



Homework 1 – for Friday, Sept. 29, 8:30!!!, A211

- What is the oxidation state of Os in $K_2[OsCl_5N]$ (potassium pentachloridonitridoosmate(2-))?
- In 19th century, a series of Pt “ammonochlorides” was synthesized, the following composition and properties were found:

composition	number of Cl^- precip. Ag^+	electr. conductivity	no of geom. isomers
$PtCl_2 \cdot 4NH_3$	2	high	1
$PtCl_2 \cdot 3NH_3$	1	medium	1
$PtCl_2 \cdot 2NH_3$	0	very low	2

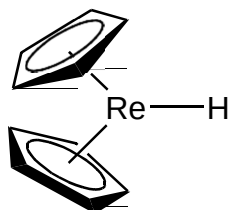
Draw their structure formulas

- in Jørgensen’s chain style
- in Werner’s main and secondary valence style
- in contemporary manner

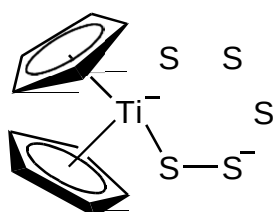
What may the geometry of these compounds look like?

- Try to draw structural formulas of the following complexes:
 - $[(\mu-\eta^5:\eta^5-C_{10}H_8)\{(\mu-H)(\eta^5-C_5H_5)Ti\}_2]$
 - $[N,N'\text{-bis(2,4,6-trimethylphenyl)ethane-1,2-diimine-}\kappa^2N,N']\text{tetracarbonylchromium}$
 - nonaammine- $1\kappa^5N, 2\kappa^4N$ - μ -hydroxido-(methanamine- $2\kappa N$)dichromium(III)
 - pentaammine- $1\kappa^3N, 2\kappa^2N$ -di- μ -hydroxido- μ -nitrito- $1\kappa N: 2\kappa O$ -(pyridine- $2\kappa N$)dicobalt(III)
- Name the following compounds:

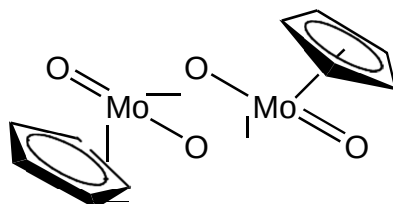
A)

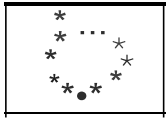


B)



C)





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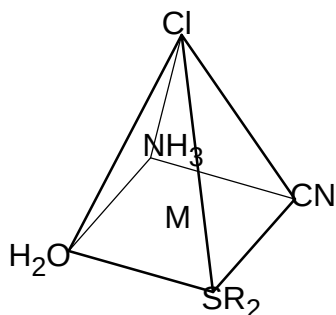


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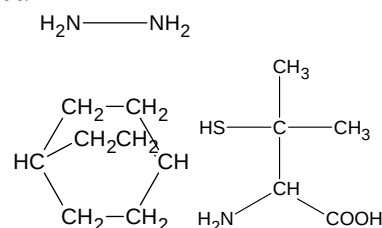
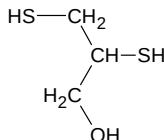
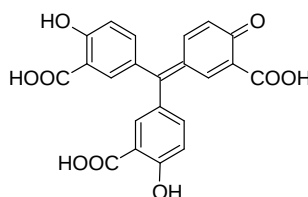
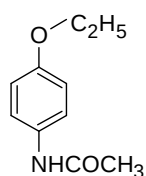


Homework 2 – for Friday, Oct. 6, 8:30-9:45, A211

- 1) $[\text{PtBr}_2\text{Cl}(\text{NH}_3)]^-$: draw structural formulas of all possible diastereoisomers of this planar ion and name them (incl. configuration numbers)
- 2) $[\text{CoCl}_2(\text{trien})]^+$: name this ion [trien = N,N'-bis(2-aminoethyl)ethane-1,2-diamine] and try to find all possible diastereoisomers. Are any of them chiral?
- 3) In the compound $[\text{Pt}(\text{NH}_2\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{NH}_2)(\text{NH}_2\text{CH}_2\text{CMe}_2\text{NH}_2)]$, Pt is situated in the centre of the square formed by 4 N. Nevertheless, the compound is chiral. Explain.
- 4) The following structure is surely chiral. Try to describe it with the help of a configuration index and its chirality by an appropriate convention.



