



Symmetry & Bonding

Answers to the Questions 22(optional), 23-24



Ex.22

考虑一个八面体过渡金属配合物，关注其金属基非键 $1t_{2g}$ 和反键 $2e_g$ 分子轨道，金属提供的d电子将填充在这些分子轨道组中。

- (a) 针对0到10个d电子的情况，制作表格显示 $1t_{2g}$ 和 $2e_g$ 分子轨道的电子排布情况，并采用常规符号（即“↑”和“↓”）标注电子自旋方向。当存在两种可能排布时，需分别列出低自旋与高自旋的排布方式。
- (b) 设 $1t_{2g}$ MO的能量为0， $2e_g$ MO的能量为 Δ_0 ，假设每对平行自旋会使能量降低K值。请在原有表格中增加使用这些参数计算出的各构型能量。
- (c) 假设 $K = 1$ & $\Delta_0 = 1/2$ (任意单位)，画图表示电子排布能量随d电子数变化的关系，必要处需同时绘制高、低自旋排布的数据点。
- (d) 现假设 $K = 1$ & $\Delta_0 = 4$ (任意单位)，重新计算各电子排布能量，重新画图。
- (e) 根据上述图形对高低自旋态的倾向性进行评述。



Ex.22



(a-d) 考虑一个八面体过渡金属配合物，关注其金属基非键 t_{2g} 和反键 e_g 分子轨道，金属提供的d电子将填充在这些分子轨道组中。

	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
HS										
$2e_g$				↑	↑↑	↑↑↑	↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑↑	↑↑↑↑↑↑↑
$1t_{2g}$	↑	↑↑	↑↑↑	↑↑↑↑	↑↑↑↑↑	↑↓↑↑↑	↑↓↑↓↑	↑↓↑↓↑↑	↑↓↑↓↑↑↑	↑↓↑↓↑↑↑↑
E	0	$-K$	$-3K$	$-6K + \Delta_o$	$-10K + 2\Delta_o$	$-10K + 2\Delta_o$	$-11K + 2\Delta_o$	$-13K + 2\Delta_o$	$-16K + 3\Delta_o$	$-20K + 4\Delta_o$
$K=1, \Delta_o = 1/2$	0	-1	-3	-5.5	-9	-9	-10	-12	-14.5	-18
$K=1, \Delta_o = 4$	0	-1	-3	-2	-2	-2	-3	-5	-4	-4
LS										
$2e_g$							↑			
$1t_{2g}$				↑↓↑↑	↑↓↑↓↑	↑↓↑↓↑↓	↑↓↑↓↑↓			
E	-	-	-	$-3K$	$-4K$	$-6K$	$-9K + \Delta_o$	-	-	-
$K=1, \Delta_o = 1/2$				-3	-4	-6	-8.5			
$K=1, \Delta_o = 4$				-3	-4	-6	-5			



ex23



- (a) Using the spin-only formula, draw up a table giving the value of μ_{eff} for an octahedral complex with 4, 5, 6 and 7 d electrons in both the low- and high-spin configurations. Express your results as decimals.

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$

		d^4	d^5	d^6	d^7
HS	n	4	5	4	3
	$\mu_{\text{eff}}/\text{BM}$	4.90	5.92	4.90	3.87
LS	n	2	1	0	1
	$\mu_{\text{eff}}/\text{BM}$	2.83	1.41	0.00	1.41



ex23



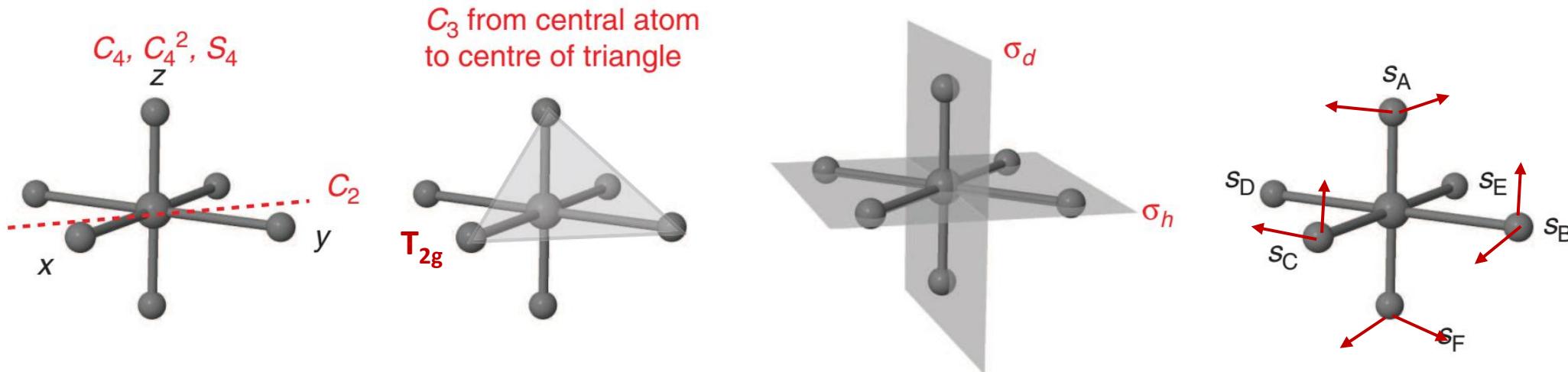
- (b) Use the following experimentally measured values of μ_{eff} to determine whether the given octahedral complex is high or low spin. (Be aware that the spin-only formula is not expected to give precise agreement with experimental data; in the complex $[\text{Co}(\text{NO}_2)_6]^{4-}$ the ligands are $[\text{NO}_2]^-$).

