner you will be able to obtain the lowest achievable moisture levels in glass vessels (the last layer of water may only be removed from glass at 400 °C in ultra-high vacuum (UHV)). In our experience even thin films of evaporated elemental cesium can be kept for more than seven days in properly flame-dried glass vessels. Residual moisture can also be removed from glass apparatuses by treatment with gaseous phosgen (a few hundred mbar).

Sometimes we prepare our flasks in a special way for crystallization purposes. To make the glass surface hydrophobic we add a small amount (1 mL) of $HN(SiMe_3)_2$ into our flasks, close the tap and open it and apply mild vacuum to the flask and then close it again. After that the liquid is gently warmed up with a heat gun until it refluxes up to the neck of the closed flask, such that all of the glass surface is in contact with $HN(SiMe_3)_2$. Then the tap is opened and the refluxing $HN(SiMe_3)_2$ is evaporated into the cold-trap. After that we start the crystallization procedure.

It also has to be noted that beryllium halides can react with borosilicate glass (such as Duran or Pyrex) and even pure silica glass at elevated temperature and pressures at or above 1 bar, the synthesis conditions of BeX_2 (X = Cl, Br, I).[52] Silica glass is a lot more resistant towards attack. Borosilicate glass can be used for the sublimation of these compounds under high vacuum and no reaction occurs with it (Figure 3)

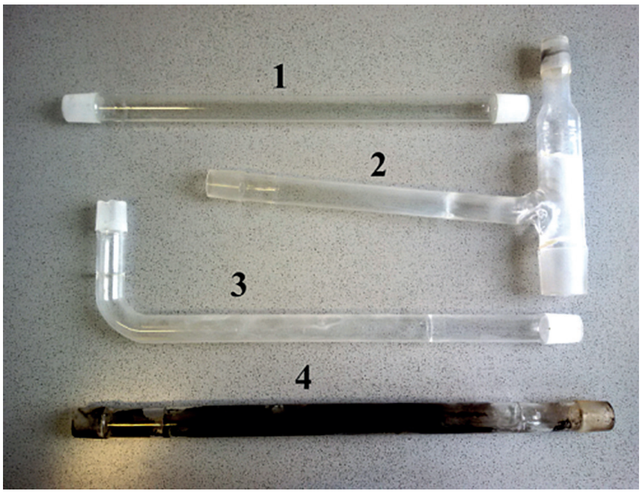


Figure 3. Different glass tubes that were used for the synthesis of Be-halides at elevated temperatures. 1) unused. 2) $BeCl_2$. 3) BeF_2 by decomp. of $(NH_4)_2BeF_4$. 4) $BeCl_2$ ($BeO + C + Cl_2 \rightarrow BeCl_2 + CO$). Picture: D. Naglav.

7. What do I do in Case of an Emergency?

The more you have prepared for accidents or unpleasant situations, the calmer, more focused you will be in such a situation.

Note: Write your accident response plans down! People from the safety and health departments may request such things.

If anything unexpected happens, such as leakage in your system, glassware breakage, or anything else getting damaged and you and/or your fumehood gets contaminated with beryllium-containing dust, aerosol, or liquid, you can be sure that the above mentioned safety equipment (Section 6) will protect you. Inform your colleagues about the incident so that no unauthorized, not suitably protected person may enter your lab. In case of fumehood contamination you can remove and deactivate dust with wet tissues and water. In this way you hydrolyze the spilled compound and transform it into hydroxide derivatives that can be removed easily by wiping over all contaminated parts. Any BeO that might be formed, when organoberyllium compounds burn in air, should also be treated that way, as the water stops the dust from swirling up again and can be wiped away as mentioned above. After disposing of the waste as described above and checking visually for any leftover contamination, we recommend to continue with a routine clean-up of the fumehood. If a powdered compound has been spilled that easily dusts, a good procedure is to spray it with a mist of water—not directly, but into the air above it in order not to blow it away. A second method is to use hair-fixing spray. Again, do not spray it directly onto the spilled powder, just let the aerosol slowly settle onto it. Then, everything can be wiped up without dust release. This is, however, only of limited use in a working fumehood but works very well outside of it. We recommend these methods also for Nano-powders or radioactive powders.

If contamination occurs as a result of not using adequate safety equipment it is completely your responsibility as you did not follow the safety rules! Follow the usual emergency procedures (shower, eye shower, wash skin with copious amounts of water, seek the advice of a physician, or call for emergency).

