

CHM 102A QUIZ 2

Total Marks: 20

Duration: 30 minutes

Name:

Roll Number:

Section:

Instructions:

1. Please write answers in the space provided (boxes).
2. Please write in ink. (Answers written in pencil will not be re-graded)

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.887	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ★	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	wolfram 74 W 183.84	reuterium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ★ ★	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [269]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]	nihonium 113 Nh [284]	flerovium 114 Fl [289]	moscovium 115 Mc [288]	livermorium 116 Lv [293]	tennessine 117 Ts [294]	oganeson 118 Og [294]					

* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

** Actinide series

Q. No.	1	2	3	4	5	6	7	Total
Marks								

Q1. Co(III) forms octahedral complexes with the general empirical formula $\text{CoCl}_m \cdot n\text{NH}_3$.

a) What values of n and m are possible?

(1+1 = 2 marks)

Answer:

m	3
n	3, 4, 5, 6

1 mark each for m and n. All values of n must be correct to get 1 mark.

Co(III) must have six ligands to form an octahedral complex. Also, it must have enough chloride ions to neutralize its 3+ charge. So, m must equal 3. With that known, it must have enough ammonia groups to achieve its octahedral structure, regardless of how many chloride ions are present. So, n can equal 6, 5, or 4 or 3.

In other words, for the given information, the complex could be any of the following: $[\text{CoCl}_3(\text{NH}_3)_3]$; $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$; $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$; $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

b) Upon the addition of excess AgNO_3 , one of the complexes precipitates 1 mole of AgCl for every mole of Co. What are the values of n and m for this complex?

(1+1 = 2 marks)

Answer:

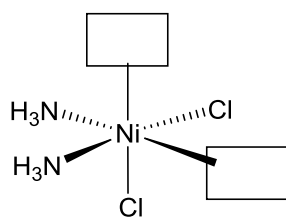
m	3
n	4

1 mark each for correct value(s) of m and n.

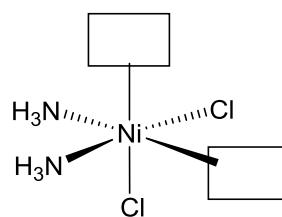
Only the free Cl^- ions will precipitate with AgCl added. The other two Cl^- will be bound to the Co and will not precipitate. With this additional information, the identity of this complex would be $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$.

Q2. Fill in the missing ligands below to complete the structures of *fac*- and *mer*- $\text{Co}(\text{NH}_3)_3\text{Cl}_3$.

(1+1 = marks)

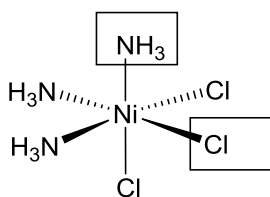


fac-Co(NH₃)₃Cl₃

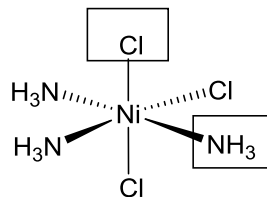


mer-Co(NH₃)₃Cl₃

Answer:



fac-Co(NH₃)₃Cl₃



mer-Co(NH₃)₃Cl₃

1 mark each for the right answer.

Q3. Assuming that the following complexes obey the 18 electron rule, answer the questions below:

- a) Determine the identity of the 3d-transition metal M in $[(\eta^3\text{-C}_3\text{H}_5)\text{M}(\text{CN})_4]^{2-}$.

(1 mark)

Answer:

M =	Co
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1 mark for the correct metal.

The complex has overall charge of -2 and it has one negatively charged ligand ($\eta^3\text{-C}_3\text{H}_5$). Therefore, the metal is in the +3 oxidation state.

The allyl anion contributes 4 electrons while the 4 cyanides donate a total of 8 electrons. Since the complex is electron precise, the number of electrons donated by M = 18 – (12) = 6.

Hence, M is a transition metal which has 6 electrons in its +3 oxidation state. So the answer is M = Co.

- b) Deduce the number of metal-metal bonds that exist in $[(\eta^5\text{-Cp})\text{Co}(\text{CO})]_2(\mu\text{-CO})$.

(1 mark)

Answer:

No. of M-M bond(s) =	1
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1 mark for the correct number of Co-Co bond.

Counting the electrons for each Co:

Co(I)	8 electrons
Cp ⁻	6 electrons
CO	2 electrons
μ-CO	1 electron
TOTAL	17 electrons

To fulfil the 18 electron rule, each Co needs one electron which can be obtained by 1 Co-Co bond.

Q4.

- a) Among the four metal ions given below, identify the two which form perfect octahedral complexes. (both metal ions have to be correct to get marks. No partial marking)

(1 mark)

Ti(III), Cr (III), Ni(II), Cu(II)

Answer:

I	Cr (III)
II	Ni (II)

1 mark for correct answers. Both answers have to be correct to get 1 mark. No partial marking.

