

## 5.3.2 Complex Chemistry of nickel

Dominik Götz

Group: J198 Moritz Bernhardt

Holiday Laboratory Course: Inorganic Chemistry

Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

**Abstract**—Complex chemistry of nickel deals with the complexes the transition metal nickel can form with different ligands and how they can be exchanged with other ligands by increasing the stability of the complex. The experiment is constructed cyclically starting with nickel(II)chloride and ending with bis(dimethylglyoximate)nickel(II). It showcases the ligand exchange reaction and recycling problems caused by the more stable complexes.

### I. INTRODUCTION

Metal complexes in inorganic chemistry are composed of two main components, the metal and the ligand. The metal acts as a binding site for other atoms or larger molecules which are called ligands. Both can be classified using the Lewis Acids and Bases concept [1]. A Lewis acid is an electron acceptor and Lewis base is an electron donor. Together they can form covalent bonds. The metal is the acid and the ligand is the base, together forming a metal complex. Ligands can be differentiated by counting how many binding sites of the metal they occupy. If they bind only once they can be classified as monodentate ligands [2]. If they do so twice, they are called bidentate ligand. Additionally, if two monodentate ligands are exchanged with a bidentate ligand, the number of particles in the solution increases, causing more entropy and thereby making it an energetically favourable reaction. Furthermore, if a ligand with two binding sites coordinates with both of them to the metal center, it is called chelate ligand. If one of the binding sites of the polydentate ligand is already bound to the metal center, the probability of the other site binding to the same metal is high. This is called chelate effect.

Depending on the coordination number, the number of binding sites, and the orbital configuration of the metal, the complex can have different geometrical shapes [3] as seen in Figure 1. For a single coordination number there can be several possible geometric shapes. To determine which one is more stable one can take a look at its orbital configuration using the ligand field theory. It can not only provide further insight into the shape of the complex but also into the excitation energy and the stability of the complex. In order to understand this more deeply we have to explore electron orbitals. An orbital is a volume in space in which the probability of finding an electron within is about 90%. Orbitals can be further subcategorized into s-, p-, d-, f- and g-orbitals. To determine the specific coordination of an atom

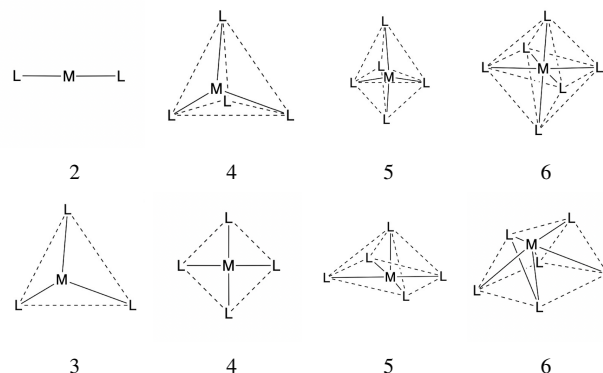


Figure 1: Complexes for Different Coordination Numbers

one must look at the periodic table. D-orbitals are the most relevant for the complex chemistry of nickel and any other transition metal since they participate in bonding with the ligand. There are five different d-orbitals of which each can host up to two electrons. They each have a distinct shape.

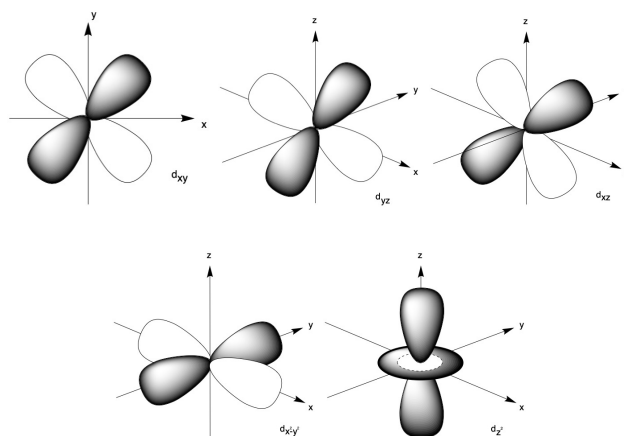


Figure 2: D-orbitals

Orbitals are filled using Hund's Rule from lowest to highest energy state. If two orbitals have the same energy level, degenerate orbitals, they are first each occupied by a single electron and only after that, if there are still electrons left, paired with a second electron of different spin. Pairing such two electrons of different spin takes some amount of energy and is thus energetically unfavourable. Every electron

