

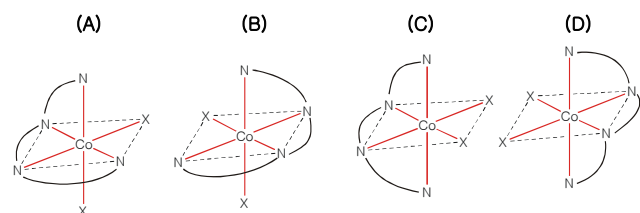
2008학년도 고급무기화학1 기말고사 (2008년 6월 10일)
[2008 Advanced Inorganic Chemistry 1 Final Exam]

- Hours: 2:00PM–5:00 PM
- Answer the questions in the boxes given.
- Total Pages: 6
- Total Problems: 9

1. 빈칸을 채워라.
1. Fill the blanks.

이름(Nomenclature)	
(a) $[\text{Cu}(\text{NH}_3)_4]^{2+}$	tetraamminecopper(II) or tetraamminecopper(2+)
(b) $[\text{PtCl}_4]^{2-}$	tetrachloroplatinate(II) or tetrachloroplatinate(2-)
(c) $\text{Fe}(\text{S}_2\text{CNMe}_2)_3$	tris(dimethyldithiocarbamato)iron(III) or tris(dimethyldithiocarbamato)iron(0) or tris(dimethylcarbamodithioato)iron(III) or tris(dimethylcarbamodithioato)iron(0)
배위구조그림(Draw coordination structure)	
(d) Diaquadiiododinitritopalladium(IV) (all ligand trans)	

2. $[\text{CoX}_2(\text{trien})_3]^+$ (trien= triethylenetetraamine)에 대한 이성질체는 다음 이 있다. 각각에 대하여 absolute configuration (Δ 또는 Λ)를 결정하여라.
2. Followings are the stereo isomers of $[\text{CoX}_2(\text{trien})_3]^+$ (trien= triethylenetetraamine). Determine the absolute configurations. (Δ or Λ)



	(A)	(B)	(C)	(D)
absolute configuration	Δ	Λ	Λ	Δ

3. 다음 착물들에 대하여 d-전자 배치 (d), 외톨이 전자 (unpaired electron)의 수 (n), spin quantum number (S), ground-state molecular term symbol (Term), LFSE를 써라. (전부 O_h 배위구조로 생각하고 풀 것) (Fig 1 참조)

3. What are the d-electron configuration (d), the number of unpaired electrons (n), spin quantum number (S), ground-state molecular term symbol (Term), and LFSE of the following complexes? (Assume all complexes have the O_h coordination geometry.) (Consult Fig 1.)

Complex	d	n	S	Term	LFSE (Δ_o)
$[\text{Co}(\text{CO})_4]^-$	d^{10}	0	0	^1S	0
$[\text{Cr}(\text{CN})_6]^{4-}$	d^4	2	1	^3H	-1.6
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (hs)	d^5	5	5/2	^6S	0
$[\text{Co}(\text{NO}_2)_6]^{4-}$ (hs)	d^7	3	3/2	^4F	-0.8
$[\text{Co}(\text{NH}_3)_6]^{3+}$ (ls)	d^6	0	0	^1I	-2.4
MnO_4^-	d^0	0	0	^1S	0
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	d^9	1	1/2	^2D	-0.6

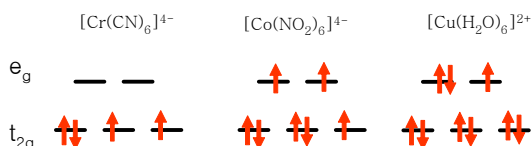
4. (a) 문제 3의 착물 중에서 Jahn-Teller effect를 보이는 착물이 3개 있다. 3개를 골라라.

4. (a) Among the complexes of problem #3, three complexes show Jahn-Teller effect. Select the complexes.

