

Name \_\_\_\_\_

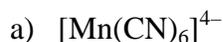
Student Number \_\_\_\_\_

## Chemistry 341 Section 01 - Mid-term Exam - 1¼ hour

October 25<sup>th</sup>, 2005

Please be sure to provide adequate explanations of your answers where it is appropriate, **including diagrams, please.**

- 1) (5 marks) For each of the following complexes give the oxidation state of the metal and its d<sup>n</sup> configuration:



Answer:  $x(\text{Mn}) + 6 \times -1(\text{CN}^-) = -4 \quad \therefore x = +2 \quad \text{Mn(II) is } d^5$



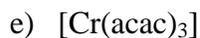
Answer:  $x(\text{Co}) + 3 \times -1(\text{Cl}^-) + 3 \times 0(\text{py}) = 0 \quad \therefore x = +3 \quad \text{Co(III) is } d^6$



Answer:  $x(\text{Re}) + 4 \times -2(\text{O}^{2-}) = -1 \quad \therefore x = +7 \quad \text{Re(VII) is } d^0$



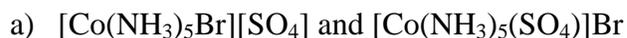
Answer:  $x(\text{V}) + 6 \times -1(\text{Cl}^-) = -3 \quad \therefore x = +3 \quad \text{V(III) is } d^2$



Answer:  $x(\text{Cr}) + 3 \times -1(\text{acac}) = 0 \quad \therefore x = +3 \quad \text{Cr(III) is } d^3$

(acac is  $\text{CH}_3\text{COCHCOCH}_3^-$ )

- 2) (2 marks) What simple chemical tests could you use to distinguish between the coordination isomers below?



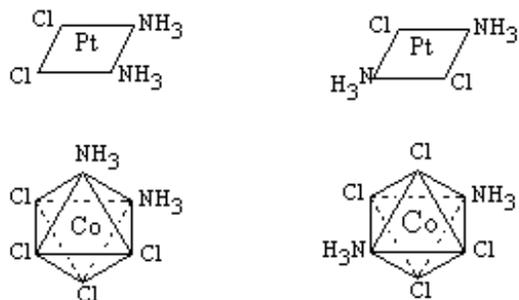
Answer: The compounds are probably inert, that is, the ligands would not exchange rapidly. Therefore, a suitable simple *chemical* test (i.e. *not* a physical measurement) would be to treat a solution of the compound with solutions of  $\text{BaCl}_2$  and  $\text{AgNO}_3$  which would give a precipitate with sulphate (white) and bromide (yellow), respectively. Only the uncoordinated counter ions would react.



Answer: The compounds are probably inert, that is, the ligands would not exchange rapidly. Therefore, a simple *chemical* test (i.e. not a physical measurement such as conductivity, which might do too) would be to treat a solution of the compound with excess  $\text{AgNO}_3$  solution, and determine how much  $\text{AgCl}$  is precipitated gravimetrically. Only the uncoordinated chloride present as the counter ion would precipitate.

3) (3 marks) Giving *real* examples, with diagrams, illustrate the meaning of the designations:

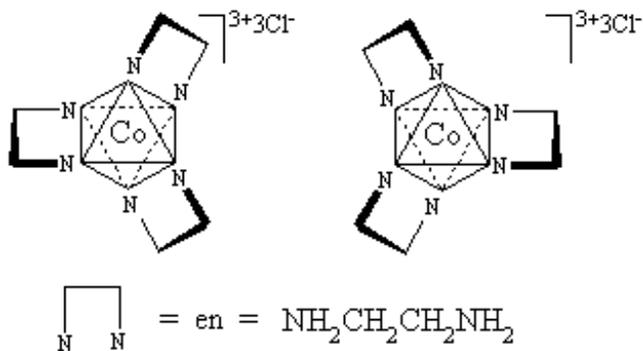
a) *cis* and *trans*



b) *fac* and *mer*



c)  $\Delta$  and  $\Lambda$



4) (5 marks) In each of the following compounds, rationalize the number of unpaired electrons:

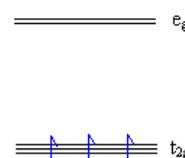
a)  $[\text{Mn}(\text{CN})_6]^{4-}$  (1 unpaired electron)

Answer: This is a Mn(II)  $d^5$  complex, and  $\text{CN}^-$  is a strong field ligand, so a spin paired octahedral ( $O_h$ ) configuration is to be expected, as depicted on the right.