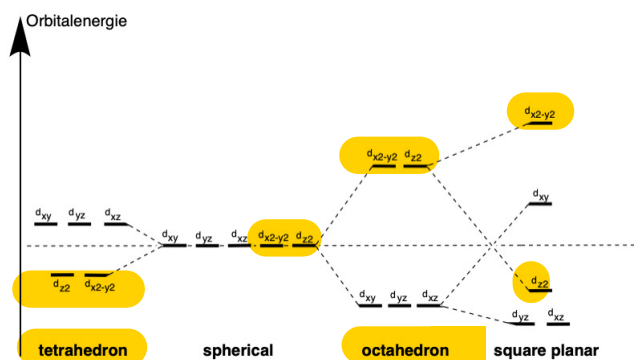


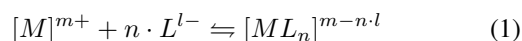
Figure 3: Energy levels for different geometric shapes

has a set of quantum numbers and according to the Pauli Exclusion Principle, this set is unique for every electron [4]. If a complex has at least one unpaired electron in its orbitals, it is called paramagnetic and therefore a high spin complex, paramagnetic [5] meaning that it will be attracted to an external magnetic field. If only paired electrons occupy the orbitals, the complex is repulsed by the external magnetic field, resulting in diamagnetic specification and low spin.

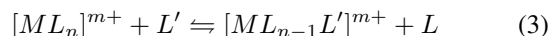
In a free metal ion all orbitals are degenerated. If a ligand comes close to the metal, energy levels of some orbitals rise due to the electrostatic repulsion between the electrons. This causes the splitting of orbital energies in the ligand field as seen in Figure 3. The energy of orbitals pointing in the direction of the ligand rises while the energy of orbitals pointing in other directions decreases. The total amount of energy must remain the same as before the splitting.

Nickel(II) is d-8-configured and therefore has 8 d-electrons. Depending on the coordination number, the geometry and ligand field of the complex can have different electron distributions. If the complex absorbs energy, one of the high energy electrons in the orbital ascends into excited state. As a consequence, its energy increases to the level above. In the relaxation phase this electrons emits light by lowering its energy and returning to its more favourable lower energy state. Some complexes absorb a specific wave length of light, thus appearing in the complementary colour to the human eye. Low spin complexes have warmer colours like red and orange, with wave lengths of  $\lambda \simeq 500nm$ . High spin complexes have cooler colours like blue and green with  $\lambda \simeq 650nm$  of wave length.

The stability of metal complexes can also be determined by analysing the d-orbitals. The lower the total energy of the orbital, the higher its stability. As a consequence, the geometric shape with the lowest energy is more favourable and thus likely to be the configuration of the complex at hand. Converting a metal to a complex with a ligand is a chemical reaction and will therefore reach an equilibrium where the ratio of products (right side of (1)) to educts (left side (1)) determines the stability with a stability constant called  $\beta$ .



$$K_n = \frac{[M(L)_n]}{[ML_{n-1}] \cdot [L]} \implies K_1 \cdot K_2 \cdot \dots \cdot K_n = \beta \quad (2)$$



A similar reaction equation can be formulated for the swap of ligands (3). The exchange happens if the following applies:

$$\beta_{product} \gg \beta_{educt}$$

In the experiment II-C this will be utilised to swap lower stability ligands with higher stability ligands and monodentate ligands with polydentate ones. The bonding strength also plays a role in ligand swap reactions. Since ligands are Lewis bases, the bonding strength correlates with the basicity. Ligands with higher basicity are more stable than the ones with lower basicity. Furthermore, is extremely important to keep the pH in a basic domain so that the ligands are not protonated. These reactions are performed in a manner that makes them form a cyclical chain of reactions starting with  $[Ni(OH_2)_6]Cl_2$  and arriving at *bis(dimethylglyoximate)nickel(II)* as a precipitate. This solid can be recycled and  $[Ni(OH_2)_6]Cl_2$  can be recovered. ~~Some reactions result in precipitation since the solubility of the complex is too high. The solids can be filtered and used for further reactions as will be explained in the recycling part of the experiment.~~

