ATOMS, MOLECULES AND RESEARCH

COORDINATION CHEMISTRY, MID-TERM EXAMINATION, SPRING 2004

NAME: Answer Key

ANSWER ALL QUESTIONS. PLEASE SHOW ALL WORK.

1. Name the following coordination compounds.

$[Co(en)_2Cl(NO_2)]Cl$

chlorobis(ethylenediamine)nitrocobalt(III) chloride

$W(CO)_5P(CH_3)_3$

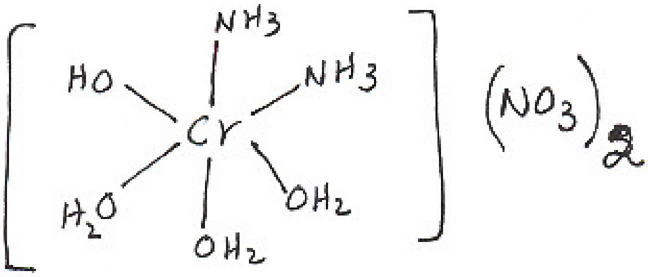
pentacarbonyltrimethylphosphinetungsten(0)

$[Pt(NH_3)_4(H_2O)_2]$ $[Fe(CN)_4(en)]$ (hint: platinum has +2 oxidation state)

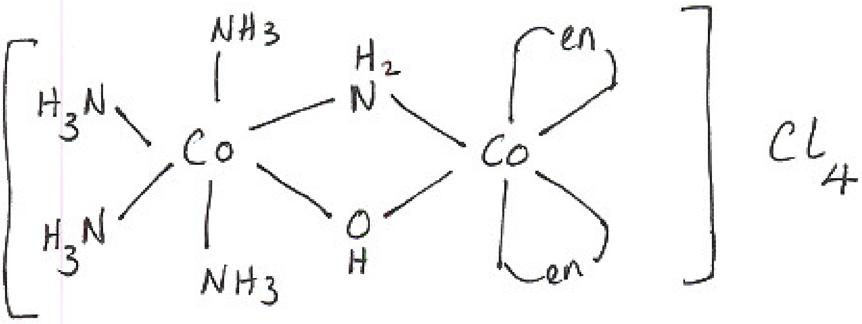
tetramminediaquaplatinum(II) tetracyanoethylenediamineferrate(II)

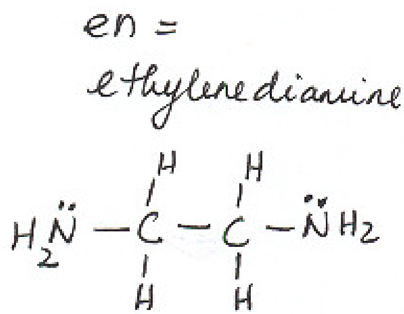
2. Write structural formulas (ignore isomers) for the following compounds.

Diamminetriaquahydroxochromium(III) nitrate

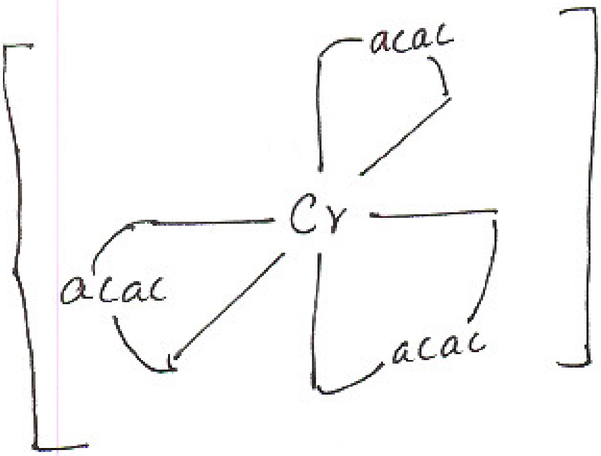


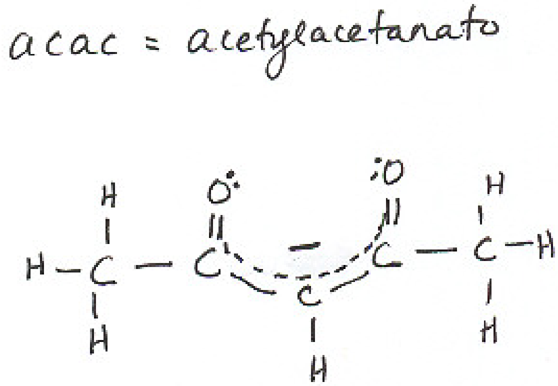
Tetraamminecobalt(III)-μ-amido-μ-hydroxobis(ethylenediamine)cobalt(III) chloride