Octahedral complexes of Cr(III) will have $t_{2g}^3 e_g^0$ configuration which will not show JT distortion. Ni(II) in octahedral complexes has the configuration $t_{2g}^6 e_g^2$ which will also not show JT distortion.

- b) Among the four metal ions given in part (a) above, identify which one shows the most prominent Jahn-Teller distortion. **(1 mark)**

Answer:

Metal ion with most prominent J-T distortion =	Cu (II)
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1 mark for the correct answer.

Cu(II) has degeneracy in the e_g level so it will show most prominent JT distortion.

Ti(III) has degeneracy in the t_{2g} level so distortion will be less prominent.

Q5. For each of the following pair of complexes, identify the one that has the larger crystal field stabilization energy (CFSE). **(1+1 = 2 marks)**

- a) $[\text{Cr}(\text{OH}_2)_6]^{2+}$ or $[\text{Mn}(\text{OH}_2)_6]^{2+}$

Answer:

Complex with higher CFSE =	$[\text{Cr}(\text{OH}_2)_6]^{2+}$
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1 mark for right answer.

Both are high-spin complexes. While Mn^{2+} is a d^5 ion and hence $\text{CFSE} = 0$, Cr^{2+} is a d^4 ion and hence $[\text{Cr}(\text{OH}_2)_6]^{2+}$ has $t_{2g}^3 e_g^1$ configuration and $\text{CFSE} = [(-0.4 \times 3) + (0.6 \times 1)]\Delta_o = -0.6 \Delta_o$. Thus, $[\text{Cr}(\text{OH}_2)_6]^{2+}$ has the larger CFSE.

- b) $[\text{Ru}(\text{CN})_6]^{3-}$ or $[\text{Fe}(\text{CN})_6]^{3-}$

Answer:

Complex with higher CFSE =	$[\text{Ru}(\text{CN})_6]^{3-}$
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1 mark for right answer.

Both Ru^{3+} and Fe^{3+} are d^6 ions that belong to the same group. Both complexes are low spin and hence have t_{2g}^6 electron configuration. However, Δ_o increases down the group and hence the ruthenium complex will have the higher CFSE.

Q6. Consider the complexes $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$ and answer the questions below: **(1 + 1 + 1 + 1 = 4 marks)**

a) What are the geometries of these complexes?

Answer :

Complex	Geometry
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	Octahedral
$[\text{CoCl}_4]^{2-}$	Tetrahedral

b) What are the oxidation states of Co in these complexes?

Answer :

Complex	Oxidation State of Metal
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	+2
$[\text{CoCl}_4]^{2-}$	+2

c) Which of these complexes will have a higher magnetic moment?

Answer :

Complex with higher magnetic moment =	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
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Both complexes have same number of unpaired electrons but orbital contribution is possible in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ which has electronic configuration $t_{2g}^5 e_g^2$ whereas in $[\text{CoCl}_4]^{2-}$, the electronic configuration is $e^4 t_2^3$ which cannot have orbital contribution.

d) Which of these complexes will show more intense colour?

Answer :

Complex which shows more intense color =	$[\text{CoCl}_4]^{2-}$
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Q7. $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic while the observed magnetic moment for $[\text{NiCl}_4]^{2-}$ complex is **2.8 B.M.** Assuming there is no significant orbital contribution, answer the following questions.