8. How do I Analyze My Compounds?

The characterization of beryllium compounds can be performed in the same way as for all chemical compounds. Typical methods include single-crystal and powder X-ray diffraction, elemental analysis, NMR, IR, Raman, and UV/Vis spectroscopy.[53–58] While performing single-crystal X-ray diffraction on beryllium compounds it must be remembered that compounds might only contain beryllium and other light elements, such as nitrogen, carbon, or oxygen. So, an absorption correction can be skipped sometimes.

For advanced NMR spectroscopic studies beryllium is very useful. ^{9}Be is a quadrupole nucleus with a spin of 3/2 and a natural abundance of 100 % which is very sensitive for NMR spectroscopy. Therefore very fine ^{9}Be spectra can be acquired in a short time that allow in situ observations of beryllium compounds. The broadness of the signal depends on the symmetry and the coordination number of the complex. The chemical shift range varies from $\delta = -20$ to $+30$ ppm and is referenced to a 0.43 M solution of $BeSO_4{\cdot}4H_2O$ in D_2O ($\delta = 0$ ppm).[58] For further details please check the literature referenced.

9. How do I Characterize My Beryllium Materials?

The most powerful tool for analysis of (partially) crystalline materials is probably X-ray diffraction (XRD).[59] It allows for identification of crystalline phases, determination of lattice parameters, and stress analysis for thin films. Beryllium metal crystallizes at ambient pressures in the hexagonal crystal system, space group $P6_3/mmm$, resulting in a simple diffraction pattern that can clearly be distinguished from other crystalline Be-containing phases, such as oxides, nitrides, and carbides by referencing the respective JCPDS standard card. Analysis of Be films is hindered by formation of thin layers of beryllium oxide that form when the metal makes contact with air owing to its strong affinity to oxygen. Chosen ex situ analytic methods should have the possibility for depth profiling. Although it is a standard method for material characterization, energy dispersive X-ray spectroscopy[61] (EDX), is often not suitable for beryllium, depending on the instrument. Most EDX devices cannot detect elements with $Z < 6$ (carbon), as the generation of X-rays becomes more unlikely with decreasing atomic number and the energy of the generated X-rays is so low that absorption of the radiation by the sample and parts of the detector leads to a strong decrease of signal intensity. In our experience, EDX can be used to check the quality of bulk beryllium which—due to its production process—is often contaminated with calcium and the halides.

In contrast to EDX, Auger electron spectroscopy[60] is very sensitive to light elements. In this case this is due to the KVV transition of metallic Be that can be observed at 105 eV. X-ray photoelectron spectroscopy[60] is a surface sensitive method for the determination of the chemical environment of an element; the 1s peak of metallic Be at 110.5 eV can be distinguished from the 1s of Be bonded to oxygen at 113 eV, bonded to nitrogen at 114 eV and bonded to carbon at 112 eV. A very powerful tool for the determination of small amounts of Be in thin films is secondary-ion mass spectrometry (SIMS). Beryllium can easily by ionized, so this technique is very sensitive, with a detection limit in the sub-ppm range and allows the determination of doping levels and diffusion behavior.

Atomic emission spectroscopy (AES) is the standard method for the quantification of Be. For example, the air of your laboratory may be passed over fine filters to retain the Be compounds, then all is dissolved in HNO_3 and analyzed. You could set up your own beryllium air-level monitoring.

10. What Curiosities did We Observe while Working with Beryllium?

10.1. Organometallic Beryllium Compounds are Highly Reactive

While doing research on beryllium we experienced several situations, in which the extremely electrophilic nature of beryllium compounds was observable.[62] While working on oxidative fluorination reactions in order to obtain Cp*BeF (Cp* = 1,2,3,4,5-methylcyclopentadienyl) we wanted to treat Cp*BeX (X = Br, I) with XeF_2, AgF_2, and p-F-$C_6H_4IF_2$ by mixing the two solid compounds in the glovebox. But it didn't work out the way we planned. We weighed both compounds separately on a set of scales in the glovebox under argon atmosphere and placed the weighing papers close to each other without mixing. This lead to a tremendous fire that evolved between the two solids, which yielded in black and purple smoke and an intense and bright flame only leaving behind a black smoldering ash. The driving force for this reaction was certainly the exothermic formation of HF and BeF_2. On the one hand this demonstrates the power of oxidative fluorination, but also underlines the high reactivity of organometallic compounds of beryllium with strong fluorinating agents, because we had never observed such an extreme behavior when we performed similar reactions with other Cp*MX_n (M = metal, X = halide) compounds.