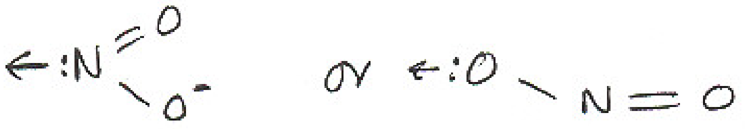
Triacetylacetanatochromium(III)





3. Give one example for each of the following.

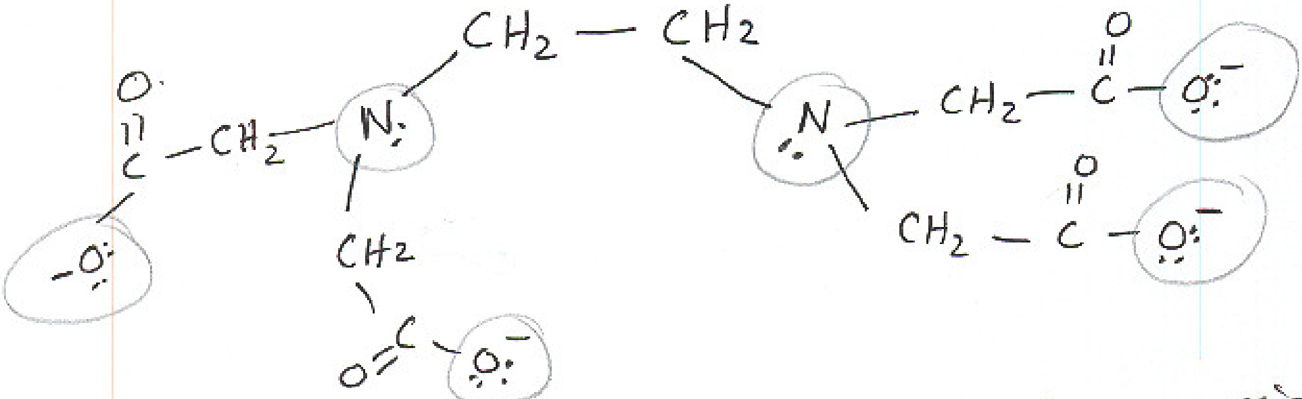
a) An ambidentate ligand NO_2^- can bond through N or O



b) A metal ion with a +3 oxidation state that has 6 electrons in the valence d orbital

Co^{3+}, Rh^{3+} or Ir^{3+}

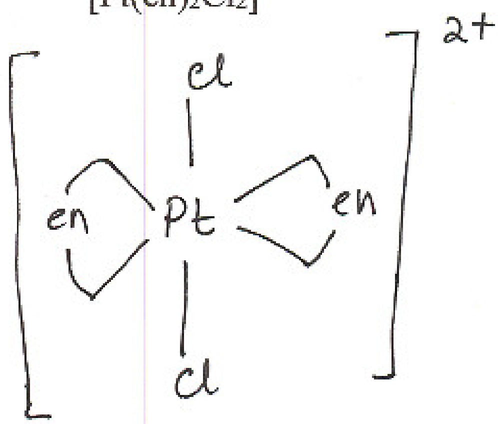
c) Draw EDTA clearly showing all the donor atoms. How many donor atoms are there on EDTA? Use this diagram to explain why EDTA is a chelating ligand.



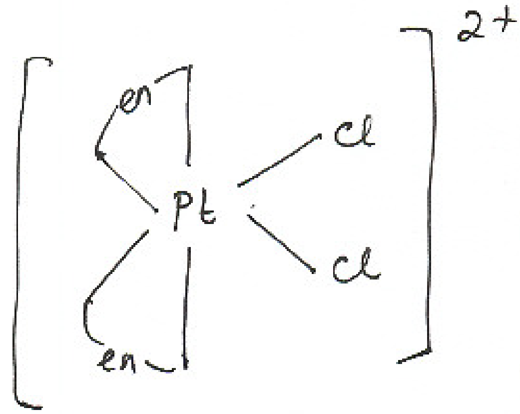
The donor atoms (all 6 of them) are circled.
There are 6 donor atoms that coordinate simultaneously with the metal atom, forming a ring (or a chelate), which includes the metal atom. Hence EDTA is called a chelating ligand.