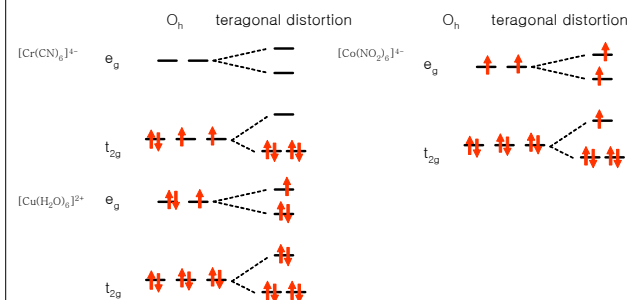
complexes	$[\text{Cr}(\text{CN})_6]^{4-}$	$[\text{Co}(\text{NO}_2)_6]^{4-}$	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
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- (b) 위 세 착물이 Jahn-Teller effect를 보이는 이유를 설명하여라.
(b) Explain why the three complexes show Jahn-Teller effect.

위에서 Jahn-Teller Effect가 일어난다고 표시한 착물들의 전자배치는 다음과 같다.

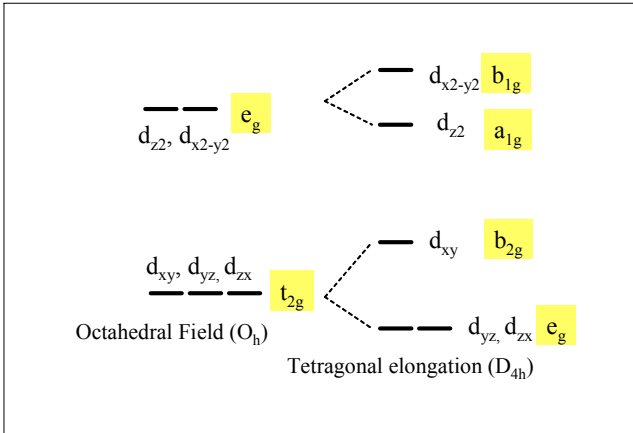


그림에서 보는 바와 같이 degenerate되어 있는 orbital에 전자배치가 균등하지 않다. ($[\text{Cr}(\text{CN})_6]^{4-}$ 와 $[\text{Co}(\text{NO}_2)_6]^{4-}$ 에는 t_{2g} , $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ 에서는 e_g) 이러한 경우에 착물은 대칭성을 무너뜨림으로써 degeneracy를 없앤다. 이럴 경우에 전자들은 degenerate된 orbital에 균등하게 배치되고 더 낮은 에너지 상태가 될 수 있다.



5. Crystal field theory 에 바탕하여 octahedral 구조에서의 d-오비탈 갈라짐과 octahedral 구조에서 tetragonal elongation이 일어날 때의 d-오비탈 갈라짐을 그려라.

5. Based on the crystal field theory, draw d-orbital splittings in the octahedral field and the d-orbital splittings when the tetragonal elongation occurs from the octahedral structure.



6. 자유 Cr^{3+} 이온은 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ 의 전자배치를 한다. 착이온 $\text{Cr}(\text{NH}_3)_x^{3+}$ 에 대하여 다음에 답하라. (NH_3 는 σ -donor ligand 이다.)

6. Free Cr^{3+} ion has the electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$. Answer the following questions about $\text{Cr}(\text{NH}_3)_x^{3+}$. (NH_3 is a σ -donor ligand.)

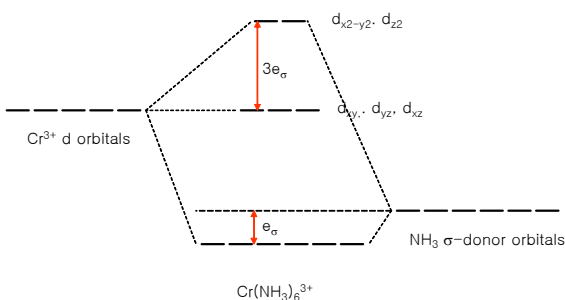
(a) 각 겹침 모델 (angular overlap model)을 이용하여 Cr^{3+} 의 d-orbital 과 NH_3 의 σ -donor orbital의 에너지 준위가 팔면체 구조인 $\text{Cr}(\text{NH}_3)_6^{3+}$ 착물을 이룰 때 어떻게 변화하는지를 에너지 준위도를 그리고 상대적인 에너지 준위를 e_σ 로 표시하여라. (구하는 과정도 쓸 것. Table 1 참조)

