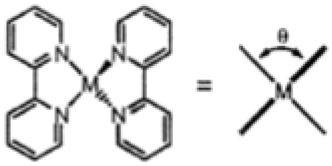
2003 2nd semester Final

Advanced Inorgnanic Chemistry 2

(Open Book Test)

1. (50 pts) What are the point groups of the following molecules? Write down all the existing symmetry elements of each molecule. (Consult character tables)

(a) Θ = 90° (b) Θ = 70°



(c) H_2O (d) cyclohexane (chair form) (e) cisplatin

2. (30 pts) What are the nomenclatures or chemical formula of the followings?

(a) *trans*-$[Cu(H_2O)_2(en)_2]^{2+}$
(b) *fac*-$[IrCl_3(PMe_3)_3]$
(c) *trans*-$[Ni(CN)_4(H_2O)_2]^{2-}$
(d) *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride
(e) *fac*-tricarbonyl-tris(trifluorophosphine)molybdenum(0)
(f) tetraamminechromium(III)-μ-oxo-μ-methoxo-bis(ethylenediamine)cobalt(III) chloride

3. (105pts) $[PtCl_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic.
(a) (10 pts) What are the geometrical structures of the above two complex ions?
(b) (20 pts) Explain why the magnetic properties differ between two compounds using VBT (Valence Bond Theory)?
(c) (20 pts) Explain why the magnetic properties differ between two compounds using CFT (Crystal Field Theory)?
(d) (10 pts) What is the point group of each compound?
(e) (5 pts) How many do vibrational modes exist for the compounds?
(f) (40 pts) There are four M-Cl stretching vibrations. What are the symmetry types of the stretching vibrations for each compound? Distinguish Raman-, IR-active modes. (Hint, Draw four M→Cl arrows and think about that.)

4. (50 pts) Equilibrium constants for the reactions between ethylenediamine (en) and Co^{2+}, Ni^{2+}, Cu^{2+} are listed in the table below. (M=Co, Ni, Cu)

$[M(OH_2)_6]^{2+} + en \rightleftharpoons [M(en)(OH_2)_4]^{2+} + 2H_2O \quad K_1$

$[M(en)(OH_2)_4]^{2+} + en \rightleftharpoons [M(en)_2(OH_2)_2]^{2+} + 2H_2O \quad K_2$

$[M(en)_2(OH_2)_2]^{2+} + en \rightleftharpoons [M(en)_3]^{2+} + 2H_2O \quad K_3$

ion	$\log K_1$	$\log K_2$	$\log K_3$
Co^{2+}	5.89	4.83	3.10
Ni^{2+}	7.52	6.28	4.26
Cu^{2+}	10.55	9.05	-1.0

(a) (10 pts) Explain why $K_1 > K_2 > K_3$ for Co^{2+} and Ni^{2+}.
(b) (20 pts) Explain why $K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+})$ for K_1 and K_2.
(c) (20 pts) Explain why $K_3(Cu^{2+}) < K_3(Co^{2+}) < K_3(Ni^{2+})$.

5. (30 pts) The spectrum of d1 Ti^{3+}(aq) is attributed to a single electronic transition $t_{2g} \rightarrow e_g$. The band shown in Fig7.10 is not symmetrical and suggests that more than one state is involved. Suggest how to explain this observation using the Jahn-Teller theorem.

6. (85 pts) Identify the ground state terms with the spin multiplicity for the following transition metal ions.

		Free Ions	Octahedral Complexes		Tetrahedral Complexes
	Cu^{2+}	^2D	^2E_g		$^2T_2$
(a)	V^{3+}				
(b)	Cr^{3+}				
(c)	Mn^{2+}		high-spin	low-spin	
(d)	Fe^{2+}				
(e)	Ni^{2+}				

7. (30 pts) Explain why $[FeF_6]^{3-}$ is colorless whereas $[CoF_6]^{3-}$ is colored but exhibits only a single band in visible.

8. (30 ts) Use Tababe-Sugano diagram to predict the ground state and the number of observable transitions for each of the following molecules.

(a) $[Cr(H_2O)_6]^{+3}$ (Octahedral structure)
(b) $[Fe(CN)_6]^{4-}$ (Octahedral structure, strong-field complex)
(c) $[NiCl_4]^{2-}$ (Tetrahedral structure)

9. (30 pts) Consider the molecular orbital diagram for a tetrahedral complex and relevant d orbital configuration. Show that the purple color of MnO_4^- ions cannot arise from a ligand-field transition (d-d transition).