- a) What are the geometries of the two complexes? **(1 + 1 = 2 marks)**

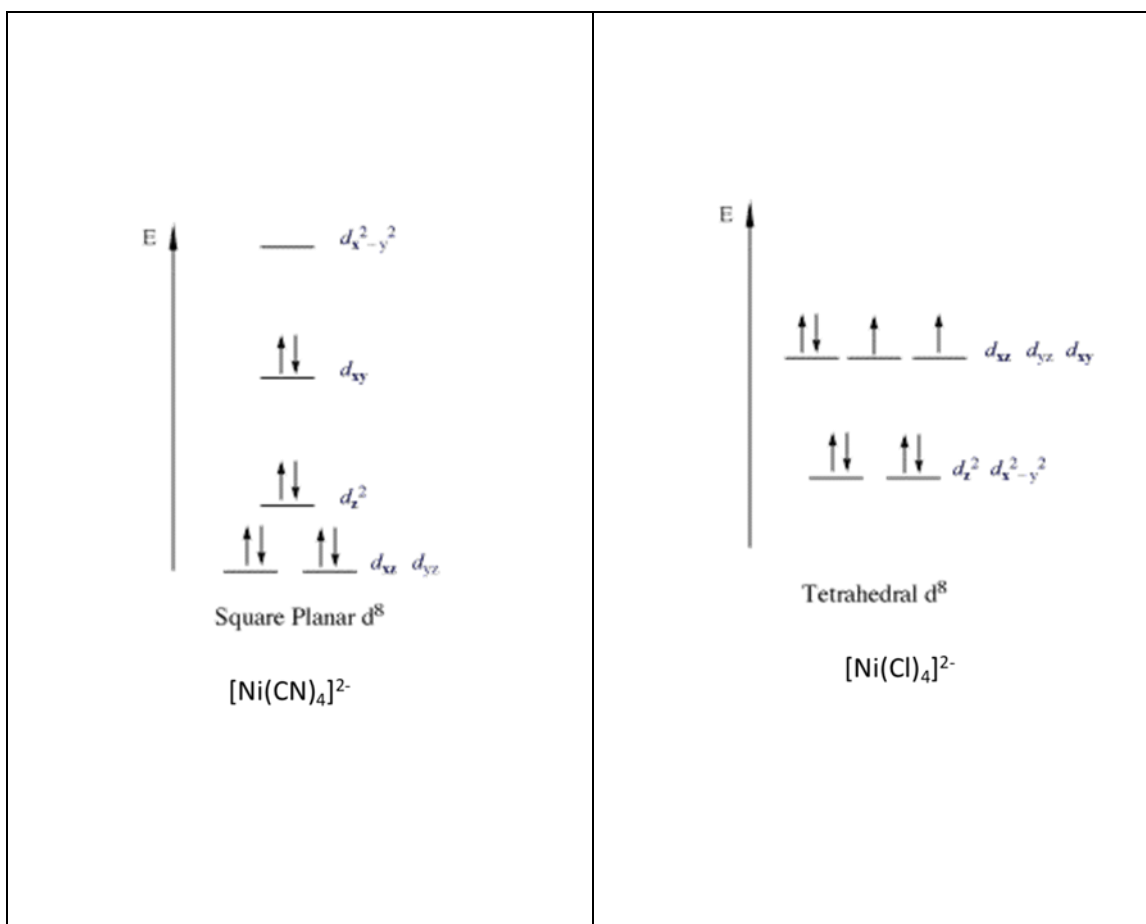
Answer:

Complex	Geometry
$[\text{Ni}(\text{CN})_4]^{2-}$	Square planar
$[\text{NiCl}_4]^{2-}$	Tetrahedral

- b) Using principles of Crystal Field Theory, draw the *d*-orbital splitting diagram and show the electron distribution for both complexes. (Answer has to be completely correct to get 1 mark each. No partial marking.)
(1 + 1 = 2 marks)

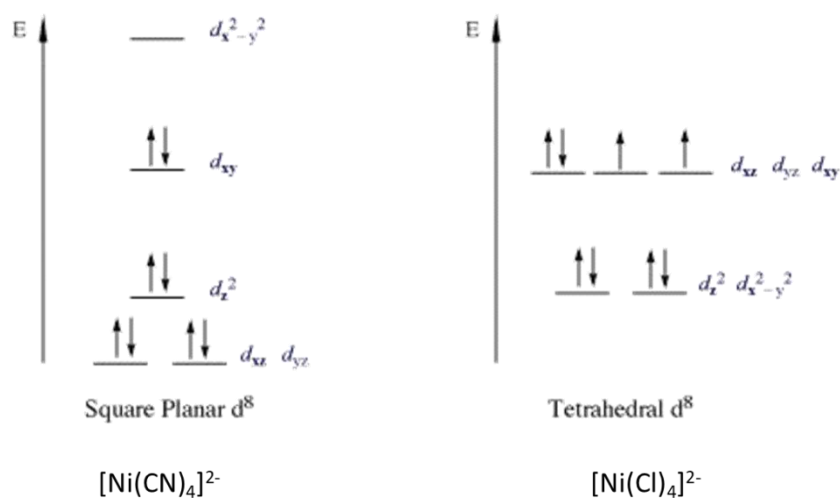
Answer:

Orbital splitting diagram and <i>d</i> -electron distribution for $[\text{Ni}(\text{CN})_4]^{2-}$	Orbital splitting diagram and <i>d</i> -electron distribution for $[\text{NiCl}_4]^{2-}$
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Answer:

For $[\text{NiCl}_4]^{2-}$, $\mu = [n(n+2)]^{1/2}$ so $n = 2$. For a 4-coordinate complex, possible structures are tetrahedral or square planar and this is a $\text{Ni}^{2+} d^8$ ion. For a d^8 ion, a square planar geometry would result in no unpaired electrons (diamagnetic) and hence $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar. For d^8 ion, a tetrahedral geometry would result in 2 unpaired electrons and hence $[\text{Ni}(\text{Cl})_4]^{2-}$ turns out to be tetrahedral.



1 mark for each correct answer.