(a) Draw the energy level diagram of the d-orbitals of Cr^{3+} and the σ -donor orbitals of NH_3 in octahedral $\text{Cr}(\text{NH}_3)_6^{3+}$ complex, based on angular overlap model. Energy levels should be noted in e_σ unit. (Write the process to get the energy level diagram. Consult Table 1.)

strength of σ -interactions

$$\begin{aligned} d_{z^2} &\Rightarrow 1 + 1/4 + 1/4 + 1/4 + 1/4 + 1 = 3 e_\sigma \\ d_{x^2-y^2} &\Rightarrow 0 + 3/4 + 3/4 + 3/4 + 3/4 + 0 = 3 e_\sigma \\ d_{xy} &\Rightarrow 0 + 0 + 0 + 0 + 0 + 0 = 0 e_\sigma \\ d_{yz} &\Rightarrow 0 + 0 + 0 + 0 + 0 + 0 = 0 e_\sigma \\ d_{xz} &\Rightarrow 0 + 0 + 0 + 0 + 0 + 0 = 0 e_\sigma \end{aligned}$$

$$\begin{aligned} \text{ligand 1} &\Rightarrow 1 + 0 + 0 + 0 + 0 + 0 = e_\sigma \\ \text{ligand 2} &\Rightarrow 1/4 + 3/4 + 0 + 0 + 0 + 0 = e_\sigma \\ \text{ligand 3} &\Rightarrow 1/4 + 3/4 + 0 + 0 + 0 + 0 = e_\sigma \\ \text{ligand 4} &\Rightarrow 1/4 + 3/4 + 0 + 0 + 0 + 0 = e_\sigma \\ \text{ligand 5} &\Rightarrow 1/4 + 3/4 + 0 + 0 + 0 + 0 = e_\sigma \\ \text{ligand 6} &\Rightarrow 1 + 0 + 0 + 0 + 0 + 0 = e_\sigma \end{aligned}$$



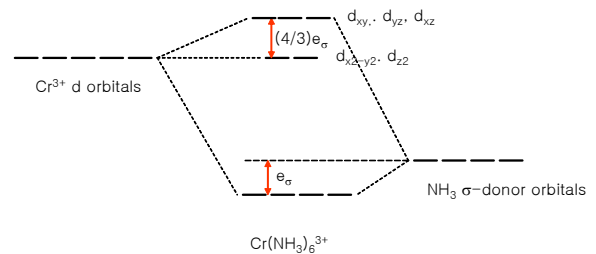
(b) 각 겹침 모델 (angular overlap model)을 이용하여 Cr^{3+} 의 d-orbital 과 NH_3 의 σ -donor orbital의 에너지 준위가 사면체 구조인 $\text{Cr}(\text{NH}_3)_4^{3+}$ 착물을 이룰 때 어떻게 변화하는지를 에너지 준위도를 그리고 상대적인 에너지 준위를 e_σ 로 표시하여라. (구하는 과정도 쓸 것. Table 1 참조)

(a) Draw the energy level diagram of the d-orbitals of Cr^{3+} and the σ -donor orbitals of NH_3 in tetrahedral $\text{Cr}(\text{NH}_3)_6^{3+}$ complex, based on angular overlap model. Energy levels should be noted in e_σ unit. (Write the process to get the energy level diagram. Consult Table 1.)