4. Write all the isomers of the following coordination complex and identify what kind of isomers they are.

$[Pt(en)_2Cl_2]^{2+}$



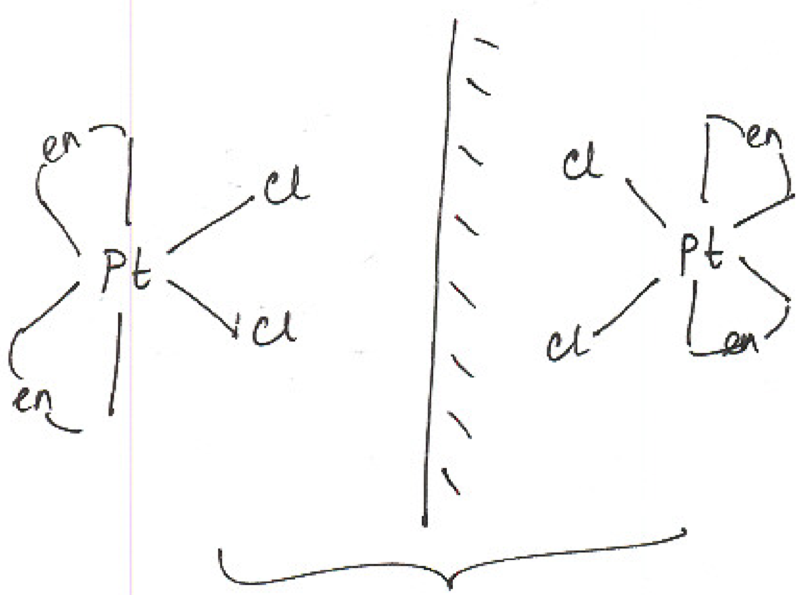
trans



cis

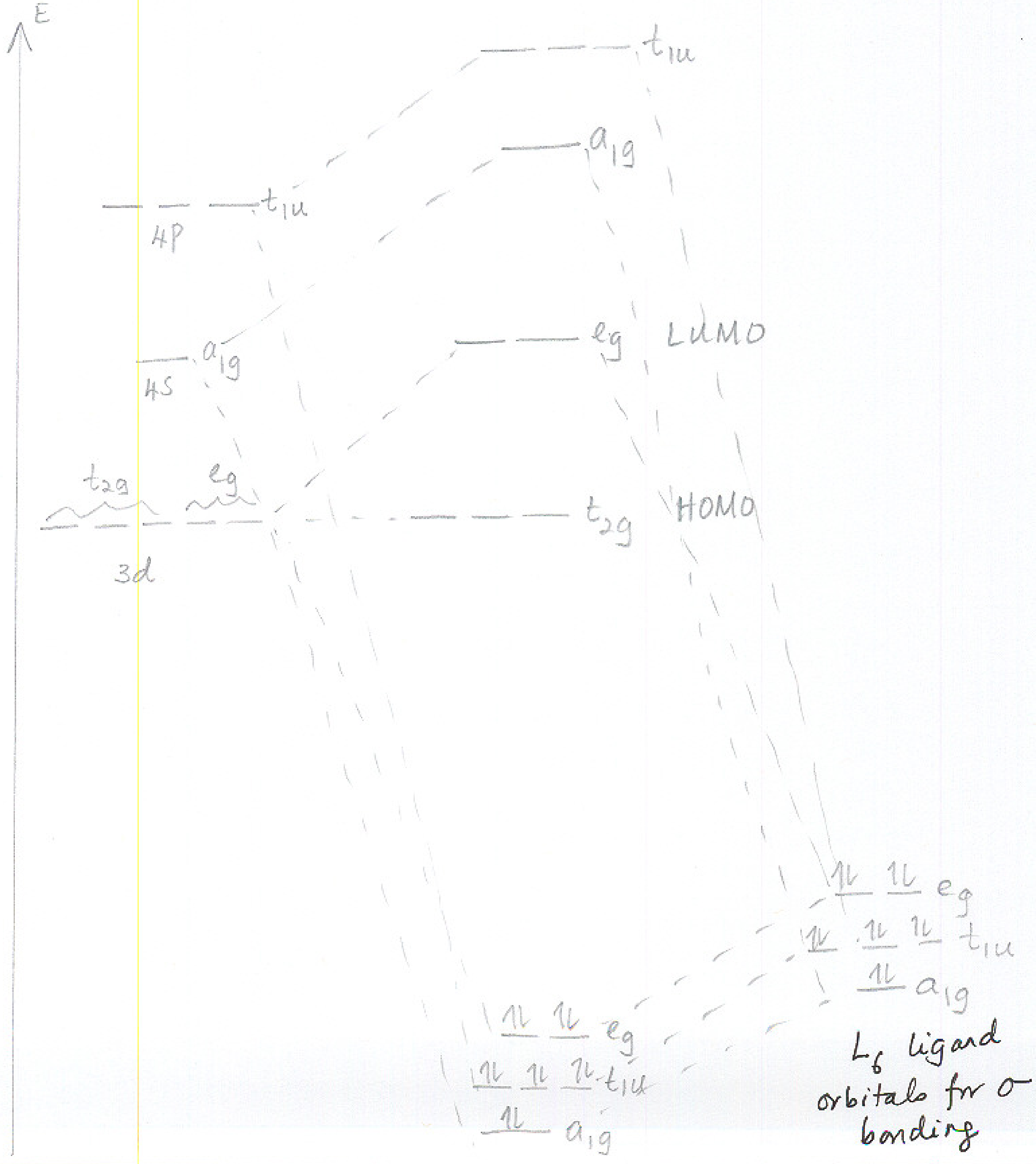
the cis and trans forms are geometric isomers.

