

Synthesis and recycling of Ni(II)-Complexes

Daniel A. Isler
DCHAB
islerd@ethz.ch

Assistant:
Seraphine Zhang
zhangs@ethz.ch

Abstract

Since metal complexes have always played a big role in nature, they have also become one of the most important subjects in inorganic chemistry. Because chemistry is an empirical science it depends a lot on experimental data and the mechanism of many reactions is yet to be elucidated, but best illustrated with examples. In the scope of this experiment various complexes were formed with the transition metal nickel and the driving force for each reaction was analyzed. In the end the initial complex was recycled in a multi-step reaction.



Zurich, September 2, 2022

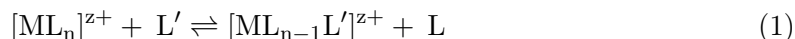
Daniel A. Isler

1 Introduction

1.1 Metal complexes

In biological metabolisms metals are not usually found in their elemental form, but rather as metal complexes with ligand spheres. This is why coordination chemistry plays a great role nowadays in a variety of fields of research ranging from biology to inorganic chemistry. A complex is built from a central atom (the metal) that is surrounded by its ligands. A complex may possess a charge and is therefore accompanied by corresponding counter ions, which need to be differentiated from the ligands, since they are outside of the ligand sphere. The ligands can vary a lot and the goal of this experiment is to show the different stabilisation effects the complex can obtain playing with an example. Furthermore, the ligands play a great influence on the color the complex obtains, as well as the geometry, which can be deduced from the orbital splitting, but this will be discussed in more depth later in section 3.4.

A metal can not only form complexes with one type of ligands, they can also be exchanged for others. When a ligand is substituted by another, we call this a ligand-substitution-reaction, which works according to the following principle:



In equation (1) M is the central atom (the metal) and L, respectively L' are two different ligands, n is the number of ligands and z is the net-charge of the complex.

There are two main driving forces for such reactions. The first one results from the σ -bonding from the metal combined with the π back donation from the ligand. The second one is the chelate effect. If a ligand binds to a metal with two or more atoms, it can substitute two ligands that bind only with one atom and therefore increases the entropy of the system, which usually is thermodynamically favorable. The chelate effect can also be explained by kinetics. When a monodentate ligand is substituted by a multidentate ligand, then the ratio of the concentration of the multidentate ligand versus the concentration of the monodentate ligand will have slightly increased.

1.2 Nickel

In the scope of this experiment a whole series of ligand substitution reactions with Nickel(II)-complexes is performed and in the end the starting material will be recycled under harsh conditions to close the cycle. The starting material was Nickel(II)chloride-hexahydrate. This was then converted through Hexaamminenickel(II)-chloride, Potassiumoxalatonickelate(II), Potassiumtriglycinatonickelate(II), Acetylacetonatonickel(II) until Bis(dimethylglyoximato)-nickel(II), which was then recycled back to the starting material. The whole process is illustrated in Figure 1.