- 5) Draw formulas of all possible isomers of the following compounds, and name them. (ox = oxalate(2-))
 - (a) $[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$
 - (b) planar $[\text{PtCl}_2(\text{PPh}_3)_2]$
 - (c) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
- 6) Rewrite each of these lists of Lewis acids and bases so that they are in increasing order of softness:
 - a. $\text{Cu}^+, \text{Cu}^{3+}, \text{Cu}^{2+}$
 - b. $(\text{CH}_3)_2\text{SO}, (\text{CH}_3)_2\text{S}, \text{Cl}_2\text{SO}$ (S-donors)
 - c. $(\text{CH}_3)_2\text{O}, (\text{CH}_3)_2\text{Se}, (\text{CH}_3)_2\text{S}$
 - d. $\text{BF}_3, \text{BCl}_3, \text{B}(\text{CH}_3)_3$
 - e. $\text{Sr}^{2+}, \text{Hg}^{2+}, \text{Pb}^{2+}$
 - f. $\text{I}^-, \text{Cl}^-, \text{Br}^-, \text{F}^-$
 - g. $\text{Ag}^{2+}, \text{As}^{3+}, \text{Ac}^{3+}, \text{Au}^+, \text{Ag}^+$
 - h. $\text{InF}_3, \text{BF}_3, \text{InI}_3, \text{TlI}_3$
 - i. $[\text{Co}(\text{NH}_3)_5]^{3+}, [\text{Co}(\text{H}_2\text{O})_5]^{3+}, [\text{Co}(\text{NH}_3)_5]^{2+}, [\text{Co}(\text{PH}_3)_5]^+$
- 7) Three of six compounds listed below are used to treat poisoning by the Hg^{2+} , Be^{2+} , and Cu^{2+} ions, the others are not useful for any of these. Identify the useless compounds; for each useful ligand identify the one metal ion that it would be used to treat.





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COOH

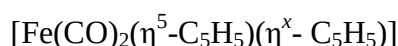
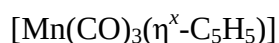


Homework 3 – for Friday, Oct. 13th

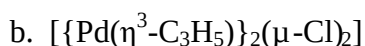
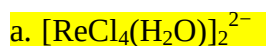
- Write each of the following complexes as $[ML_lX_x]^q$, give the oxidation state of the metal, its electronic configuration (with respect to the oxidation state), and the total number of electrons.

	$[ML_lX_x]^q$	metal oxidation state	electronic configuration of M	total number of electrons
$[Cr(\eta^6-C_6H_6)_2]$				
$[W(CO)_5]$				
$[Mn(CO)_5Cl]$				
$[Co(CO)_3Et]$				
$[Cu(SR)_3]^{2-}$				
$[ReH_9]^{2-}$				
$[Ni(H_2O)_6]^{2+}$				
$[Zr(\eta^5-C_5H_5)_2(H)(Cl)]$				

- Predict the hapticity x for a cyclopentadienyl ligand in the following complexes provided the 18-electron rule applies. Try to draw the complexes.



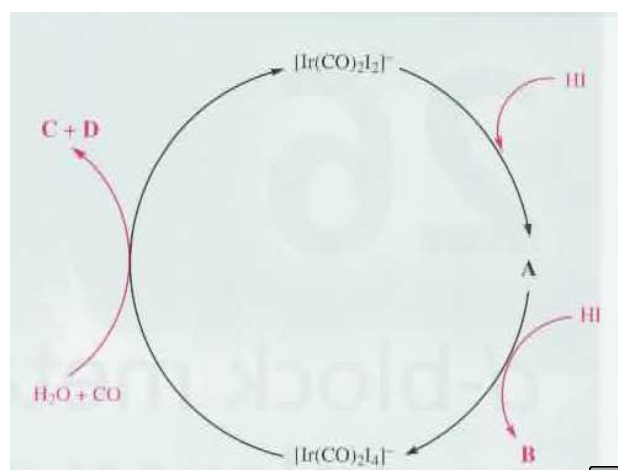
- What is the oxidation state of the metal centres in the following binuclear complexes:



- How can butadiene be classified in L_lX_x classification? Why?

- The 1. step in the Cativa process is the reaction between MeI and the catalyst. However, the catalyst may also react with HI and this step initiates a water gas shift reaction that competes with the main catalytic cycle.

Suggest identities for species **A**, **B**, **C**, and **D**.





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What changes in iridium oxidation state occur and what is the electron count in each iridium complex?
(We discussed the main cycle at the seminar.)