strength of σ -interaction

$$\begin{aligned} d_{z^2} &\Rightarrow 0 + 0 + 0 + 0 = 0 e_\sigma \\ d_{x^2-y^2} &\Rightarrow 0 + 0 + 0 + 0 = 0 e_\sigma \\ d_{xy} &\Rightarrow 1/3 + 1/3 + 1/3 + 1/3 = 4/3 e_\sigma \\ d_{yz} &\Rightarrow 1/3 + 1/3 + 1/3 + 1/3 = 4/3 e_\sigma \\ d_{xz} &\Rightarrow 1/3 + 1/3 + 1/3 + 1/3 = 4/3 e_\sigma \end{aligned}$$

$$\begin{aligned} \text{ligand 7} &\Rightarrow 0 + 0 + 1/3 + 1/3 + 1/3 = e_\sigma \\ \text{ligand 8} &\Rightarrow 0 + 0 + 1/3 + 1/3 + 1/3 = e_\sigma \\ \text{ligand 9} &\Rightarrow 0 + 0 + 1/3 + 1/3 + 1/3 = e_\sigma \\ \text{ligand 10} &\Rightarrow 0 + 0 + 1/3 + 1/3 + 1/3 = e_\sigma \end{aligned}$$



(c) (a)와 (b)로부터 Δ_t/Δ_o 값은 얼마인지 계산하라. (Δ_o = octahedral orbital splitting parameter, Δ_t = tetrahedral orbital splitting parameter)
(c) From the results of (a) and (b), calculate the value of Δ_t/Δ_o . (Δ_o = octahedral orbital splitting parameter, Δ_t = tetrahedral orbital splitting parameter)

$$\Delta_o = 3 e_\sigma$$

$$\Delta_t = 4/3 e_\sigma$$

$$\Delta_t/\Delta_o = 4/9$$

(d) Table 2를 참조하여 $\text{Cr}(\text{NH}_3)_6^{3+}$ 에서 Δ_o 는 얼마가 되는지 cm^{-1} 단위로 계산하여라.
(d) In octahedral $\text{Cr}(\text{NH}_3)_6^{3+}$, calculate Δ_o in cm^{-1} unit. (Consult Table 2.)

$$\Delta_o = 3 e_\sigma = 3 \times 7180 \text{ cm}^{-1} = 21,540 \text{ cm}^{-1}$$

(e) Table 2를 참조하여 $\text{Cr}(\text{NH}_3)_4^{3+}$ 에서 Δ_t 는 얼마가 되는지 cm^{-1} 단위로 계산하여라. (Table 2는 팔면체 구조에 대한 것이지만 그대로 적용하여라.)
(e) In tetrahedral $\text{Cr}(\text{NH}_3)_4^{3+}$, calculate Δ_o in cm^{-1} unit. (Though Table 2 is for octahedral complexes, use the table for this question.)

$$\Delta_t = 4/3 e_\sigma = 4/3 \times 7180 \text{ cm}^{-1} = 9,573 \text{ cm}^{-1}$$

(f) Crystal Field Theory 에 의한 Crystal Field Stabilization Energy (= Ligand Field Stabilization Energy) 가 $\text{Cr}(\text{NH}_3)_6^{3+}$ 와 $\text{Cr}(\text{NH}_3)_4^{3+}$ 에 대하여 각각 얼마인지 cm^{-1} 단위로 답하라.
(f) What are the Crystal Field Stabilization Energy (= Ligand Field Stabilization Energy) of the octahedral $\text{Cr}(\text{NH}_3)_6^{3+}$ and the tetrahedral $\text{Cr}(\text{NH}_3)_4^{3+}$, respectively, in cm^{-1} unit ?

$$\text{Cr}(\text{NH}_3)_6^{3+}(\text{d}^3)$$

$$\text{LFSE} = 1.2\Delta_o = 1.2 \times 21,540 \text{ cm}^{-1} = 25,848 \text{ cm}^{-1}$$

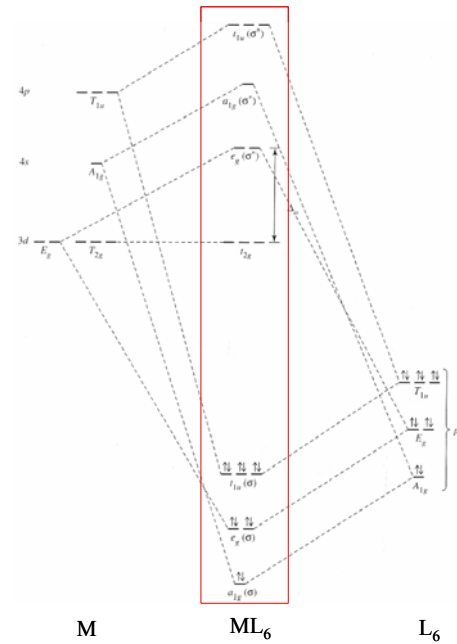
$$\text{Cr}(\text{NH}_3)_4^{3+}(\text{d}^3)$$

$$\text{LFSE} = 0.8\Delta_t = 0.8 \times 9,573 \text{ cm}^{-1} = 7,658 \text{ cm}^{-1}$$

