Self-assessment test with focus on SynCat subjects (2) (solutions)

Part 1 – Organic Chemistry

1. Which of the following hydrogen atoms is preferably abstracted by the radical R·? Draw the resulting compound and at least one mesomeric or no-bond form of it.

2. Draw a complete reaction mechanism with all intermediates for the following reaction. What is the main product?

3. Give the main product of the following transformation. Draw the complete reaction mechanism with all relevant intermediates.

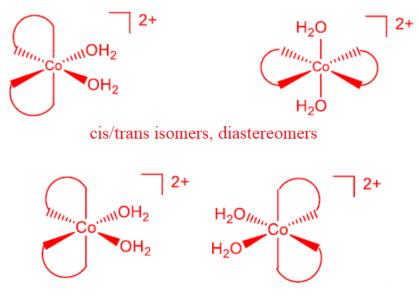
4. Draw 1,2-difluoro ethane in its two most stable conformations. Discuss the effects that lead to the stability of either of those forms.

least steric hindrance smallest dipole moment

best stereoelectronic effects $\sigma(CH)$ -> $\sigma^*(CF)$

Part 2 – Inorganic Chemistry

5. Take a look at the $[Co(en)_2(H_2O)_2]^{2+}$ complex. Sketch all of its stereoisomers and distinguish between diastereomers and enantiomers.

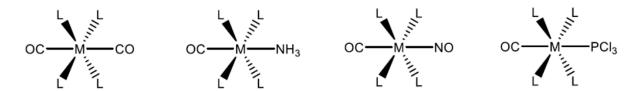


 Δ/Λ isomers, enantiomers

- 6. Explain why a complex with ethylene diamine (en) ligands is much more stable than a corresponding ammin complex. How is this effect called? en is a bidentate ligand, **chelating effect** comes into play, entropy on product side is greatly increased by coordination of bidentate ligands
- 7. Sketch the different d-Orbitals in an octahedral, tetrahedral and square-planar ligand field respectively. Also give the names of the respective orbitals.

octahedral field	tetrahedral field	square-planar field
$ \begin{array}{ccc} & & e_g \\ & d_{x2-y2} & d_{z2} \\ & & & t_{2g} \\ & d_{xz} & d_{yz} & d_{xy} \end{array} $	$ \begin{array}{cccc} - & - & - & t_2 \\ d_{xz} & d_{yz} & d_{xy} & \\ - & - & e \\ d_{x2-y2} & d_{z2} \end{array} $	$egin{array}{cccc} & - & b_{1g} \ d_{x2-y2} & & & \ & - & b_{2g} \ d_{xy} & & - & a_{1g} \ d_{z2} & & - & e_g \end{array}$
		a_{xz} a_{yz}

8. Judge the bond strength of the CO-bond in the following complexes. In which order would you expect the CO stretching bands to appear in the IR spectrum? (M and L are the same in each complex).



In general, the CO stretching bands appear at higher wavenumbers if the CO bond is stronger. By coordination of CO to a metal center, the CO bond becomes weaker because of the π -back-bonding of the metal (which donates electron density into unoccupied π^* molecular orbitals of CO). If arranged trans to each other, different ligands may compete for electron density of the metal. Thus, if a ligand is a strong π -acceptor, it will receive "more" electrons from the metal resulting in weaker π -back-bonding on the opposite coordination side.

The ability to accept electrons should be: $NH_3 < PCl_3 < CO < NO$. Thus, the order of CO stretching bands should be (from low wavenumbers to high wave numbers): $\nu(CO, NH_3 \text{ complex}) < \nu(CO, PCl_3 \text{ complex}) < \nu(CO, CO \text{ complex}) < \nu(CO, NO \text{ complex})$.

9. If you compare the properties of transition metal rows you will notice similar behavior between 4d and 5d elements while 3d elements show a huge deviation. Rationalize this peculiarity.

4d and 5d elements have nearly the same atomic radii in contrast their 3d analogues. This is due to lanthanoid contraction and the effect of "inert electron pair".