Homework 4 – for Friday, Oct. 20th

1. Two famous iron cyanido complexes, potassium hexacyanidoferrate(+II) (“yellow prussiate”) and potassium hexacyanidoferrate(+III) (“red prussiate”) differ not only in colour but also in toxicity: in the aqueous solution, one of them hydrolyses and releases cyanide ligands (i.e. it is *kinetically labile*) and is therefore highly toxic (category T +, highly toxic). The other hydrolyses very slowly (*kinetically inert*) and is therefore non-toxic.

Write formulas of both prussiates. Decide which of the two salts is toxic, which is nontoxic, and base your decision on the CFSE and the possible mechanism of hydrolysis.

2. Use data from the table “Energy Levels of *d* orbitals..” (paper 3/2017) and compare CFSE values for a trigonal bipyramid and a square pyramid (both CN 5). Which high-spin electronic configuration is the most stable? What do you mean about LS configuration – is it more probable in *TBPY* or in *SPY* arrangement?
3. When an octahedral field is tetragonally elongated along the *z* axis, a square planar field is formed at the end (see paper 3/2017). Suppose an octahedral field is tetragonally **compressed** instead (that is, the *z*-axis ligands move closer to the metal while the *x* and *y* axis ligands move farther away). Which geometry results?

Draw a labelled *d*-orbital diagram.

4. Suppose that both high- and low-spin cases are possible for tetrahedral complexes. What numbers of *d* electrons would have both possibilities? Give the electronic configurations for these possibilities (*e*, *t*₂).
5. Arrange the following ions in order of increasing split between the *t*_{2g} and *e*_g sets of *d* orbitals (increasing Δ_{oct}):
[CoF₆]³⁻, [CoF₆]⁴⁻, [Ir(CN)₆]³⁻, [Rh(H₂O)₆]³⁺, [Rh(CN)₆]³⁻, [RhF₆]³⁻.
6. How many unpaired electrons would there be in each of the following cases?
 - a. *d*⁴, octahedral, LS
 - b. *d*⁶, tetrahedral, HS
 - c. *d*⁹, square planar
 - d. [Co(H₂O)₆]²⁺, HS
 - e. [PtCl₆]²⁻, LS



Homework 5 – for Friday, Oct. 27th

1. Find the ground terms of following ions: Cu^{2+} , Co^{2+} , Sm^{3+} , Ho^{3+} . How many times are they degenerated?
2. Electronic configuration d^2 forms 45 microstates and from these microstates 5 terms are constituted. The ground term is 3F . Which of the following microstates can take part in this term?
 - a) $2(\uparrow)1()0(\uparrow)-1()-2()$
 - b) $2(\uparrow)1(\downarrow)0()-1()-2()$
 - c) $2()1(\uparrow\downarrow)0()-1()-2()$
 - d) $2(\uparrow\downarrow)1()0()-1()-2()$

One of the higher terms is labelled 1S . Again, which of the following microstates can take part in this term?

- a) $2(\downarrow)1(\uparrow)0()-1()-2()$
 - b) $2()1(\uparrow\downarrow)0()-1()-2()$
 - c) $2()1()0(\uparrow\downarrow)-1()-2()$
 - d) $2(\uparrow)1()0()-1()-2(\downarrow)$
3. UV-Vis spectra of the following complexes are characterised by the presence of a highly intense absorption band with following λ_{max} . What is the nature of this band (MLCT, LMCT, d-d)? Try to explain the correlation between an appropriate central metal property and the band energy.
 $[\text{MnO}_4]^-$ 528 nm; $[\text{TcO}_4]^-$ 286 nm; $[\text{ReO}_4]^-$ 227 nm.
 $[\text{OsCl}_6]^{3-}$ 282 nm; $[\text{OsCl}_6]^{2-}$ 370 nm.
 4. The ligand-field splitting parameter Δ is normally larger for octahedral complexes than for tetrahedral complexes of the same metal ion with the same ligand atoms. How do you account for the observation that the energy for the first $d-d$ transition is around 11000 cm^{-1} for $\{\text{Fe}^{\text{III}}\text{O}_6\}$ chromophores but around 22000 cm^{-1} for $\{\text{Fe}^{\text{III}}\text{O}_4\}$ chromophores (ground state term 6A_1 in both cases)?
 5. When the blue, paramagnetic *trans*-diaquabis(*N,N*-diethylethane-1,2-diamine)nickel(II) chloride, *trans*- $[\text{Ni}(\text{deen})_2(\text{H}_2\text{O})_2]\text{Cl}_2$, is heated, it forms the paramagnetic, green *trans*- $[\text{NiCl}_2(\text{deen})_2]$ complex. (deen is a bidentate ligand). Rationalize the paramagnetism of these two complexes and the colour change that occurs.