(g) (f)의 결과로 보아 Cr^{3+} 와 NH_3 가 배위결합 할 때 선호하는 것은 팔면체 $\text{Cr}(\text{NH}_3)_6^{3+}$ 이겠는가 사면체 $\text{Cr}(\text{NH}_3)_4^{3+}$ 이겠는가?
(g) When Cr^{3+} and NH_3 form a coordination complex, will it be an octahedral $\text{Cr}(\text{NH}_3)_6^{3+}$ or a tetrahedral $\text{Cr}(\text{NH}_3)_4^{3+}$? Predict the answer, based on the answer of (f).

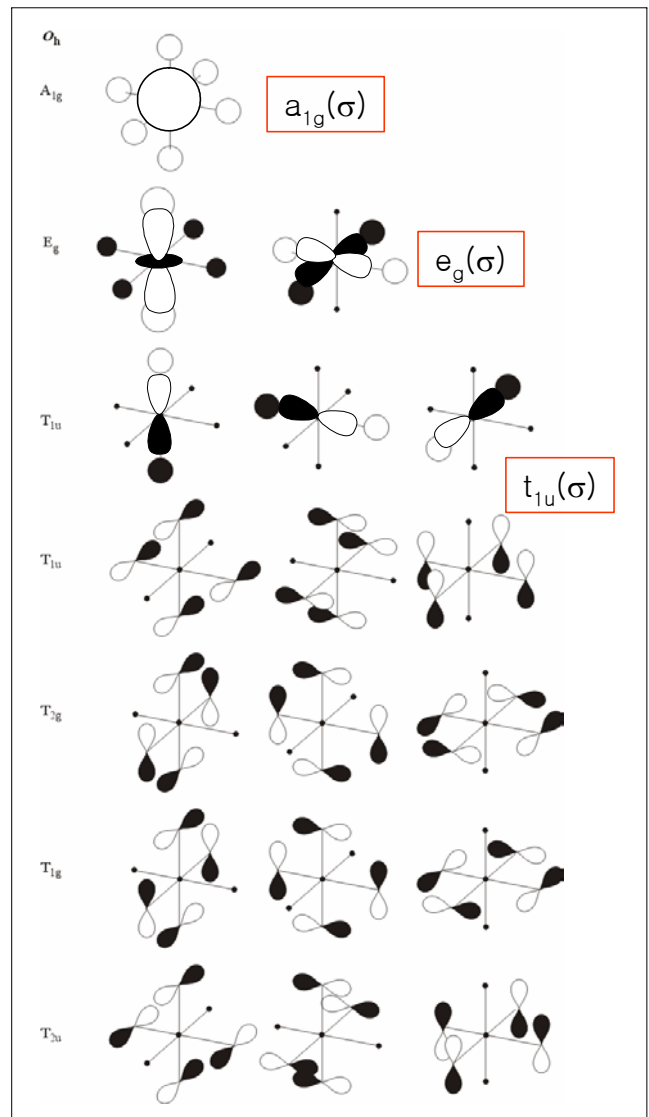
octahedral $\text{Cr}(\text{NH}_3)_6^{3+}$