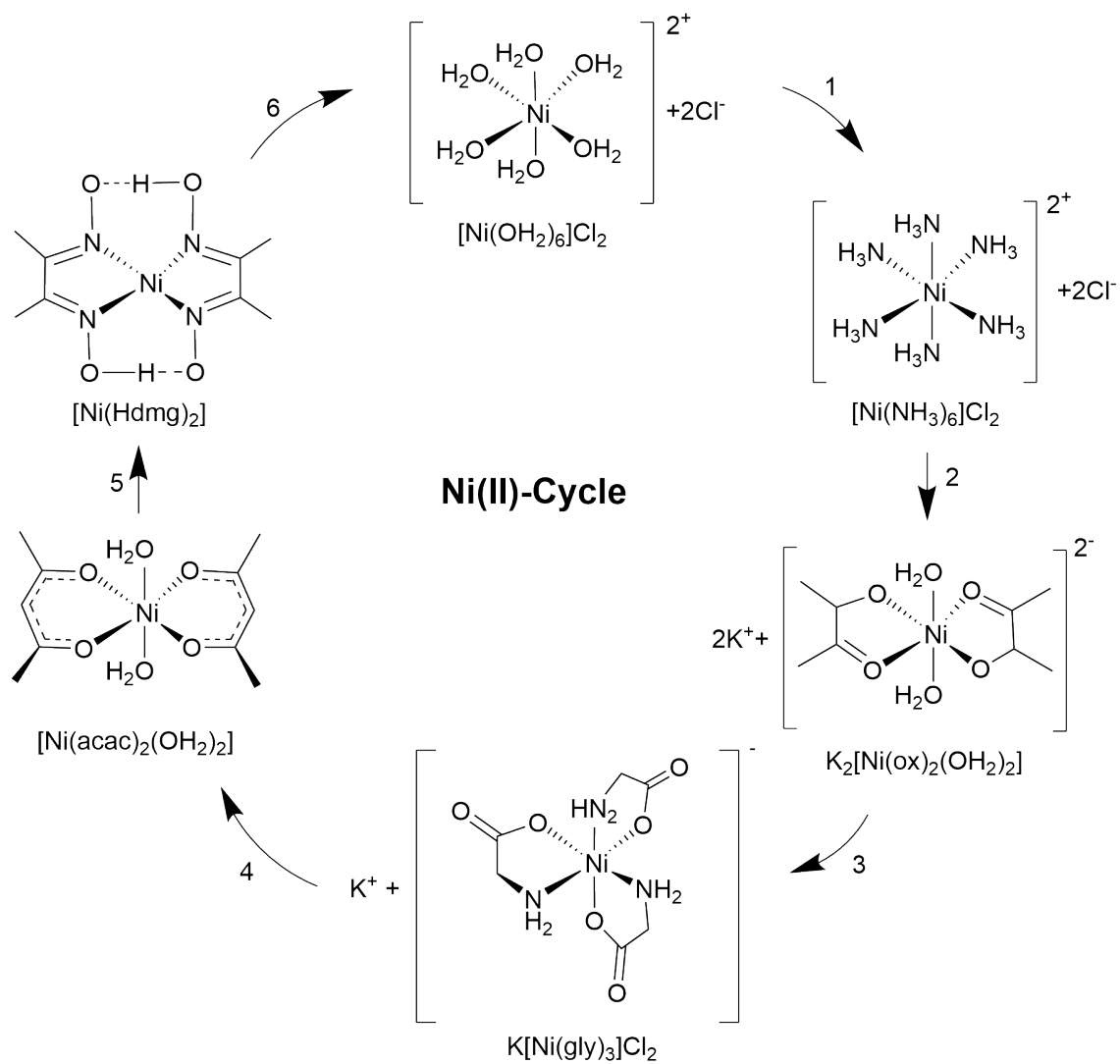












Figure 1: Complex-chemistry of Nickel(II) according to [2]

2 Experimental

2.1 Chemicals

All chemicals were provided by the Schönberg-lab and were used without further purification. The Hazard-&Precautionary-Phrases, for which the abbreviation H-&P will be used, are listed in the appendix. They were researched on PubChem [1].