We also worked with $BeEt_2$ and Be$i$$Bu_2$ which we used to handle in syringes since they are liquids at room temperature. After the addition of these compounds to a reaction mixture we wanted to dispose the syringes and therefore pulled out the plunger of the assumed to be empty syringe in the fumehood. The remaining minimum amounts of liquid left in the syringe caused tremendous flames under the evolution of white fine dust and it seemed to us that they are more reactive than the well-known analogous compounds of aluminum or zinc. Because of this we developed the method for the safe disposal of beryllium compounds as mentioned above (Section 6.4).

10.2. Beryllium Compounds are Sweet? Yes Indeed

However, what most chemists know is that beryllium is famous for the sweetness of some of its salts that originally gave the element the name glucinium in France before the IUPAC nomenclature was introduced in 1957. Those findings were based on taste self-experiments, which was common in earlier days of chemistry.[1] Since we were working intensively on the Cp* complexes of beryllium we can present findings that circumstantiate these "observations" in a similar way. Due to the relatively high volatility of Cp* compounds we found out that Cp*Be compounds, such as Cp*BeR (R = Cl, Br, I, Cp*) have an extremely intensive but marvelous odor that is comparable with strong perfume. This perfumed sweetness has not been reported yet as far as we know and also underlines the beauty of this element, which—as in life—often comes with the risks of a beast. Those observations where made while preparing single crystals of these compounds for X-ray diffraction experiments at room temperature. The number of crystals ($0.380 \times 0.220 \times 0.070$ mm) was always between four and ten and they were kept under perfluorinated oil. While mounting crystals on nylon loops under the microscope we always experienced this extreme strong odor even in such small concentrations. During the preparation of single crystals at -50 to $-40\,°C$ we never observed such smells, possibly due to the decreased volatility of the compounds at such low temperatures. Additionally we noticed a sweetish smell when anhydrous $BeCl_2$ was accidentally released from a reaction vessel due to overpressure.

Note: As particle filter masks are penetrated by particles of sizes smaller than 0.6 μm, filter masks containing active carbon (such as the above mentioned ABEK2P3 filters) are recommended for such cases. However, you will not be able to smell the compounds then. If however you start smelling something, you know it is time to change the filter.

11. What is the Current Status of Beryllium Chemistry?

The following Section does not claim completeness but it is a selection of highlights from our point of view.

11.1. Coordination Compounds

The aqueous coordination chemistry of beryllium has been investigated much more than its chemistry in organic solvents. Therefore, a lot of compounds are known and studied and reviewed in several articles (see Table 3). The chemistry of beryllium is dominated by its need for electron density owing to its electron deficiency as a Group 2 metal. In aqueous solution the coordination compounds of beryllium have a tetrahedral coordination mode which is the most favored one for beryllium compounds. Beryllium also tends to form six-membered rings in which three Be^{2+} cations are bridged with an anion $[Be_3(\mu\text{-}A^-)_3(donor)_6]^{3+}$, in which all beryllium cations are coordinated tetrahedrally (Figure 4)

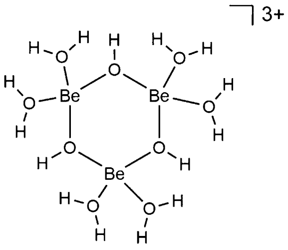


Figure 4. $[Be_3(\mu\text{-}OH^-)_3(H_2O)_6]^{3+}$.

The coordination compounds of beryllium in non-aqueous solutions have only been studied in classic organic solvents, such as toluene, tetrahydrofuran, CH_2Cl_2 and such. One exception is our research on the coordination chemistry of beryllium in anhydrous liquid ammonia, which yielded very interesting results, such as the action of the Be^{2+} cation as a fluoride acceptor or the formation of the $[Be(NH_3)_4]^{2+}$ cation. As a part of a deliberate hydrolysis process in this medium we also found the $[Be_3(\mu\text{-}OH)_3(NH_3)_6]^{3+}$ structural motive typical of the six-membered rings known from the aqueous coordination chemistry.[63,64]

The basic knowledge on beryllium coordination chemistry in non-aqueous solvents has been reviewed by two of the pioneers in this field Prof. Kurt Dehnicke (†2011, his death was not related to Be chemistry) and Prof. Bernhard Neumüller in 2008, which seems to be a state-of-the-art report about classical coordination chemistry.[65] It summarizes the advances in this field up to 2008 and describes the complex behavior of beryllium halides with numerous ligands in non-aqueous solutions.