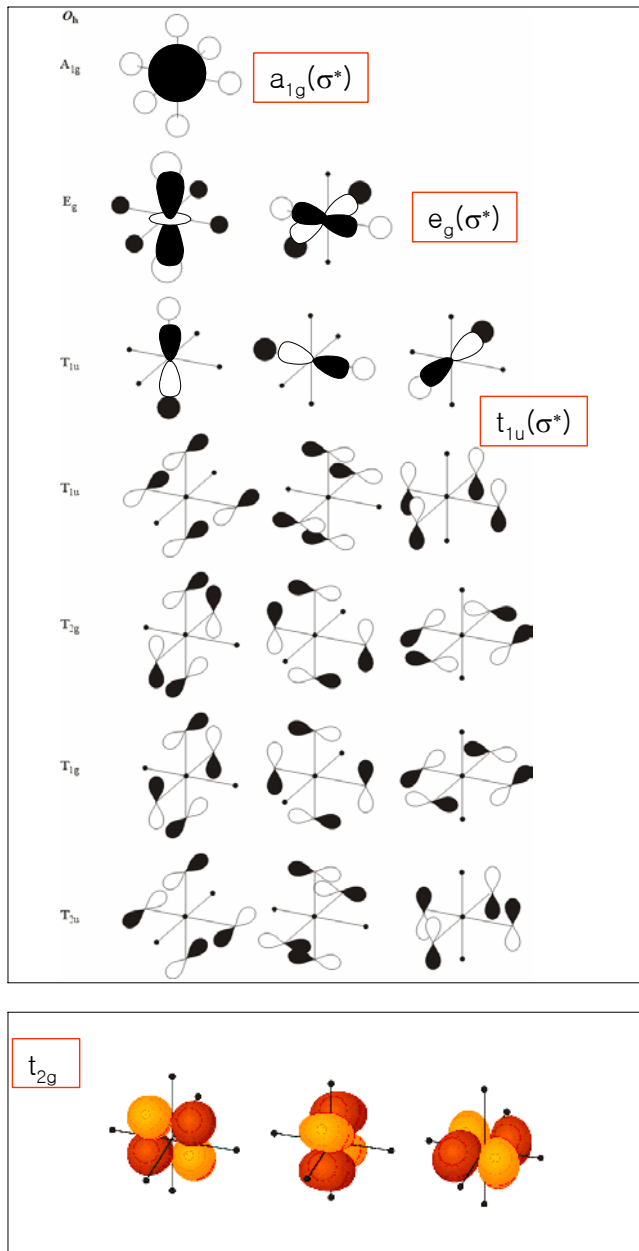
7. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ 와 같이 octahedral 구조를 가지는 착물의 MO의 에너지 준위 그림은 다음과 같다.
7. Following is the energy level diagram of MOs of an octahedral complex like $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.



다음에 주어진 symmetry adapted orbital 그림 위에 모든 MO들의 그림을 그려라. 만일 non-bonding orbital이 있다면 빈 네모에 그려라.

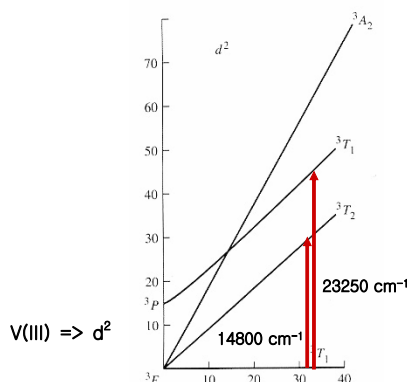
Draw the all MOs on the given symmetry adapted orbitals. If there is(are) non-bonding MO(s), draw the non-bonding orbital(s) in the empty box.)





8. $[\text{VF}_6]^{3-}$ 는 14800 cm^{-1} 와 23250 cm^{-1} 에서 두 개의 흡수선을 갖는다. (세번째 흡수선은 자외선 영역) Fig 1의 여러 Tanabe-Sugano diagram 중에서 해당하는 diagram을 찾아 diagram 위에 두 흡수선이 어느 상태에서 어느 상태로의 전이에 해당하는지 화살표로 표시하여라.

8. $[\text{VF}_6]^{3-}$ has the electronic absorption bands at 14800 cm^{-1} and 23250 cm^{-1} . (The third absorption band is in ultraviolet range.) Select the appropriate Tanabe-Sugano diagram for $[\text{VF}_6]^{3-}$ in Fig 1 and mark arrows the corresponding transitions to the above two bands on the diagram in Fig 1.