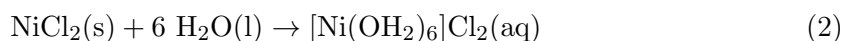
Substance, CAS-Nr.	GHS H-&P-Phrases	
Nickel(II)chloride, 7718-54-9		H301, H317, H334, H350, H360, H373, H402 - P201, P202, P260, P261, P264, P270, P272, P273, P280, P281, P285, P301+P310, P302+P352, P304+P341, P308+P313, P314, P321, P330, P333+P313, P342+P311, P363, P405, and P501
Concentrated ammonia, 7664-20-0		H221, H314, H331, H400 - P210, P260, P261, P264, P271, P273, P280, P301+P330+P331, P303+P361+P353, P304+P340, P305+P351+P338, P310, P311, P321, P363, P377, P381, P391, P403, P403+P233, P405, and P501
Glycine, 56-40-6		
Acetylacetone, 123-54-6		H226, H302 - P210, P233, P240, P241, P242, P243, P264, P270, P280, P301+P312, P303+P361+P353, P330, P370+P378, P403+P235, and P501
Dimethylglyoxim, 95-45-4		H228, H301 - P210, P240, P241, P264, P270, P280, P301+P310, P321, P330, P370+P378, P405, and P501
Sodium hydroxide, 1310-73-2		H314 - P260, P264, P280, P301+P330+P331, P303+P361+P353, P304+P340, P305+P351+P338, P310, P321, P363, P405, and P501
Sulfuric acid, 7664-93-9		H314 - P260, P264, P280, P301+P330+P331, P303+P361+P353, P304+P340, P305+P351+P338, P310, P321, P363, P405, and P501

Activated charcoal, unknown		H335, H351 - P201, P202, P261, P271, P281, P304+P340, P308+P313, P312, P403+P233, P405, and P501
Hydrogen peroxide, 7722-84-1		H271, H302, H314, H332 - P210, P220, P221, P260, P261, P264, P270, P271, P280, P283, P301+P312, P301+P330+P331, P303+P361+P353, P304+P312, P304+P340, P305+P351+P338, P306+P360, P310, P312, P321, P330, P363, P370+P378, P371+P380+P375, P405, and P501
Potassium oxalate, 6487-48-5		H302, H312, H319 - P264, P270, P280, P301+P312, P302+P352, P305+P351+P338, P312, P322, P330, P337+P313, P363, and P501
Hydrochloric acid, 7647-01-0		H314, H331 - P260, P261, P264, P271, P280, P301+P330+P331, P303+P361+P353, P304+P340, P305+P351+P338, P310, P311, P321, P363, P403+P233, P405, and P501

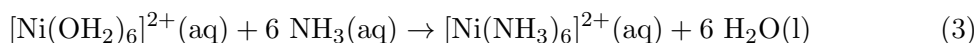
3 Results and Discussion

3.1 Synthesis

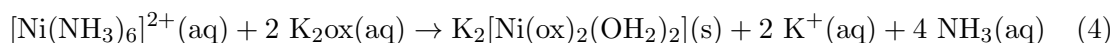
The starting material **Nickel(II)chloride-hexahydrate** was formed by dissolving $NiCl_2$ (111.8 mg, 0.86 mmol, 1 eq) in water.



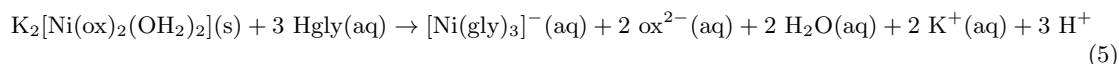
The solution turned greenish. Concentrated NH_3 (a few drops) was added until the solids had dissolved into the complex **Hexaamminenickel(II)** chloride which turned the solution blue. This ligand-exchange-reaction was thermodynamically driven, because NH_3 is the stronger Lewis base than H_2O .



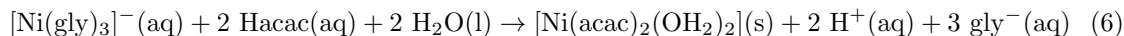
Potassiumoxalate-monohydrate (0.31 g, 1.7 mmol, 2 eq) to the boiling solution and 30 minutes cooling in ice allowed the formation of the turquoise **Oxalatonickelate(II)**. This ligand exchange reaction is driven by the chelate effect, since four monodentate ligands were replaced by two bidentate ligands.



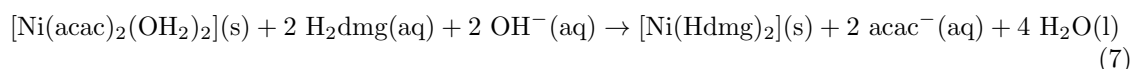
After warming up to room temperature glycine (185 mg, 2.46 mmol, 3 eq) was added to form **Triglycinatonickelate(II)** which has a light blue color. Again the reaction was driven by the chelate effect.