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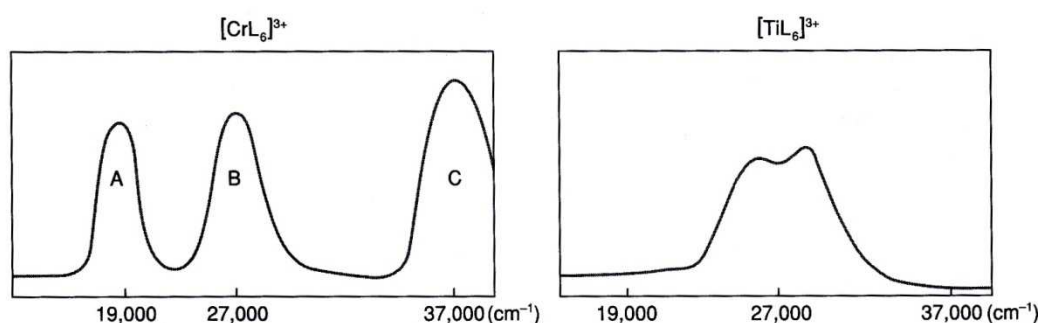


6. When the blue, paramagnetic *trans*-diaquabis(*N,N*-diethylethane-1,2-diamine)nickel(II) bromide, *trans*-[Ni(deen)₂(H₂O)₂]Br₂, is heated, it forms the orange, diamagnetic, *trans*-[Ni(deen)₂] Br₂ complex. Rationalize the colour and magnetic changes that occur during this reaction. Why there is a difference between this reaction and the precedent one?



Homework 6 – for Friday, November 3rd

1. Charge transfer bands of appropriate coordination complexes are often used for colorimetric determination of metal ions. There are two popular methods for Fe determination: Fe(+III) with SCN^- ligands, or Fe(+II) with phenantroline (by chance both of them are red ☺). What types of CT bands are present in these complexes? Justify your answer (remember redox properties of the Fe ions).
2. The energy of the lowest energy charge-transfer band decreases across the series $[\text{VO}_4]^{3-}$, $[\text{CrO}_4]^{2-}$, $[\text{MnO}_4]^-$, we have discussed it, but it increases across the series $[\text{V}(\text{CO})_6]^-$, $[\text{Cr}(\text{CO})_6]$, $[\text{Mn}(\text{CO})_6]^+$. How do you account for this?
3. The d^9 ion Cu^{2+} is often found in a distorted octahedral environment, in which two Cu–L distances are longer than the other four. How many d – d bands would you expect for such an ion?
4. Below are shown two spectra: the first is of a Cr^{3+} octahedral complex ion, the second is of a Ti^{3+} octahedral complex ion.



- a) Explain the number of absorption bands in the spectra.
- b) Which absorption band, A, B, or C, would you use to determine the value of Δ_o of the Cr^{3+} ion?
- c) Which are approximately the colours of these two complexes?



Homework 7 – for Friday, November 10th

1. The experimental magnetic moments of four manganese complexes are given below. State whether the complexes are high-spin or low-spin. Also write down the electronic configurations (within the t_{2g} and e_g sets of d orbitals) that are consistent with these observed magnetic moments and values of the spin-only magnetic moment.

	oxid. number of Mn	electronic configuration	μ_s [BM]	μ_{exper} [BM]
$[\text{Mn}(\text{CN})_6]^{4-}$				1,8
$[\text{Mn}(\text{CN})_6]^{3-}$				3,2
$[\text{Mn}(\text{NCS})_6]^{4-}$				6,1
$[\text{Mn}(\text{acac})_3]$				5,0

acac⁻ stays for 2,4-pentadionato-, traditionally acetylacetonato-. Draw an electronic formula of this ligand, show the possible donor atoms.