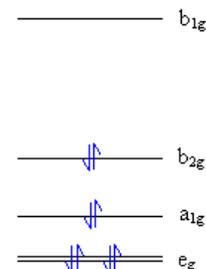
b)  $[\text{Mn}(\text{CN})_6]^{2-}$  (3 unpaired electrons)

Answer: This is a Mn(IV)  $d^3$  octahedral ( $O_h$ ) complex. The configuration is as shown below (whatever the strength of the field due to the ligands ( $\text{CN}^-$ ). (That is, the designations “high spin” or “low spin” are not applicable.) The configuration is depicted on the right.



c)  $[\text{Pd}(\text{CN})_4]^{2-}$  (no unpaired electrons)

Answer: This is a 4-coordinate Pt(II)  $d^8$  complex, and as such (metal ion from 3<sup>rd</sup> transition row and  $d^8$ ) is certainly square-planar ( $D_{4h}$ ). If it were tetrahedral, there would be 2 unpaired electrons: see (e) below. The configuration is shown on the right



d)  $[\text{CoCl}_4]^{2-}$  (3 unpaired electrons)

Answer: This is a 4-coordinate Co(II)  $d^7$  complex. Chloride does not provide a particularly strong ligand field, so the complex must be tetrahedral ( $T_d$ ). The configuration is depicted on the right.



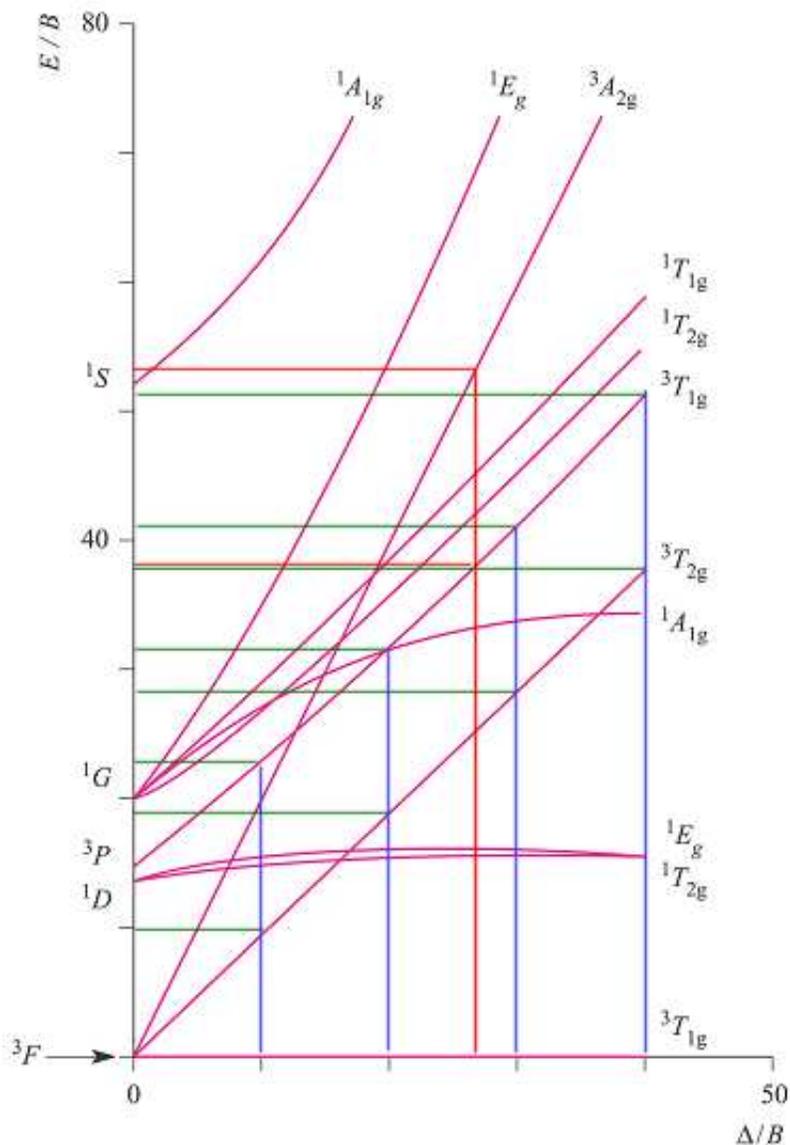
e)  $[\text{NiBr}_4]^{2-}$  (2 unpaired electrons)

Answer: This is a 4-coordinate Ni(II)  $d^8$  complex. Bromide does not provide a particularly strong ligand field, so the complex must be tetrahedral ( $T_d$ ). If it were square-planar, there would be no unpaired electrons: see (c) above. The configuration is depicted on the right.



5) Aqueous solutions of  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  show absorptions at  $17200$  and  $25600 \text{ cm}^{-1}$  which are assigned to the transitions:  ${}^3\text{T}_{2g} \leftarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{T}_{1g}(\text{F})$ .

- a) (1 marks) How many absorptions would you expect to observe, and why might they not all be reported?
- b) (4 marks) Estimate the values of  $B$  and  $\Delta_o$  from the Tanabe-Sugano diagram for the  $d^2$  configuration given below. (By convention, transitions are specified in the form: (final term symbol)  $\leftarrow$  (initial term symbol)).



**Answer (a):** See after (b)

**Answer (b)**

We have to find the  $\Delta/B$  value on the T-S diagram that corresponds to the ratio of the two absorption energies reported. Then using one of the corresponding  $E/B$  values we can calculate  $B$ , and hence  $\Delta$ .