complex	$\mu_{\text{eff}} / \text{B.M.}$	complex	$\mu_{\text{eff}} / \text{B.M.}$
$[\text{Co}(\text{NO}_2)_6]^{4-}$	1.9	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	3.8
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	4.8	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	5.9
$[\text{Fe}(\text{CN})_6]^{3-}$	2.3	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	5.3

- b i) $[\text{Co}(\text{NO}_2)_6]^{4-}$: Co^{2+} d⁷ & n = 1 ($\mu_{\text{eff}} = 1.9$) \rightarrow LS
- ii) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$: Cr^{2+} d⁴ & n = 4 ($\mu_{\text{eff}} = 4.8$) \rightarrow HS
- iii) $[\text{Fe}(\text{CN})_6]^{3-}$: Fe^{3+} d⁵ & n = 1 ($\mu_{\text{eff}} = 2.3$) \rightarrow LS
- iv) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$: Cr^{3+} d³ & n = 3 ($\mu_{\text{eff}} = 3.8$) \rightarrow no HS/LS issue
- v) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$: Mn^{2+} d⁵ & n = 5 ($\mu_{\text{eff}} = 5.8$) \rightarrow HS
- vi) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: Fe^{2+} d⁶ & n = 4 ($\mu_{\text{eff}} = 5.3$) \rightarrow HS



S&B Ex. 24(a) Considering an octahedral complex in which each ligand is a single anion, such as Cl^- . Suppose that each ligand also contributes two p orbitals arranged at right angles to the M–L bond. Find the representation generated by these **12** orbitals and show it reduces to $\text{T}_{1g} \oplus \text{T}_{2g} \oplus \text{T}_{1u} \oplus \text{T}_{2u}$



Use local axis system for each ligand! 每个配体有两个垂直键轴的p轨道

O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$	
Γ	12	0	-4	0	0	0	0	0	0	0	(xz, xy, yz)

这些配体p轨道组成的 T_{2g} SOs



S&B Ex. 24(a) Considering an octahedral complex in which each ligand is a single anion, such as Cl^- . Suppose that each ligand also contributes two p orbitals arranged at right angles to the M–L bond. Find the representation

O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
E_g	2	-1	2	0	0	2	-1	2	0	0
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
E_u	2	-1	2	0	0	-2	1	-2	0	0
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1

$$\Gamma \quad 12 \quad 0 \quad -4 \quad 0 \quad = T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$$

-2-2 4-4



Ex. 24(b) With the aid of a suitable diagram explain why the presence of low-lying (in energy terms) filled π -type orbitals on the ligands generally results in a decrease in Δ_o .

(c) Similarly explain why the presence of higher-lying empty π -type orbitals generally results in an increase in Δ_o . What kind of ligand has such orbitals?

(b) 配体上 π 轨道组合成的 T_{2g} SOs 可与金属基的 T_{2g} SOs (即金属 d_{xy}, d_{xz}, d_{yz}) 组合成 $1t_{2g}$ 成键和 $2t_{2g}$ 反键分子轨道(如下左图)。当配体 π 轨道为占据轨道时, 金属基 t_{2g} 轨道为反键轨道, 能量升高, 与 $2e_g$ 间的能差缩小, 即配位场分裂能 Δ_o 降低 (如下右图) ;

(c) 当配体 π 轨道为空轨道时, 金属基 t_{2g} 轨道为成键轨道, 能量降低, 与 $2e_g$ 间的能差增大, 即配位场分裂能 Δ_o (如下右图) 增大.