2. The magnetic susceptibilities of the following two ruthenium complexes, $[\text{RuF}_6]^{4-}$ and $[\text{Ru}(\text{PR}_3)_6]^{2+}$, are $\chi = 1,01 \cdot 10^{-2} (\text{BM})^2 \text{K}^{-1}$ and approximately zero, respectively. With how many unpaired electrons are these results consistent? (Assume $T = 298 \text{ K}$.) Briefly justify your answer.
3. Two following vanadium complexes were characterised by UV-Vis spectroscopy. From the data, estimate Δ_o and B values and explain whether these values are in accordance with the spectroscopic series of ligands. Which complex, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{V}(\text{CN})_6]^{3-}$, exhibits more covalent M – L bond? Use either a Tanabe-Sugano diagram or equations describing term energies.

$[\text{cm}^{-1}]$	$\nu_1 (^3T_{1g}(F) \rightarrow ^3T_{2g}(F))$	$\nu_2 (^3T_{1g}(F) \rightarrow ^3T_{1g}(P))$	$\nu_3 (^3T_{1g}(F) \rightarrow ^3A_{2g})$
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	17 400	25 600	a shoulder of a CT band at 38000 cm^{-1}
$[\text{V}(\text{CN})_6]^{3-}$	22 000	28 500	not identified

4. Magnetic moments: spin-orbit coupling.

Calculate μ_{eff} for $[\text{Ni}(\text{en})_3]^{2+}$ taking into account spin-orbit coupling. Compare the result with μ_s (spin-only value) and the experimental value $\mu_{\text{exp}} = 3.16 \text{ B.M.}$

Δ_o value for $[\text{Ni}(\text{en})_3]^{2+}$ is $11\,500 \text{ cm}^{-1}$.

[I repeat here the relationship between μ_{eff} and μ_s :

$\mu_{\text{eff}} = \mu_s (1 - 4\lambda/\Delta)$ for A ground terms, or $\mu_{\text{eff}} = \mu_s (1 - 2\lambda/\Delta)$ for E ground terms]



Homework 8 – for Friday, November 24th ???

1. Bonding in cyanido complexes

- A. By writing a Lewis structure, show that $\text{C}\equiv\text{N}$ is an X-type ligand.
- B. Assuming that the order of increasing energy for the MO is the same in $\text{C}\equiv\text{N}$ as in $\text{C}\equiv\text{O}$,
 - indicate the nature of the MO that has a σ interaction with a metal centre;
 - give the shape and the occupation of the π -type MO;
 - indicate whether this ligand is a π acceptor or a π donor;
 - indicate whether the CN ligand binds to the metal through carbon or nitrogen in the η^1 coordination mode.
- C. How can you explain the following data:
 - ionic radius of Fe^{2+} is 92 pm and ionic radius of Fe^{3+} is 78 pm. The Fe–CN bond is shorter in $\text{K}_3[\text{Fe}(\text{CN})_6]$ (190.3 pm) than in $\text{K}_4[\text{Fe}(\text{CN})_6]$ (192.2 pm), but the difference does not correspond with the ionic radii.
 - the Fe – N distance is 303.7 pm in $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 309.0 pm in $\text{K}_4[\text{Fe}(\text{CN})_6]$. What can you say about the length of the C–N bond? Is this result in accordance with the different lengths of Fe–C bonds?

2. Discuss the following observations:

- A. The μ_{eff} observed for $[\text{Cr}(\text{CN})_5(\text{NO})]^{3-}$ and $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ show that both complexes have one unpaired electron. Analysis of the (anisotropic) EPR g-values indicates that the odd electron occupies the d_{xy} orbital in $[\text{Cr}(\text{CN})_5(\text{NO})]^{3-}$ but, instead, the d_{z^2} orbital in $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$.
- B. The complex $[\text{MoOCl}_5]^{2-}$ also has one unpaired electron ($\mu_{\text{eff}} = 1.67 \mu_{\text{B}}$ and $g_{\text{av}} = 1.947$ in its K^+ salt, the components of g showing that this resides in the d_{xy} orbital. The complex $[\text{Mo}(\text{NO})\text{Cl}_5]^{2-}$ is diamagnetic.



Homework 9 – for Friday, December 1st (!!!)