Next, Acetylacetone (0.24 mL, 2.46 mmol, 3 eq) was added and after a few minutes the precipitation of the light blue **Acetylacetonatonickel(II)** could be observed. The reaction resulted in an increase in stability, because the two acac-ligands formed an aromatic system.

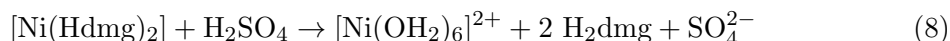


Finally a solution of dimethylglyoxime (292 mg, 2.52 mmol, 3 eq) in diluted sodium hydroxide was added to form the complex **Bis(dimethylglyoximato)nickel(II)** which precipitates and caused a color change to bright red. This complex is favourable because hydrogen bridges can be formed between the two ligands.



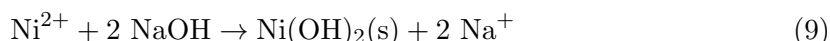
3.2 Recycling

After filtration, the red precipitate was dissolved in water that was strongly acidified with sulfuric acid, so that the pH was below 1. The solution was heated up until it obtained the greenish color of $[\text{Ni}(\text{OH}_2)_6]^{2+}$.

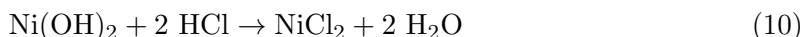


Any possible organic precipitate is filtered and activated charcoal (2 g, 0.17 mol, excess) was added to the filtrate, which was boiled and then filtered again. Then activated charcoal (1.5 g, 0.13 mol, excess) along with 30% hydrogen peroxide (5 mL, 48.95 mmol, excess) was added to decompose the organics.

Through the addition of sodium hydroxide, nickel hydroxide precipitated and was separated through filtration.



To finish the recycling, the obtained nickel hydroxide was dissolved in a small amount of concentrated hydrochloric acid to form the initial substance nickel(II) chloride.



To obtain the solid the solution was heated until all water was evaporated and just the solid nickel(II) chloride is left.

3.3 Efficiency

To validate the efficiency of the performed synthesis, the dried precipitate that resulted from the recycling process was found to be 98 mg, which corresponds to 0.41 mmol. Dividing by the initially added 0.86 mmol results in a yield of 47.9%.

The low yield shows how difficult the process of efficient recycling is. The largest amount of the initial substance was probably lost during the two filtrations that were required in the recycling process. The recycling process showed that you not only have to expect low yields, but also harsh conditions have to be applied.

3.4 Magnetism and geometry

All complexes obtained during the synthesis were octahedral except for **Bis(dimethylglyoximato)nickel(II)**, which was square planar. This can be deduced from the ligand field splitting model, shown in Figure 2. Ni(II) has a d^8 electron-configuration. As can be seen in Figure 2, in the octahedral as well as the tetrahedral geometry, the two most energetic orbitals are on the same energy level, whereas in the square planar field the energy difference of the two most energetic orbitals is severe. **Bis(dimethylglyoximato)nickel(II)** must have the square planar geometry, since Δ_{oct} is greater than the energy required to pair two electrons in one orbital. As shown in Figure 2, for the square planar geometry all electrons are paired up which results in diamagnetism. For all the other complexes obtained during the synthesis, the two most energetic orbitals are degenerated and are therefore each filled with only one electron, which results in paramagnetism.