## II. EXPERIMENT

### A. Chemicals

The following Chemicals were available in the laboratory without further preparation: nickel(II)chloride-hexahydrat  $[Ni(OH_2)_6]Cl_2$ , deionised water  $H_2O$ , concentrated ammonia solution  $NH_3$  25%, potassiumoxalat-monohydrat  $K_2C_2O_4$ , glycin  $C_2H_5NO$ , acetylaceton  $C_5H_8O_2$ , dimethylglyoxim  $C_4H_8N_2O_2$ , sulfuricacid  $H_2SO_4$ , activated carbon C, hydrogenperoxid  $H_2O_2$ , sodium hydroxide  $NaOH$ , nitric acid  $HNO_3$ , bariumchloride  $BaCl_2$ , concentrated hydrochloric Acid  $HCl$ .

### B. Equipment

~~The Equipment was provided by the Laboratory J 198 supervised by assistant Moritz Bernhardt: Scale: Mettler Toledo Pb303, Heating Plate: Heidolph MR Hei Standart and a stationary fume hood.~~

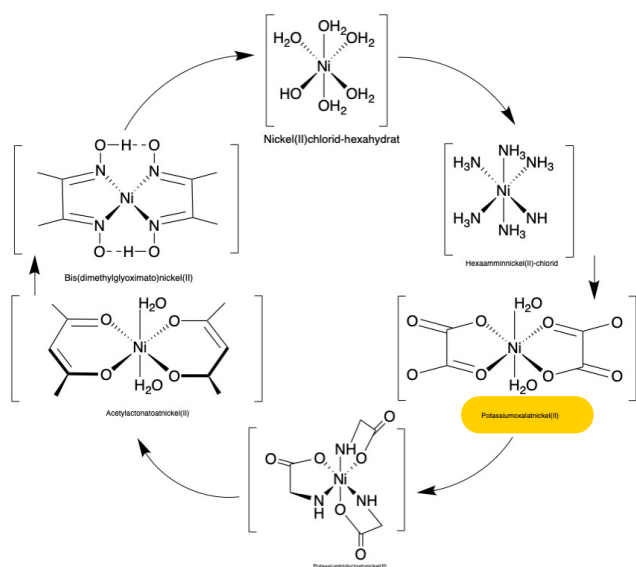


Figure 4: Ni(II) Cycle

### C. Execution

Because the experiment was constructed cyclically, each step depended on the steps executed beforehand. ~~An exception to this is the first nickel(II)chlorid-hexahydrat complex which was provided at the laboratory.~~ The experiment is divided into 5 ligand swaps with increasing stability. The last experiment of this series of experiments is recycling and the the refurbishment of the solution.

1) *Reaction:* 201mg of  $[\text{Ni}(\text{OH}_2)_6]\text{Cl}_2$  (0.844mmol, 1 equiv.) were weighed in ~~on a weighing plate and then transferred into a 100ml Erlenmeyer flask and then dissolved~~ with 2ml of deionised water measured with a 10ml graduated pipette. After all of the green nickel salt had dissolved, concentrated ammonia (25%, 6.857 M) was added ~~under the fume hood. Using an eye dropper,~~ the ammonia was added in droplets until the just formed precipitation of nickelhydroxid had fully dissolved again. A clear deep blue solution formed indicating the ligand swap was successful and contained Hexaaminnickel(II)-chloride.

2) *Reaction:* The solution from reaction one was diluted with roughly 5ml of deionised water. ~~The Erlenmeyer flask was covered in order to prevent the smell of ammonia filling the room.~~ Afterwards, the solution was heated to its boiling point. ~~After reaching the boiling point,~~ the in advance prepared solution containing 311mg of potassiumoxalat (1.7mmol, 2 equiv.) dissolved in 5ml deionised water was added. ~~The magnetic stirrer made sure that the solution was well mixed.~~ After the heating process the solution was cooled down to room temperature and then placed into an ice bath to ~~cool down further.~~ During the cooling process turquoise potassiumoxalatnickelat(II) crystals formed.