9. Ni^{2+} 착물에 대한 다음의 데이터가 있다. (Fig 1 참조)

9. Following data are obtained from the experiments of Ni^{2+} complexes. (Consult Fig 1.)

착물 (Complexes)	흡수선(Absorption bands) (cm^{-1})		
	A	B	C
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	8,500	15,400	26,000
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	10,750	17,500	28,200
$[\text{Ni}(\text{OS}(\text{CH}_3)_2)_6]^{2+}$	7,728	12,970	24,038
$[\text{Ni}(\text{dma})_6]^{2+}$	7,576	12,738	23,809

(a) 흡수선 A, B, C는 각각 어느 상태에서 어느 상태로의 전이에 해당하는가?

(a) Which transitions do the absorption bands, A, B, and C correspond to, respectively?

	Ground state term symbol $\rightarrow$ Excited state term symbol
A	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$
B	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$
C	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$

(b) 팔면체 Ni^{2+} 착물에 대하여 Δ_o 값은 ground state 와 first excited state 사이의 에너지 차이에 해당한다. 각 착물에 대하여 Δ_o 값이 어떻게 되는지 적어라.

(b) For the octahedral Ni^{2+} complexes, Δ_o corresponds to the energy difference between the ground state and the first excited state. What are the Δ_o of each complex?

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	8,500 cm^{-1}
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	10,750 cm^{-1}
$[\text{Ni}(\text{OS}(\text{CH}_3)_2)_6]^{2+}$	7,728 cm^{-1}
$[\text{Ni}(\text{dma})_6]^{2+}$	7,576 cm^{-1}

(c) (b)의 결과를 바탕으로 위 Ni^{2+} 착물에 있는 리간드들 사이의 spectrochemical series의 순서를 써라.

(c) Based on the answers of (b), write the spectrochemical series of the ligands in the above Ni^{2+} complexes.

$\text{NH}_3 > \text{H}_2\text{O} > \text{OS}(\text{CH}_3)_2 > \text{dma}$

Fig 1. Simplified Tanabe-Sugano diagrams for d^2 - d^8 electron configuration

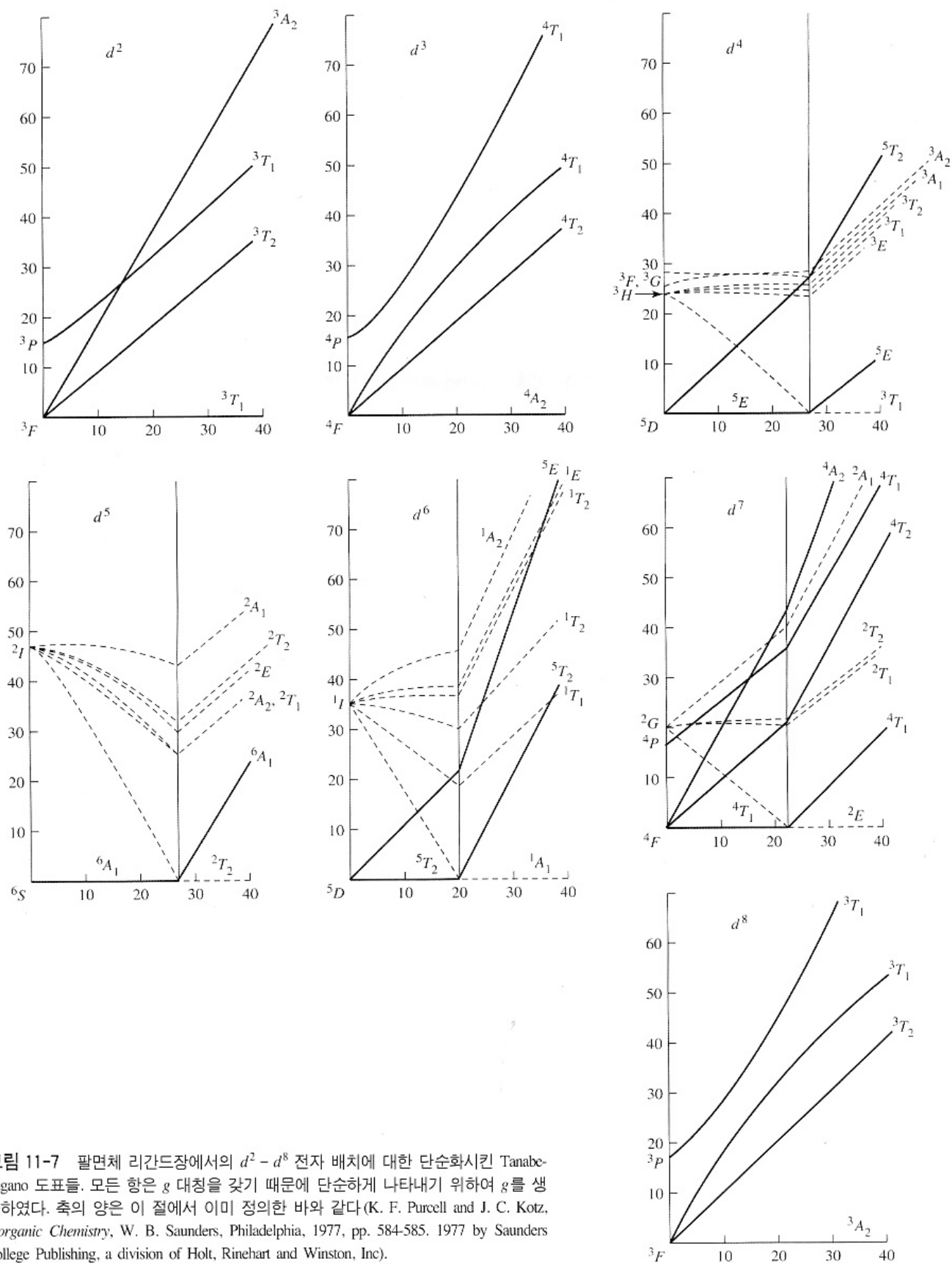
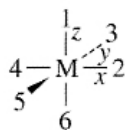