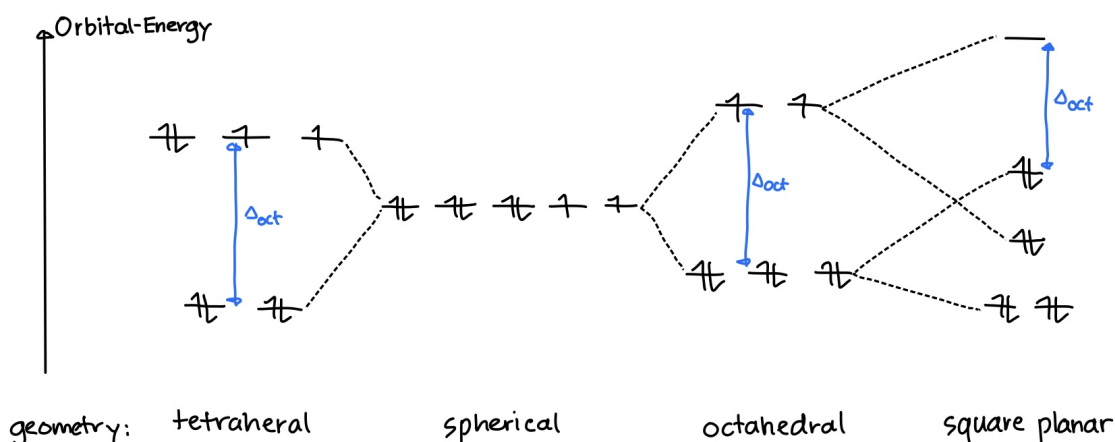


Figure 2: Energy diagram of the ligand field splitting from Ni(II)-complexes with the electrons illustrated as arrows.

With the orbital splitting model 2, the great variation of colors observed during the synthesis can also be explained. The color is directly related to the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, which is noted as Δ_{oct} in Figure 2. A complex can only absorb portions of energy, which is provided by electromagnetic waves of distinct wavelengths. If a wavelength is visible to the human eye, then the complex will appear in the complementary color. Because Δ_{oct} can be varied by ligand exchange reactions, the color of the solution was changed many times during the synthesis.

4 Conclusion

The synthesis was facile, since all reactions had a strong driving force and resulted in an increase in stability of the complex. Most reactants were added in surplus.

By watching the color of the solution/suspension change from blue over turquoise, light blue to red, one could very well observe the ligand exchange reactions. This showed how much the ligand can change the orbital splitting of the central atom. The connection between the magnetism and the structure showed nicely that Bis(dimethylglyoximato)nickel(II) must have diamagnetic properties, since it appears in square planar geometry.

Finally, the recycling process was more difficult, since it involved multiple steps and the

solution always looked black from the activated charcoal that was added in large amounts. The yield of 47.9% shows how difficult it is to recycle efficiently, it was more than expected and with an industrial setup one could surely accomplish a better score to save our natural resources. Furthermore, the purity of the complex was not analyzed.

A Appendix

A.1 Lab journal copies

Exp. 5.3.2
Komplexchemie des Nickels (Recycling) 10.01.2022
24

Ziel: Einblick in die Komplexchemie von Ni gewinnen, indem mehrere Ligandenaustauschreaktionen durchgeführt werden, und schlussendlich der Ausgangsstoff wiedervergestellt wird.

Schematischer Kreislauf (Vorgehen):

genauere Einwaage: 111.8 mg NiCl_2
2.4772 mg \rightarrow verworfen

1) $0.2\text{g } [\text{Ni}(\text{OH})_2]_3\text{Cl}_2 \rightarrow 100\text{ ml EtOH, } 2\text{ ml H}_2\text{O lösen}$
 \cdot Tropfenweise NH_3 (konz.) bis Niederschlag gelöst
 \hookrightarrow Tiefblaue Lsg. von $[\text{Ni}(\text{NH}_3)_6]^{2+}\text{Cl}_2^-$
 \hookrightarrow nur sehr wenig NH_3 gebraucht

2) \cdot Erhitzen zum Sieden
 $+ 0.37\text{g K(ox)}$ in $5\text{ ml H}_2\text{O}$
 \hookrightarrow Nach 30 min kühlen im Eisbad $\rightarrow \text{K}_2[\text{Ni}(\text{ox})_2]_3$ auf.
 \hookrightarrow türkischblau