The cis form has two optical isomers given below



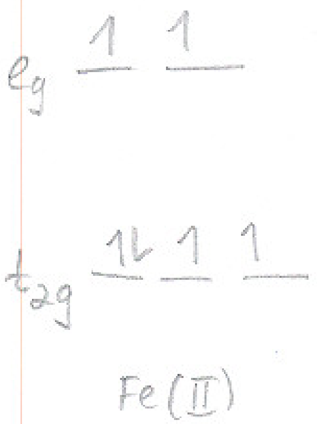
enantiomeric pair

5. Draw a molecular orbital diagram to show the ~~valence~~ molecular orbitals of a generic octahedral complex, ML_6. On this diagram, show the valence orbitals of the metal (M) and the ligands (L) that participate in σ bonding. Clearly label all of the orbitals (before and after they combine) with the appropriate symmetry symbols. Clearly label the HOMO and the LUMO on this diagram.



b) Draw a diagram showing the **HOMO and the LUMO only**, assuming that the ligands are "weak field ligands" and the metal is Fe(II). Calculate the expected spin-only magnetic moment. Show all work. Will this complex show paramagnetic properties or diamagnetic properties? Explain.

$\mu_s = \sqrt{n(n+2)}$ B.M. where
n = # of unpaired electrons



$n = 4$ $\quad \mu_s = \sqrt{4(6)}$ B.M.

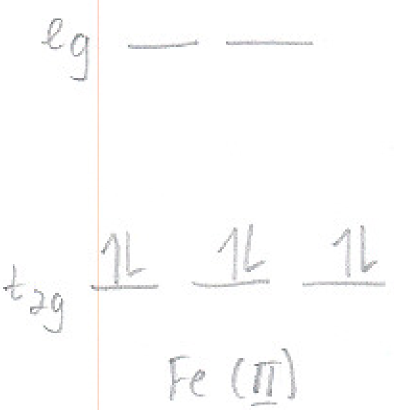
$= \underline{4.89 \text{ BM}}$

This will be paramagnetic since there are unpaired electrons.

c) Draw a diagram showing the **HOMO and the LUMO only**, assuming that the ligands are "strong field ligands" and the metal is Fe(II). Calculate the expected spin-only magnetic moment. Show all work.

$n = 0 \quad \therefore \mu_s = 0$

diamagnetic, since there are no unpaired electrons.