Besides that Review there have only been a few though significant reports about coordination complexes of beryllium in the last 15 years.[66–90] A lot of investigations were concentrated on the synthesis of coordination complexes with NHCs (N-heterocyclic carbenes), which led to the discovery of the activation of these carbenes by a beryllium-induced ring-enhancement reaction and the synthesis of a NHC-$BePh_2$ complex (Figure 5).[82,83] It was also possible to isolate the first example of a structurally characterized beryllium borohydride as NHC:$Be(BH_4)_2$, which has been subject of ongoing discussion since its first reported synthesis over 70 years ago.[85] One of the leading authors in this field is Prof. M. Hill, who also studied the reduction chemistry and reaction behavior of β-diketiminate beryllium complexes (*N*-acetyl-*N*-acetonate = nacnac) in which he could show that coordinated beryllium alkyl complexes cause ether-cleavage reactions with thf as well as polymerization reactions.[81,82,85,86] We focused on the synthesis of heteroleptic scorpionate beryllium complexes (trispyrazolylborates (Tp)) and studies on the nature of homoleptic linear beryllium amides like $Be[N(SiMe_3)_2]_2$.[88,89]

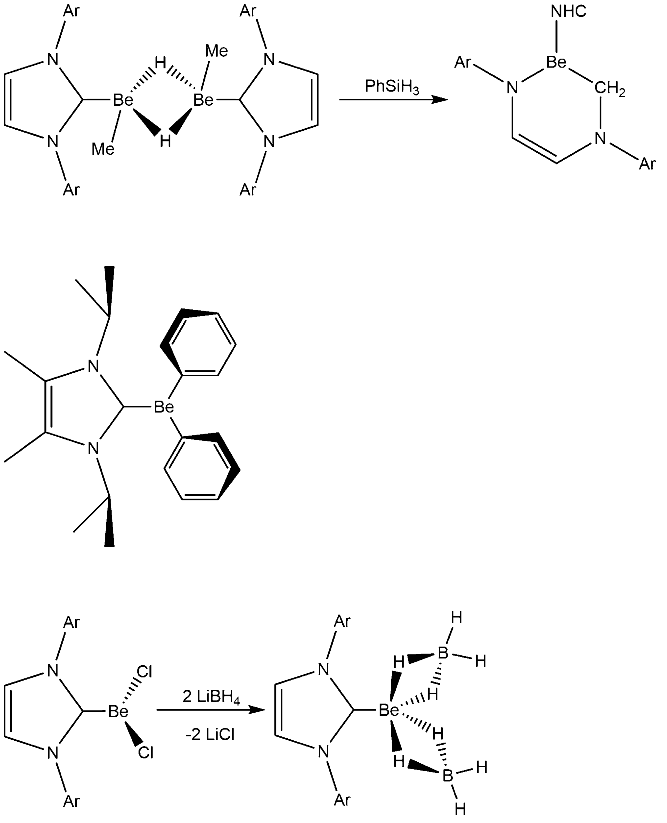


Figure 5. beryllium chemistry with N-heterocyclic carbenes (NHCs).

11.2. Organometallic Compounds

It seems that the organometallic chemistry of beryllium has awakened during the last 15 years, in which several groups started to investigate these highly reactive compounds (Figure 6).[90–100] Significant contributions were made by Power and co-workers, who published the synthesis of the homoleptic $BeMes_2\cdot(Et_2O)$ (Mes = 1,3,5-trimethylbenzene) and the heteroleptic sterically encumbered $ArBeX\cdot(Et_2O)$ (Ar = C_6H_3-2,6-Mes_2; X = Cl, Br, SMes, NHPh, $NHSiPh_3$, N-$(SiMe_3)_2$) compounds together with intensive ^{9}Be-NMR spectroscopy studies.[97,98] Carmona and Fernández published the structural characterization of $BeCp^*_2$ (Cp^* = pentamethyl cyclopentadienyl) and several derivatives.[100]

11.3. Theoretical Investigations

In several Reviews about beryllium chemistry the authors always mentioned the lack of experimental investigations in comparison to the huge amount of theoretical work that is published about beryllium chemistry.[3] This is probably due to