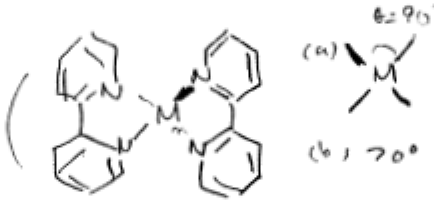
10. (Bonus 60 pts) Essay: Write good thing, bad thing, ugly thing, suggestion, to be improved, thing you want to learn in inorganic chemistry lecture,.......anything about this lecture. Write at least <u>12 lines</u> (Korean, 5 points/line, at least 40 characters/line, max point 60) or <u>6 lines</u> (English, 10 points/line, at least 50 characters/line, max point 60). Of course, you can write as much as you want. Just maximum point is 60.

• **Exam score and term grade will be posted in my web site within a week.** Check the site frequently.
Put a password (4 digit number) as well as your name and student # in your answer sheet. The password will be used for web posting.

2003 2학기 대학원 무기화학2 기말고사

1 (10 × 5 = 50점)

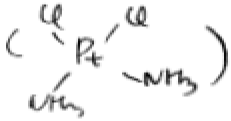
(a) D_{2d} , $E, 2S_4, C_2, 2C_2', 2\sigma_d$



(b) D_2 , $E, C_2(z), C_2'(y), C_2(x)$

(c) C_{2v} , $E, C_2, \sigma_v(xz), \sigma_v'(yz)$ (H_2O)

(d) D_{3d} , $E, 2C_3, 3C_2, i, 2S_6, 3\sigma_d$ ()

(e) C_{2v} , $E, C_2, \sigma_v(xz), \sigma_v'(yz)$ ()

2 (5 × 6 = 30점)

(a) trans-$[Cu(H_2O)_2(en)_2]^{2+}$

: trans-diaqua bis(ethylenediamine) copper(II)

(b) fac-$[IrCl_3(PMe_3)_3]$

: fac-trichloro tris(trimethyl phosphine) iridium(III)

(c) trans-$[Ni(CN)_4(H_2O)_2]^{2-}$

: trans-diaquatetracyanonickelate(II)

(d) trans-dichlorobis(ethylenediamine)cobalt(III) chloride

: trans-$[CoCl_2(en)_2]^+Cl^-$

(e) fac-tricarbonyl-tris(trifluoro phosphine) molybdenum(0)

: fac-$[Mo(CO)_3(PF_3)_3]$

(f) tetraammine chromium(III)-μ-oxo-methoxo-bis(ethylenediamine) cobalt(III) chloride

: μ-oxo-methoxo-$[Co(en)_2][Cr(NH_3)_4]Cl$?

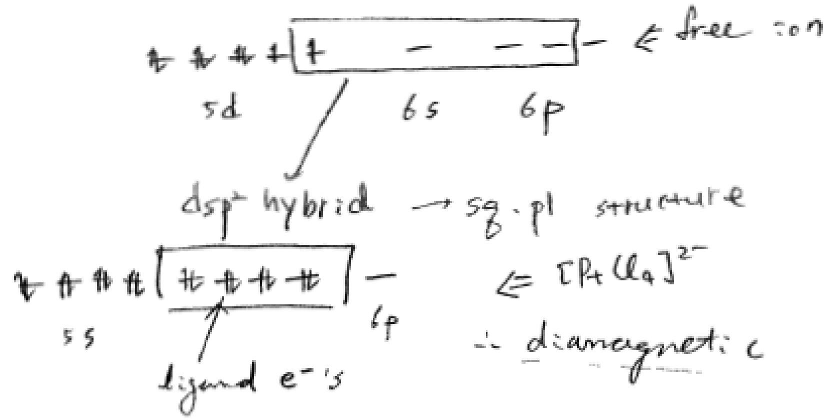
[3] (105)

a) $[PtCl_4]^{2-}$: square planar 5

$[NiCl_4]^{2-}$: tetrahedral 5

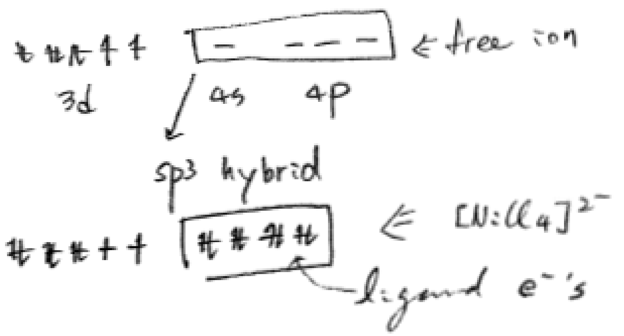
(b)