3) *Reaction:* The solution from Reaction 3 was reheated to room temperature and 185mg of Glycin (2.46mmol, 3 equiv.) dissolved in 5ml of ~~deionised~~ water alongside a few

drops of ammonia were added ~~in same process as in II-C1.~~ Subsequently, the solution was heated up using a water bath ~~in a 400 ml beaker.~~ After the brief heating, a light blue solution formed containing potassiumtriglycinatonickelat(II).

4) *Reaction:* To the solution of the previous step 0.24ml of Acetylacton (2.4mmol, 3 equiv.) were added dropwise and stirred until a lightblue precipitate had formed.

5) *Reaction:* To the suspension of reaction 4 a solution of 290mg dimethylglyoxim (2.52mmol, 3 equiv.) in 5ml diluted sodium hydroxide was added. This caused the light blue precipitate to convert into a red precipitate of bis(dimethylglyoximato)nickel(II).

6) *Recycling and Refurbishment:* The red precipitate formed in II-C5 was then filtered and acidified with sulfuric acid until a pH of less than 1 was reached. It was then heated until the outcrop had taken on the green colour of the Hexa-aquanickel(II) complex. This procedure can leave behind a precipitation, that consists of organic ligand molecules. After the filtration, 2000mg of active carbon (170mmol) were added to the filtrate. It was reheated and filtered while still hot. After it had cooled down to room temperature, 1500mg of active carbon (120mmol) and 5ml of hydrogenperoxide (210mmol, 30%) were added. Thereafter it was stirred for an hour, boiled up and filtered again. In order to achieve a pH of eleven to twelve, sodiumhydroxide was added. The precipitate nickelhydroxide was filtered out and the light green compound was isolated. The precipitation was washed with deionised water to clean it from any sulphate. To check if all the sulphate had been washed out, add a few drops nitric acid were added. After adding bariumchloride no precipitation was observed, indicating that indeed the precipitation was cleansed of all sulphate.

The clean precipitation was dissolved with hydrochloric acid and slowly heated to a temperature of 150C. At this point, all of the liquid had evaporated and only the complex which the experiment cycle had started with, nickel(II)chlorid-hexahydrate, was left. Therefore the recycling process was completed.

## III. RESULT AND DISCUSSION

With every ligand swap reaction the stability of the complex increases. Either by swapping a monodentate ligand with a bidentate one or by swapping them with ligands of higher basicity. Nickel(II) has 8 d electrons. By having a look at figure 3 and applying the earlier mentioned rules for filling orbitals, it is obvious that for reaction one to four, the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals are filled with two electrons and the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are solely occupied. This leads to the conclusion that they are paramagnetic and should have a blue or green colour. The last complex only has a coordination number of four and applying the same logic, this complex is diamagnetic and is expected to have a orange or red colour.

### A. Reaction 1

In the first ligand swap reaction we swapped the  $H_2O$  ligands with the more basic  $NH_3$  ligands in the octahedral nickel(II)chloride-hexahydrat. This was indicated by the change in colour to a clear deep blue. This solution contained the octahedral hexaaminnickel(II)-chloride.

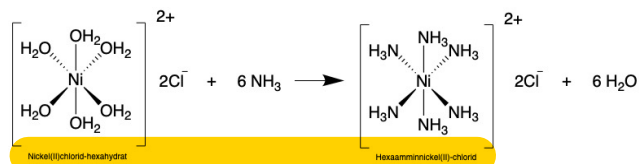


Figure 5: to hexaaminnickel(II)-chloride

### B. Reaction 2

In this reaction the monodentate ligand  $NH_3$  was swapped the bidentate ligand Potassiumoxalat. The swap was indicated by the turquoise crystals that had formed. potassiumoxalatonnickelat(II) has an octahedral geometry.

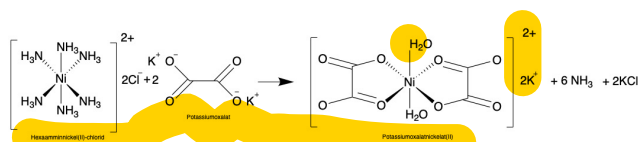


Figure 6: to potassiumoxalatonnickelat(II)

### C. Reaction 3

In this step the potassiumoxalat ligand was swapped with the more basic ligand glycine. But not only the two bidentate ligands were swapped, but also the monodentate ligands that had still occupied two coordination points. This reaction is also energetically favourable since, as explained in I, the entropy of the system increases due to a rising number of particles in the solution. The light blue colour of the solution showed that potassiumtriglycinatonickelat(II) was contained in it. The complex had a octahedral configuration.