1. Ligand exchange reaction of dialkyl chalcogenides ER_2 (E =S, Se, and Te; R = Me and Et) with $[TaCl_5(ER_2)]$ in inert solvents is very much slowed down when R is Et rather than Me, and shows very negative entropies of activation ($\Delta S^\ddagger$ from -96 to $-108 \text{ J mol}^{-1} \text{ K}^{-1}$). Is this reaction dissociative or associative? Give 2 reasons.
2. The room temperature rate of exchange of metal carbonyls with free CO decreases dramatically from $[Ni(CO)_4]$ ($1 \cdot 10^{-2} \text{ s}^{-1}$) to $[Fe(CO)_5]$ ($5 \cdot 10^{-10} \text{ s}^{-1}$) to $[Cr(CO)_6]$ (estimated at $9 \cdot 10^{-14} \text{ s}^{-1}$). Offer an explanation.
3. You want to enhance the rate of replacement of the anionic ligand by solvent water in each of the following complexes, and can choose to do this by adding either
 - a strong acid,
 - a strong base,
 - Ag^+ .

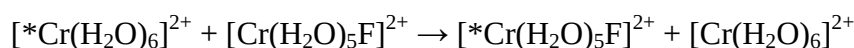
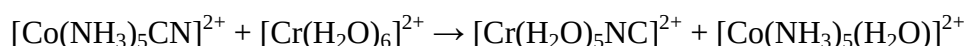
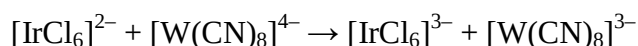
Which would be effective in each case, and why?

- a. $[Co(NH_2Me)_5ONO_2]^{2+}$ (*nitrato*)
 - b. $[Co(py)_5Br]^{2+}$
 - c. $[Co(py)_5OMe]^{2+}$
 - d. $[Co(NH_3)_5(CN)]^{2+}$
 - e. $[Cr(H_2O)_5F]^{2+}$
4. Design syntheses of the *cis* and *trans* isomers of $[PtCl_2(NO_2)(py)]^-$ using $[PtCl_4]^{2-}$, pyridine, and NO_2^- .

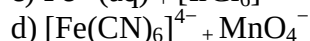
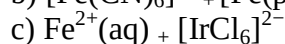
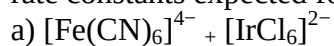


Homework 10 – for Friday, December 8th

- For each of the following electron transfer reactions, speculate whether the mechanism is outer sphere or inner sphere. Write the mechanism for an inner sphere reaction.



- Using given values (slides) of E° a k_{11} , identify the products and calculate the approximate rate constants expected for the following outer sphere one-electron transfer reactions:



- The standard redox potential of the pair $\text{Co}^{3+}(\text{aq})/\text{Co}^{2+}(\text{aq})$ is +1,82 V. Formation constants values, $\log \beta$, of the Co^{3+} and Co^{2+} complexes with ethane-1,2diimine (ethylenediamine) are 48.7 and 13.8, resp.. Calculate the standard redox potential of the pair $[\text{Co}(\text{en})_3]^{3+}/[\text{Co}(\text{en})_3]^{2+}$.
- In the synthesis of which of the following complexes would it be *unsatisfactory* to employ a plain substitution reaction on a hydrated metal ion in aqueous solution?
 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Fe}(\text{py})_6]\text{Cl}_3$, $[\text{Ni}(\text{py})_6]\text{Cl}_2$, $[\text{Tc}(\text{NH}_3)_6](\text{PF}_6)_4$
- The reaction of CrCl_3 with liquid NH_3 to give yellow $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ often has a low yield, since the reaction tends to stop with the production of pink $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. However, adding a small piece of Na metal result in complete conversion of the CrCl_3 to $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$. Offer two plausible explanations of this rate enhancement for the final step of the substitution process.



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1. Using Wade-Mingos (PSEPT) rules, decide which of the following cluster molecules is *closo*-, *nido*-, *arachno*- or *hypho*-, specify the shape of the original polyhedron and try to draw the structure: B_4H_{10} , $C_2B_4H_6$, B_6H_{10} , $NB_{10}H_{13}$, $[Os_5(CO)_{16}]$, $[Os_5C(CO)_{15}]$, $[Co_6H(CO)_{15}]^-$. Colored atoms are included in a metal cluster.
2. Determine which shape of skeleton (*closo*-, *nido*- ...) has a cluster $[Fe_2(CO)_6(C-CH_3)_2(C-OH)_2]$.
3. Determine which shape of skeleton has a cluster $[Co_8(CO)_{18}C]^{2-}$, what should be the position C and why?
4. Given the formulas and geometries of the following cluster anions, predict their ionic charge (if any):
 - a. $[Rh_7(CO)_{16}]$, capped octahedron
 - b. bicapped tetrahedral $[Os_6(CO)_{18}]$
 - c. octahedral $[Ru_6(CO)_{18}]$
 - d. square pyramidal B_5H_5