$[PtCl_4]^{2-}$: Pt(II), d^8



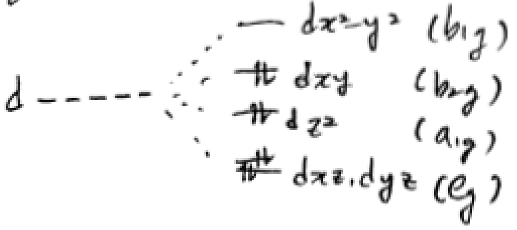
10

$[NiCl_4]^{2-}$: Ni(II), d^8



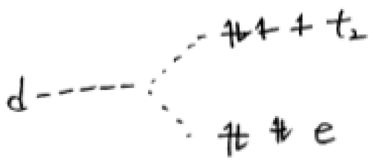
∴ paramagnetic 10

(c) $[PtCl_4]^{2-}$: sq. pl (D_{4h}) 10



∴ diamagnetic

$[NiCl_4]^{2-}$: T_d 10

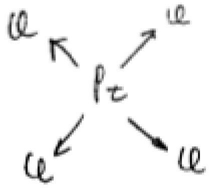


∴ paramagnetic

(d) $[PtCl_4]^{2-}$: D_{4h} 5　　(e) $3N-6 = 3\times5-6 = 9$ 5

$[NiCl_4]^{2-}$: T_d 5

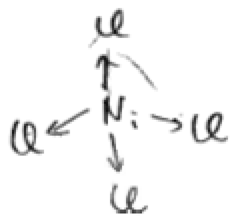
(f)



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	h=16
$\Gamma_\uparrow$	4	0	0	2	0	0	0	4	2	0	

$\therefore \Gamma_\uparrow = A_{1g} + B_{1g} + E_u$

(A_{1g}, B_{1g} ↑ Raman-Active; E_u ↑ IR-active) 20



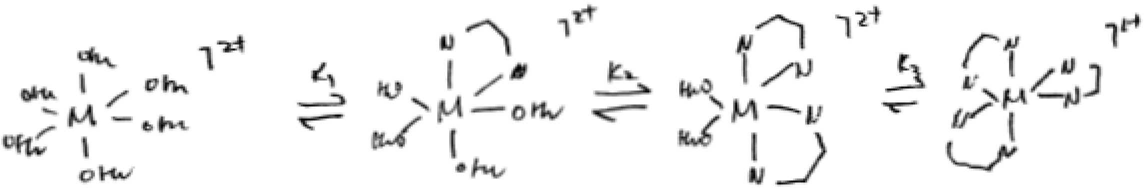
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	h=24
$\Gamma_\uparrow$	4	1	0	0	2	

$\therefore \Gamma_\uparrow = A_1 + T_2$

(A_1, T_2 → Raman-active; T_2 → IR-active) 20

4 (50)

(a)



$K_1 \rightarrow K_2 \rightarrow K_3$ 로 갈 수록 치환되어야 할 H_2O ligand의

선택에 대한 자유의 수가 줄어든다

$\therefore K_1 > K_2 > K_3$ 10

(b) 전이금속 착물의 안정도는 Coulombic interaction과 LFSE가 클수록 증가한다

	Co^{2+}	Ni^{2+}	Cu^{2+}
반지름	→	→	감소
Coulombic interaction	→	→	증가

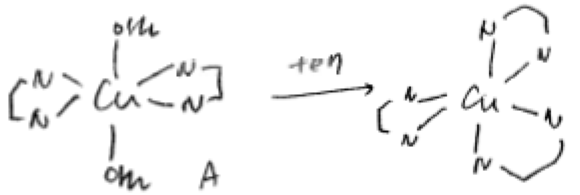
	d^7	d^8	d^9
Oh LFSE	$-0.8\Delta_o$	$-1.2\Delta_o$	$-0.6\Delta_o$

그런데 $Cu^{2+}(H_2O)_6$의 경우 Jahn-Teller distortion에 의하여 Oh의 LFSE인 $-0.6\Delta_o$보다 더 많이 안정화 될 수 있다.