The ratio of the two reported absorptions energies is:

$$E_2/E_1 = 25600/17200 = 1.49$$

From the T-S diagram we see that:

$$86.5 \text{ mm} \equiv 50\Delta/B$$

$$141.0 \text{ mm} \equiv 80E/B$$

Distances were read off the Tanabe-Sugano diagram (blue and green lines) and the ratios plotted on a graph (see next page):

$\Delta/B$	Ratio (mm/mm)
10	$40.5/17 = 2.38$
20	$56/33 = 1.69$
30	$72/50 = 1.44$
40	$90/66 = 1.36$

From the graph below, at ratio = 1.49, we find  $\Delta/B = \sim 26.5$ .

This is equivalent to  $26.5 \times 86.5/50 = 45.8 \text{ mm}$  on the T-S diagram.

(Note that  $\Delta$  may not be exactly equal to  $17500 \text{ cm}^{-1}$  ( $E_1$ ), due to crossing avoidance involving  ${}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{T}_{1g}(\text{P})$ , so we should not calculate  $B$  directly from the  $\Delta/B$  value.)

From the Tanabe-Sugano diagram at  $\Delta/B = 45.8$  mm, we find  $E_2/B = 67$  mm (red lines).

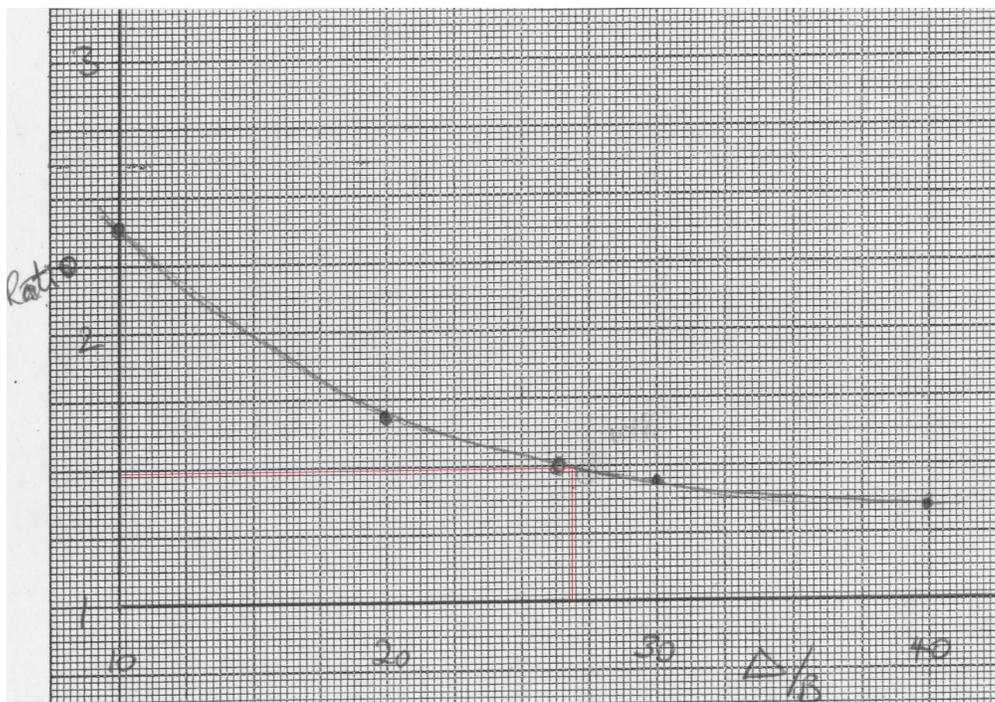
This is equivalent to  $67 \times 80/141 = 38.0$ .

Therefore,  $B = 25600/38.0 = 674 \text{ cm}^{-1}$ .

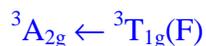
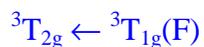
Since  $\Delta/B = 26.5$  and  $B = 674 \text{ cm}^{-1}$ ,  $\Delta = 674 \times 26.5 = 17860 \text{ cm}^{-1}$

(That should be  $17900 \text{ cm}^{-1}$  rounded to 3 significant figs, which is probably optimistic!).

( $E_2$  was used for greater precision in obtaining  $B$ . Better still would have been to use both  $E_1$  and  $E_2$ , and average the  $B$  values obtained.)



Answer (a): The only spin allowed absorptions, three of them, are from the triplet ground term to other triplet terms:



The third absorption,  $E_3$ , at  $\Delta/B = \sim 26.5 \equiv 45$  mm is found at  $E/B = 94 \text{ mm} \equiv 53.3$  (red lines),  
Therefore,  $E_3$  should be observed at  $53.3 \times 674 = 35900 \text{ cm}^{-1}$  (279 nm).

If this absorption was not reported, it was probably because it was hidden under a strong charge transfer band (or perhaps it was beyond the range of the spectrophotometer).