3) \cdot Erw. auf RT, Lsg. v. 0.105g Glycin , Tropfen konz. NH_3
in $5\text{ ml H}_2\text{O}$ dazugeben.
 \hookrightarrow Nach erhitzen blau $\text{K}[\text{Ni}(\text{gly})_3]$

4) $0.24\text{ ml Acetylaceton} \rightarrow 10\text{ min rühren}$
 \hookrightarrow hellblauer Niederschl. $[\text{Ni}(\text{acac})_2(\text{OH})_2]$

5) $0.292\text{g Dimethylglyoxim}$ in 5 ml verd. NaOH $\rightarrow 2\text{ M}$
 \hookrightarrow himbeerrotes Bis(dimethylglyoximato)nickel(II)
 \hookrightarrow sehr trübe Lösung

6) Aufarbeitung & Recycling:

- \cdot Roter Niederschlag abfiltrieren, H_2SO_4 ansäuern: $\text{pH} < 1 \rightarrow$ erhitzen bis grüne Farbe (von $[\text{Ni}(\text{OH})_2]_3^{2+}$) \rightarrow Filtrieren
- \cdot Filtrat + $2\text{g Aktivkohle} \rightarrow$ Metall \rightarrow ~~...~~
- \hookrightarrow aufkochen, weiss filtrieren \rightarrow abkühlen + 1.5g Aktivkohle , $5\text{ ml H}_2\text{O}$ (langsam), 30% $\rightarrow 1\text{h rühren}$, aufkochen & filtrieren \rightarrow hat sehr nettes gebrochelt
- \cdot Filtrat + $\text{NaOH} \rightarrow \text{pH zw. } 11, 12$, ausgefallenes Ni(OH)_2 abfiltrieren
- \cdot Niederschlag mit H_2O sulfatfrei waschen, prüfen durch ansäuern mit HNO_3 & einige Tropfen $\text{BaCl}_2 \rightarrow$ kein Ausfall \rightarrow sonst weiter waschen
- \hookrightarrow Niederschlag + wenig konz. HCl vollst. lösen \rightarrow langsam trocknen, $T < 150^\circ\text{C}$
 \rightarrow gelber Rückstand, wird aber durch 1 Tag an der Luft zu grünem $[\text{Ni}(\text{OH})_2]_3\text{Cl}_2 \rightarrow$ Ausgangsstoff gewonnen \checkmark

Filtration $m_{\text{Becherglas, mit Ni}} = 47.9059\text{g}$

~~$m_{\text{abfiltrierter}} = 29.3425\text{g}$~~ \rightarrow

$\Delta m = 98.1\text{mg} \Rightarrow n_{[\text{Ni}(\text{OH})_2]_3\text{Cl}_2} = \frac{98\text{mg}}{237.7\frac{\text{mg}}{\text{mmol}}} = 0.413\text{mmol}$

$\hookrightarrow \text{yield} = \frac{n_{[\text{Ni}(\text{OH})_2]_3\text{Cl}_2}}{n_{\text{NiCl}_2, \text{start}}} = \frac{47.8\%}{\text{wow!}}$

$m_{\text{Becherglas, gewaschen}} = 47.8078\text{g}$

A.2 H-Phrases

H221: Flammable gas.
H226: Flammable liquid and vapour.
H228: Flammable solid.
H271: May cause fire or explosion; strong oxidiser.
H272: May intensify fire; oxidiser.
H301: Toxic if swallowed.
H302: Harmful if swallowed.
H314: Causes severe skin burns and eye damage.
H317: May cause an allergic skin reaction.
H331: Toxic if inhaled.
H332: Harmful if inhaled.
H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335: May cause respiratory irritation.
H350: May cause cancer.
H351: Suspected of causing cancer.
H360: May damage fertility or the unborn child.
H373: May cause damage to organs through prolonged or repeated exposure.
H400: Very toxic to aquatic life.
H402: Harmful to aquatic life [Hazardous to the aquatic environment, acute hazard].