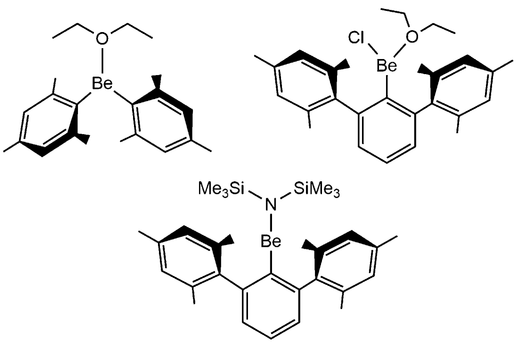


Figure 6. beryllium chemistry with bulky organic ligands.

the uniqueness of beryllium because of its exposed position in the periodic table that results in interesting bonding properties. This high interest in the nature of beryllium compounds should be another huge motivation for preparative chemists to confirm or disprove theoretical results. Most articles are focused on the special bonding properties of beryllium with its two empty p-orbitals (under sp-hybridization) and the resulting high Lewis acidity.[101–108] Recent work has also tried to evaluate the requirements for ligands that might be suitable for the synthesis of stable Be^{I} compounds (Figure 7).[106] Another field of study is the unique bonding situations that are possible with beryllium in noble-gas compounds,[109,110] Be clusters,[111,112] and coordination compounds.[113,114]

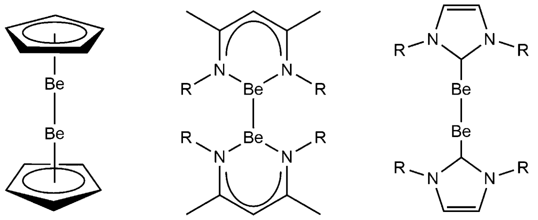


Figure 7. theoretical beryllium chemistry.

11.4. Materials Chemistry

From the materials scientist's point of view, beryllium is a kind of dream material owing to its unique properties. Among these its low density, which is comparable with magnesium and lower than that of aluminum (the "classical" light metals) combined with the high melting point and its high elastic modulus are interesting for application in aerospace and space technology. Although, in industry, Be and its oxidation product BeO are still considered to be remarkably "toxic", especially as dust, though even skin contact is problematic. Thus the dream becomes a nightmare. Therefore, as a result of the high safety levels needed, when industrially processing beryllium metal, its use is limited to applications, where costs only play a minor role. Being almost transparent to X-rays, only showing a small cross-section for the capture of thermal neutrons, and having a large coefficient for neutron scattering makes Be indispensable in the nuclear industry and nuclear research. In the last years, research is strongly fueled by its use in nuclear fusion reactors for plasma-facing inner parts, where Be resists the harsh conditions during operation.[115]

The growth of beryllium thin films is dominated by physical vapor deposition (PVD) methods.[116,117] For example, Be films were fabricated by the evaporation of beryllium under high vacuum on rock-salt substrates.[118] The necessary molten beryllium and its vapor are described as extremely corrosive and the choice of the crucible material is critical (tungsten was recommended). Another possibility is ion beam sputtering. Using a metallic Be target, Wu et al. investigated the growth of Be films on Si(100) substrates and the effect of Cu-doping on the microstructure of the film.[119] A strong reduction of the grain size and a decreasing surface roughness was found with increasing Cu content. Thick Be coatings (ca. 150 μm) can be generated using direct current magnetron sputtering on spherical polymer substrates.[120] The chemical vapor deposition (CVD) technique is a superior way for forming thin metal coatings. While information describing the CVD of most metals fill whole books, only little can be found for the CVD of Be. The classic CVD precursors—halides and hydrides—are unsuitable for Be CVD, because Be halides are thermally very stable and BeH_2 forms an inorganic chain polymer without a notable vapor pressure. One alternative is the use of thermolabile metal–organic precursors in a MOCVD process. Chemistry is strongly linked to MOCVD and novel compounds often get investigated for their suitability leading to a huge number of precursors for most elements, but only few simple beryllium compounds have been tested as possible Be sources. To our knowledge, only two detailed studies of organometallic Be compounds including $BeMe_2$, $BeEt_2$, $Be\textit{t}Bu_2$, and $BeCp_2$ in MOCVD were reported.[121,122] This lack of research might be caused by the increased hazard level, when working with highly volatile solids or liquids, which react violently even with small quantities of water or oxygen forming highly "toxic" dust instead of bulk Be. The operator should avoid even the smallest leak in the MOCVD machine to avoid intake of oxygen and leakage of beryllium. More common is the use of $BeCp^*_2$ and $BeEt_2$ for the doping of III–V semiconductors, such as GaAs and GaN.[123,124] Beryllium acts here as p-type dopant and the low vapor pressure of metallic Be prevents the evaporation from hot reactor parts in contrast to zinc and magnesium,and the high tendency of diffusion helps the doping process being more reproducible.[125] Beside the deposition of metallic Be films, another possible area of application of MOCVD are Be_2C, α-Be_2N_3 and BeO coatings. To date, such coatings were grown only by PVD, for example, α-Be_2N_3 was grown on silicon using reactive laser ablation of Be foil in nitrogen atmosphere at 700 °C,[126] Be_2C was grown by magnetron sputtering of beryllium in methane atmosphere on different substrate materials including Si, glass, Al foil, and polymers.[127] Amorphous BeO films were deposited by reactive sputtering of Be in oxygen-containing Ar atmosphere.[128] Organometallic Be compounds can act as so called single-source precursors, and the ligand as a possible source for oxygen, carbon, or nitrogen. Rare examples are the formation of Be_2C films using $BeEt_2$ in combination with H_2 as reactive gas in plasma-enhanced CVD (PECVD) process at 250 °C[129] and the use of $BeMe_2$ as precursor for ALD