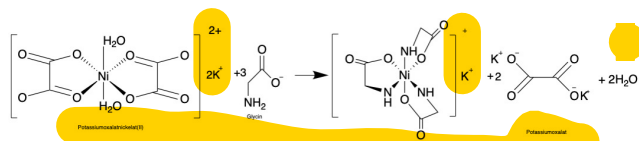


Figure 7: to potassiumtriglycinatonickelat(II)

### D. Reaction 4

The glycine ligands were now swapped with acetylaceton which is a ligand that has higher basicity. The octahedral configuration was kept during the swap but there were only two instead of three bidentate acetylaceton ligands. Its high basicity stabilises the complex more than the three glycine ligands. The swap was visible because of the light blue acetylacetonatnickel precipitation in the solution.

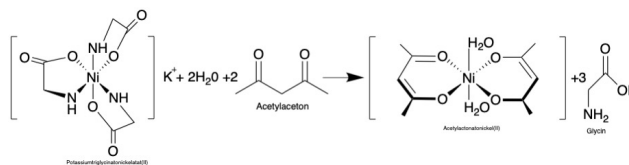


Figure 8: to acetylacetonatnickel(II)

### E. Reaction 5

By adding dimethylglyoxim, the precipitation turned red and formed the complex bis(dimethylglyoximato)nickel(II) with a coordination number of four. The two dimethylglyoxim molecules built hydrogen bonds with each other, making the complex even more stable. The geometry of this complex was square planar. Since the difference in energy between two energy levels was higher than the spin pairing energy, all orbitals were filled up completely, making it diamagnetic. The prediction for the colour of the complex using the knowledge from the introduction proved to be right. This experiment is helpful for gaining a deeper insight into how complexes are coordinated, what low and high spin complexes are and what geometry they can have and which are favourable and why.

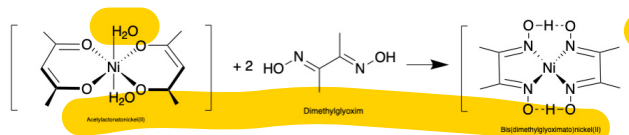
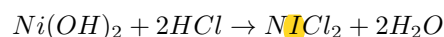
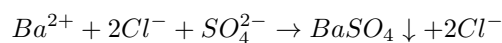


Figure 9: to bis(dimethylglyoximato)nickel(II)

### F. Recycling

At the end of the experiment, the hexaaquanickel(II)chloride was refurbished by a complex series of filtrations and reactions. In the first steps, the organic ligand molecules were filtered out and ideally only nickelsulfate should have remained. With only nickelsulfate in the solution, sodium hydroxide was added to achieve the precipitate nickelhydroxide.

The nickelhydroxide was then separated from the solution by filtration, resulting in a green solid. This solid was then washed with deionised water to cleanse it from sulphate. Subsequently, a sulfate check with bariumchloride was performed.



Thereafter, the washed precipitation was acidified with hydrochloric acid resulting in the production of the nickelchloride complex which the experiment was started with. The recycling part of the experiment was done and the cycle was closed.

## REFERENCES

- [1] A. Abudra and T. Badial, "Lewis concept of acids and bases," *Libretexts*, 2020. [Online]. Available: [https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Supplemental\\_Modules\\_\(Physical\\_and\\_Theoretical\\_Chemistry\)/Acids\\_and\\_Bases/Acid/Lewis\\_Concept\\_of\\_Acids\\_and\\_Bases](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Acids_and_Bases/Acid/Lewis_Concept_of_Acids_and_Bases)
- [2] C. E. Housecroft and E. C. Constable, *Chemistry 4th Edition*. Mastering CHEMistry, 2020.
- [3] H. Schönberg, *Praktikum Allgemeiner Chemie. Anorganische und analytische Chemie*. Laboratorium für Anorganische Chemie ETH Zürich, 2020.
- [4] —, *Praktikum Allgemeiner Chemie. Anorganische und analytische Chemie*. Laboratorium für Anorganische Chemie ETH Zürich, 2020.
- [5] "Paramagnetismus." [Online]. Available: <https://www.chemie.de/lexikon/Paramagnetismus.html>