A.3 P-Phrases

P201: Obtain special instructions before use.
P202: Do not handle until all safety precautions have been read and understood.
P210: Keep away from heat/sparks/open flames/hot surfaces. — No smoking.
P220: Keep/Store away from clothing/burnable/combustible materials.
P221: Take any precaution to avoid mixing with combustibles .
P233: Keep container tightly closed.
P240: Ground/bond container and receiving equipment.
P241: Use explosion-proof electrical/ventilating/lighting/. equipment.
P242: Use only non-sparking tools.
P243: Take precautionary measures against static discharge.
P260: Do not breathe dust/fume/gas/mist/vapours/spray.
P261: Avoid breathing dust/fume/gas/mist/vapours/spray.
P264: Wash skin thoroughly after handling.
P270: Do not eat, drink or smoke when using this product.
P271: Use only outdoors or in a well-ventilated area.
P272: Contaminated work clothing should not be allowed out of the workplace.
P273: Avoid release to the environment.
P280: Wear protective gloves/protective clothing/eye protection/face protection.
P281: Use personal protective equipment as required.
P283: Wear fire/flame resistant/retardant clothing.
P285: In case of inadequate ventilation wear respiratory protection.
P301: IF SWALLOWED:+P310: Immediately call a POISON CENTER or doctor/physician.
P301: IF SWALLOWED:+P312: Call a POISON CENTER or doctor/physician if you feel unwell.

P301: IF SWALLOWED:+P330: Rinse mouth.+P331: Do NOT induce vomiting.
P302: IF ON SKIN:+P352: Wash with plenty of soap and water.
P303: IF ON SKIN (or hair):+P361: Remove/Take off immediately all contaminated clothing.+P353: Rinse skin with water/shower.
P304: IF INHALED:+P312: Call a POISON CENTER or doctor/physician if you feel unwell.
P304: IF INHALED:+P340: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P304: IF INHALED:+P341: If breathing is difficult, remove victim to fresh air and keep at rest in a position comfortable for breathing.
P305: IF IN EYES:+P351: Rinse cautiously with water for several minutes.+P338: Remove contact lenses, if present and easy to do. Continue rinsing.
P306: IF ON CLOTHING:+P360: Rinse immediately contaminated clothing and skin with plenty of water before removing clothes.
P308: IF exposed or concerned:+P313: Get medical advice/attention.
P310: Immediately call a POISON CENTER or doctor/physician.
P311: Call a POISON CENTER or doctor/physician.
P312: Call a POISON CENTER or doctor/physician if you feel unwell.
P314: Get medical advice/attention if you feel unwell.
P321: Specific treatment (see symbol on this label).
P330: Rinse mouth.
P333: If skin irritation or rash occurs:+P313: Get medical advice/attention.
P342: If experiencing respiratory symptoms:+P311: Call a POISON CENTER or doctor/physician.
P363: Wash contaminated clothing before reuse.
P370: In case of fire:+P378: Use . . . for extinction.
P371: In case of major fire and large quantities:+P380: Evacuate area.+P375: Fight fire remotely due to the risk of explosion.
P377: Leaking gas fire: Do not extinguish, unless leak can be stopped safely.
P381: Eliminate all ignition sources if safe to do so.
P391: Collect spillage.
P403: Store in a well-ventilated place.
P403: Store in a well-ventilated place.+P233: Keep container tightly closed.
P403: Store in a well-ventilated place.+P235: Keep cool.
P405: Store locked up.

Bibliography

- [1] National Center for Biotechnology Information (2022). *PubChem Compound LCSS*. URL: <https://pubchem.ncbi.nlm.nih.gov>. (accessed: 13.01.2022).
- [2] H. Schönberg. "Praktikum in allgemeiner Chemie". In: *Laboratorium für anorganische Chemie ETH Zürich*, 2020. Chap. 5.3.2.