(ALD = atomic layer deposition, a process related to CVD) of BeO on Si, GaAs,[130] and GaN.[131] The use of beryllium is strongly dominated by the nuclear industry, in which, an interesting possible application can be found. Uranium dioxide UO_2 is the widely used fuel in nuclear reactors and typically used in form of pellets. Unfortunately, the glasslike low thermal conductivity of UO_2 hinders the heat dissipation out of the pellet. To avoid the damage of the pellets due to thermal stress, the operation temperature is limited. Beryllium oxide has a high thermal conductivity, resists the strong radiation, and is chemically inert even at high temperatures. So a composite of UO_2 and BeO is discussed as possible solution to improve the thermal conductivity of the fuel which could allow the enhancement of the fuel temperature and therefore a higher overall efficiency of the process.[132]

For a better overview we list and highlight a selection of publications in Table 3. It distinguishes between the above mentioned topics and works as a guide for further literature research.

Table 3: Overview of publications related to a particular topics aspect.

Topic	Reference
toxicology	[2, 5, 6, 10–50]
safety	[6, 10, 12, 29–36, 48, 49]
characterization	[53–61, 115–131]
coordination compounds—aqueous	[3, 65]
coordination compounds—non aqueous	[65–89]
coordination compounds—ammonia	[63, 64]
organometallic compounds	[62, 66, 81, 90–100]
theoretical investigations	[62–64, 100–108]
Reviews	[3, 4, 47, 65, 66, 81]

12. Why should I Work with Beryllium?

In case this Review has not been enough to motivate you to start your own research on beryllium chemistry, we would like to summarize and finish with a highly committed personal statement.

As a scientists our intrinsic and instinctive motivation for our work is the interest in the discovery of new things, which—for chemists—means that we are destined to find new compounds and concepts to shed some light into the darkness of undiscovered chemistry. This stimulus and the aspiration for new discoveries always comes with the often cited "*pleasure of finding things out*".[133] There are few elements in the periodic table that have been treated with such reserve by researchers as beryllium. Beryllium needs to be rediscovered with all its chemical properties, concepts, and maybe new classes of compounds and materials. We hope that more modern inorganic chemists will ambitiously take part in this new phoenix-like rise that will force the trend to initiate a renaissance for the chemistry of long neglected elements as it was described for uranium—one of the other chemically unacknowledged elements—in a Review by Stephen Liddle last year.[134]

If this outlook is not catchy enough for you, here are some open questions that might motivate you to jump onto the bandwagon driven by the preparative chemist:

- Is it possible to make Be^I compounds?
- Can beryllium be used for Grignard-type reactions?
- What are suitable precursors for CVD (chemical vapor deposition) or PVD (physical vapor deposition) of beryllium?
- Do beryllium compounds form π bonds?
- How can you synthesize beryllium–metal bonds?
- and many more …

If you think your ideas might answer one of the questions above or can lead to new findings then our primary aim was successful. We hope we could catch your attention and turn it into curiosity.

Acknowledgements

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