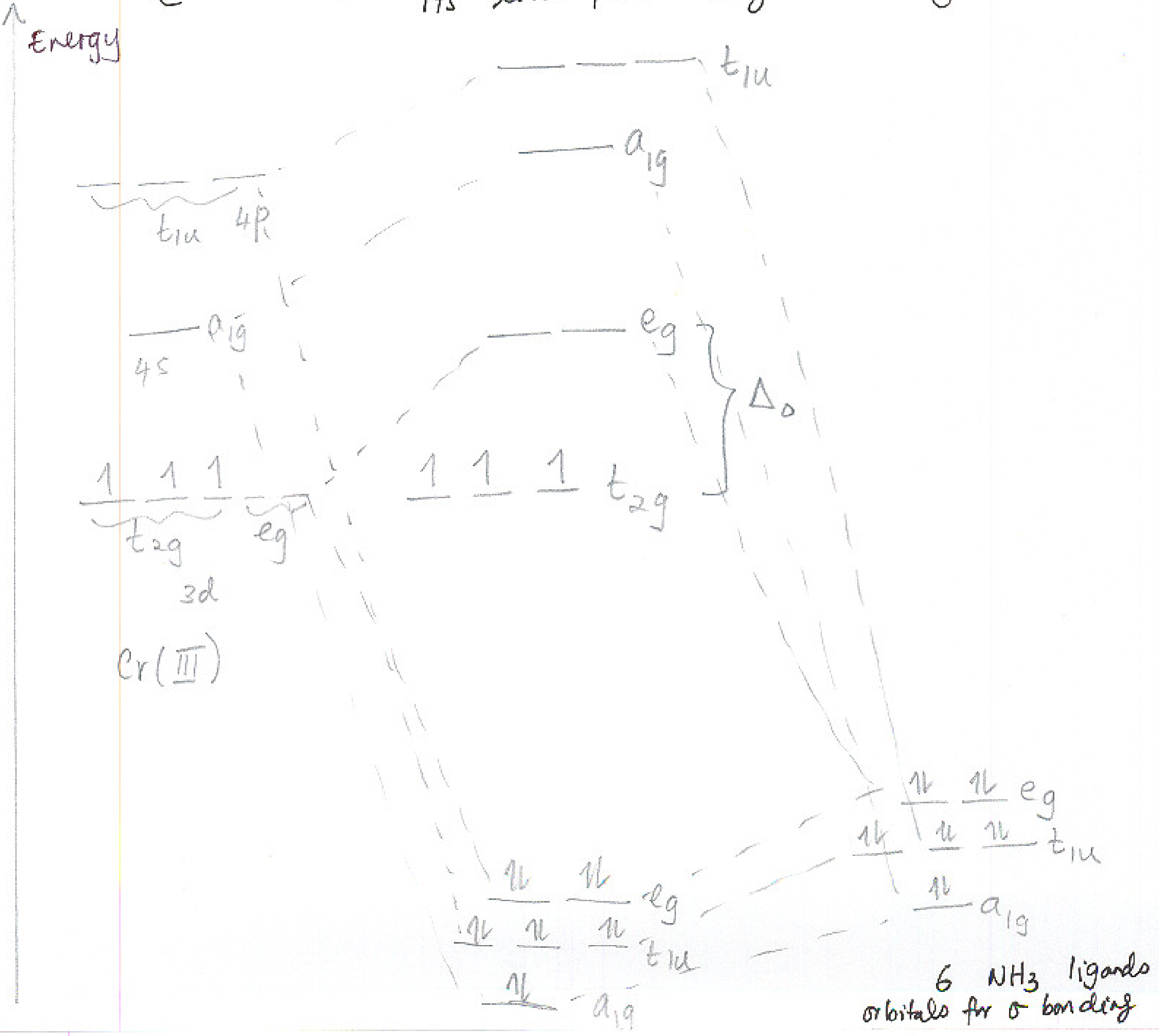


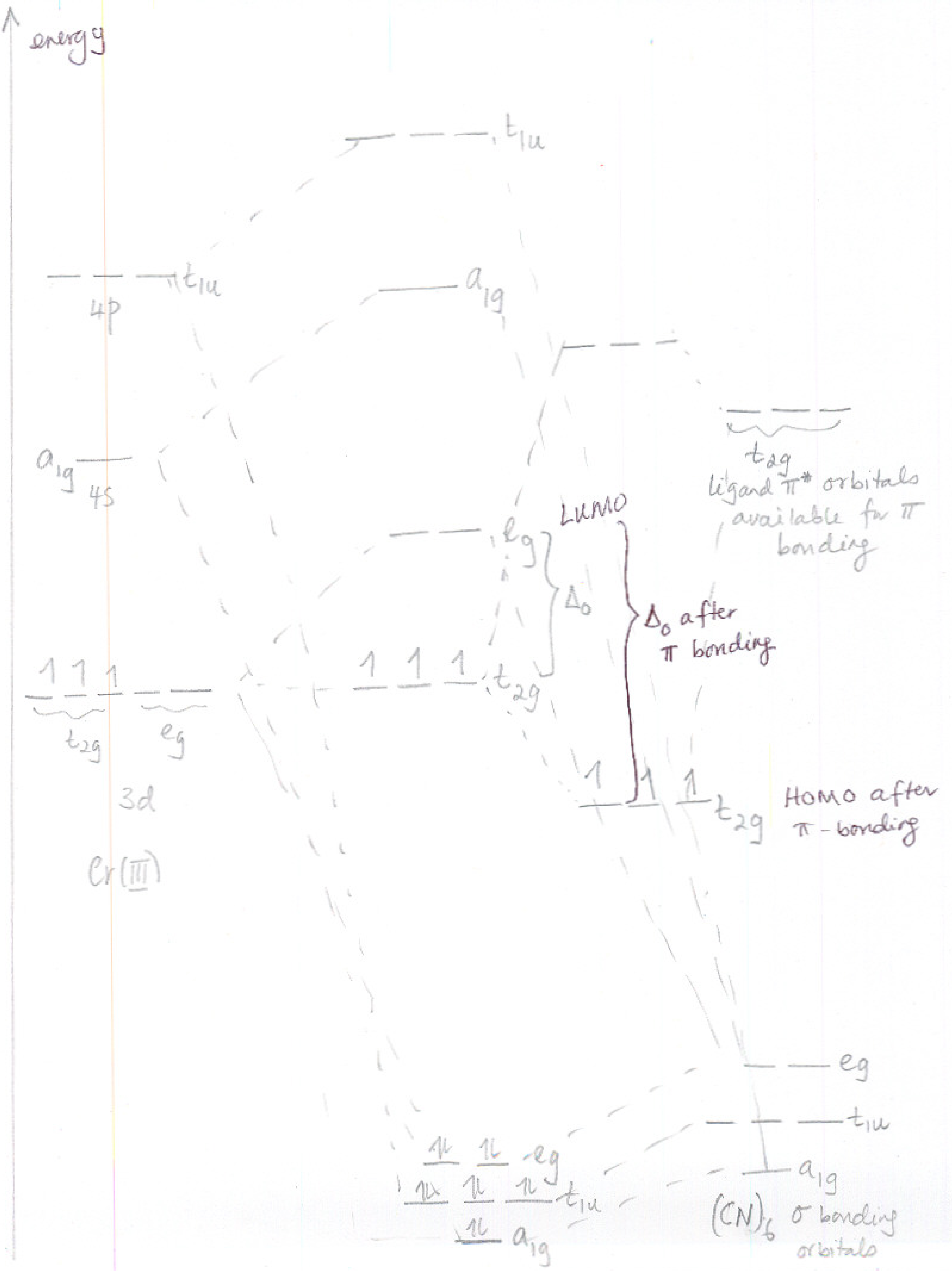
6. A student recorded the UV/VIS spectrum of the following compounds and obtained the given data. Note that in both cases chromium is in the +3 oxidation state.

$[Cr(NH_3)_6]^{3-}$	transition in the visible region at 21,600 cm^{-1}
$[Cr(CN)_6]^{3-}$	transition in the UV region at 33,500 cm^{-1}

Draw two separate molecular orbital diagrams for the two complexes. Clearly explain the reasons for these observations with the aide of your diagrams. Be sure to include the σ and π donor and acceptor properties of the ligands in your reasoning.

$[Cr(NH_3)_6]^{3+}$:NH_3 bonds to the metal donating its lone pair. Only σ bonding is involved.





energy
t_{1u}
t_{1u}
4p
a_{1g}
a_{1g}
4s
t_{2g}
ligand π^* orbitals available for π bonding
LUMO
e_g
Δ_o
Δ_o after π bonding
t_{2g}
t_{2g}
e_g
3d
t_{2g}
HOMO after π-bonding
Cr(III)
e_g
t_{1u}
e_g
t_{1u}
a_{1g}
a_{1g}
$(CN)_6$ σ bonding orbitals

CN^- is a strong field ligand. It also has vacant π^* orbitals with the correct symmetry (t_{2g}) to overlap with the HOMO (t_{2g}) of the σ-bonded $[Cr(CN)_6]^{3-}$ complex. This lowers the energy of the HOMO, increasing Δ_o as a result of π-bonding [π back bonding].

Therefore it is clear from the two MO diagrams that Δ_o for the $[Cr(CN)_6]^{3-}$ ion is much larger than Δ_o for the $[Cr(NH_3)_6]^{3+}$ ion.

∴ The electronic transition (HOMO → LUMO) of the cyano complex will occur at a much higher energy than that of the ammine complex. This is indeed the observation made by the student.