따라서 $K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+})$. 20

(c) (b)의 이유로 $K(Co^{2+}) < K(Ni^{2+})$

Cu^{2+}의 경우 K_3는 다음 반응의 평형상수이다.

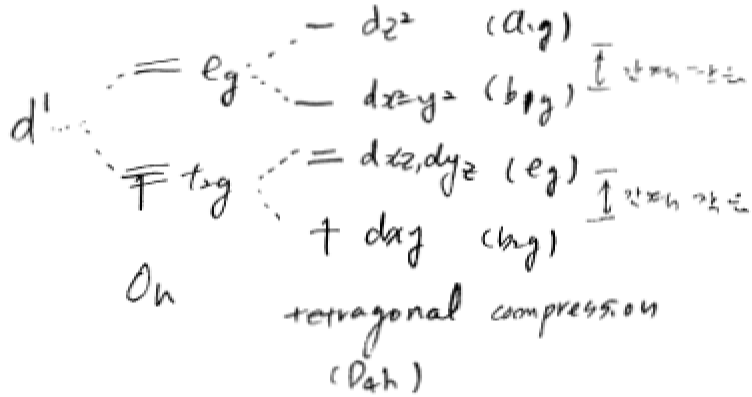


Jahn-Teller effect로 인해 안정한 A의 구조보다 복수로 좀 더 불안정한 형태로 가야 하므로 $K_3(Cu^{2+})$는 매우 작다

$\therefore K_3(Cu^{2+}) < K_3(Co^{2+}) < K_3(Ni^{2+})$ 25

15 ㉚

$Ti^{3+}(aq)$. d^1



d^1 complex의 경우 O_h 구조보다 tetragonal compression 에 의한 D_{4h} 구조를 가지는 것이 더 안정하다. 따라서 O_h 에서의 $t_{2g} \rightarrow e_g$ transition 이 아니라 $b_{2g} \rightarrow b_{1g}$, $b_{2g} \rightarrow a_{1g}$ 의 transition 이 일어나서 흡수 스펙트럼이 asymmetric 하게 보인다 30

16 5×17=85

		free ions	O_h complexes		T_d complexes
	Cu^{2+}	(d^9) ^2D	^2E_g		$^2T_2$
(a)	V^{3+}	(d^2) ^3F	$^3T_{1g}$		$^3A_2$
(b)	Cr^{3+}	(d^3) ^4F	$^4A_{2g}$		$^4T_1$
			high spin	low spin	
(c)	Mn^{2+}	(d^5) ^6S	$^6A_{1g}$	$^2T_{2g}$	$^6A_1$
(d)	Fe^{2+}	(d^6) ^5D	$^5T_{2g}$	$^1A_1$	^5E
(e)	Ni^{2+}	(d^8) ^3F	$^3A_{2g}$		$^3T_1$

(6)

7 (30) $[FeF_6]^{3-}$: Fe^{3+} (d^5) high-spin (weak field), ground state = ${}^{6}A_{1g}$

$[CoF_6]^{3-}$: Co^{3+} (d^6) 〃 〃 , 〃 = ${}^{5}T_{2g}$

$[FeF_6]^{3-}$의 경우 ground state (${}^{6}A_{1g}$)와 spin-multiplicity가 같은 excited state가 없어서 흡수가 일어나지 않는다. (흡광계수가 낮다)

$[CoF_6]^{3-}$의 경우 ${}^{5}T_{2g} \rightarrow {}^{5}E_g$로의 전이가 일어날 수 있다.

8 ($10 \times 3 = 30$)

(a) $[Cr(H_2O)_6]^{3+}$. Cr^{3+}, d^3 (O_h)

${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$

${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$ 3개

${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$

(b) $[Fe(CN)_6]^{4-}$, Fe^{2+}, d^6 (O_h)

${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$

${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$

${}^{1}A_{1g} \rightarrow {}^{1}E_g$ 3개

${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ (I)

${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ (F)

(c) $[NiCl_4]^{2-}$. Ni^{2+} d^8 (T_d)

${}^{3}T_1(F) \rightarrow {}^{3}T_2$

${}^{3}T_1(F) \rightarrow {}^{3}T_1(P)$ 3개

${}^{3}T_1(F) \rightarrow {}^{1}E$

[9] 은 $[MnO_4]^-$, Mn^{7+}, d^0

즉, d-electron이 없다 따라서 ligand-field transition이 없다