그림 11-7 팔면체 리간드장에서의 $d^2 - d^8$ 전자 배치에 대한 단순화시킨 Tanabe-Sugano 도표들. 모든 항은 g 대칭을 갖기 때문에 단순히 나타내기 위하여 g 를 생략하였다. 축의 양은 이 절에서 이미 정의한 바와 같다(K. F. Purcell and J. C. Kotz, *Inorganic Chemistry*, W. B. Saunders, Philadelphia, 1977, pp. 584-585. 1977 by Saunders College Publishing, a division of Holt, Rinehart and Winston, Inc.).

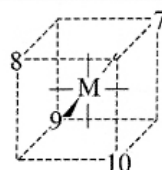
Table 1. Angular Overlap Parameters: Sigma interactions

표 10-11

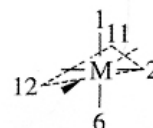
각겹침 변수들: 시그마 상호 작용



정팔면체 위치들



정사면체 위치들



삼각쌍뿔 위치들

금속 d 궤도함수의 시그마 상호 작용
(e_σ 단위로 표시)

배위수 (CN)	모양	위치들
2	선형	1, 6
3	삼각형	2, 11, 12
3	T 모양	1, 3, 5
4	정사면체	7, 8, 9, 10
4	평면사각형	2, 3, 4, 5
5	삼각쌍뿔	1, 2, 6, 11, 12
5	사각 피라미드	1, 2, 3, 4, 5
6	정팔면체	1, 2, 3, 4, 5, 6

리간드 위치	z^2	$x^2 - y^2$	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0
7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0

Table 2. Angular Overlap Parameters

표 10-13

각겹침 변수들

금속	X	$e_\sigma (cm^{-1})$	$e_\pi (cm^{-1})$
정팔면체 MX_6 착화합물들	Cr^{3+}		
	CN^-	7530	-930
	en	7260	
	NH_3	7180	
	H_2O	7550	1850
	F^-	8200	2000
	Cl^-	5700	980
	Br^-	5380	950
Ni^{2+}	I^-	4100	670
	en	4000	
	NH_3	3600	