

一、常见配体、EAN规则计算

1. 卤原子(离子)、OH⁻及含氧酸根

常提供一对电子进行配位,也可做桥联接配体

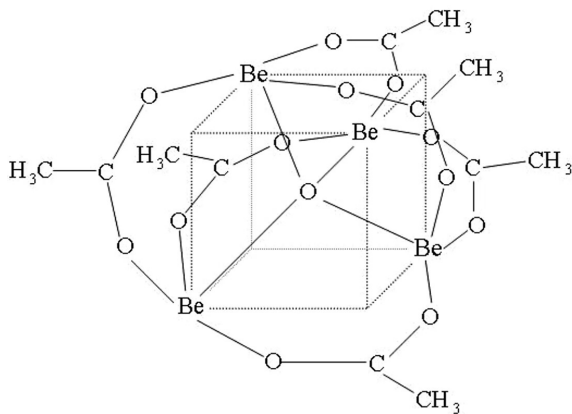
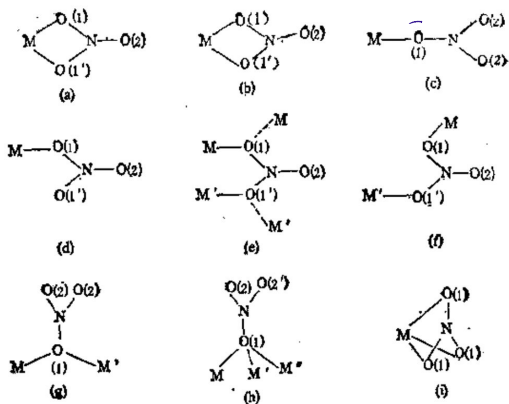
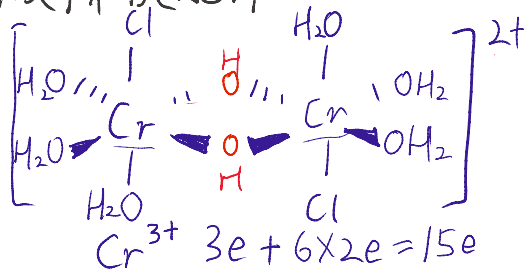
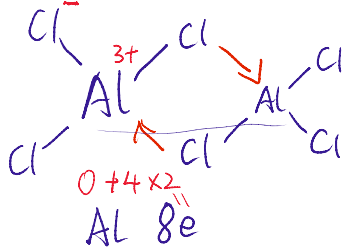
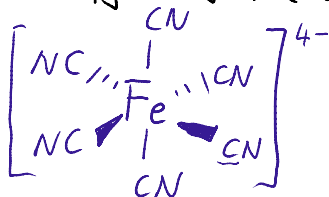


图 12.35 硝酸根和金属离子 (M) 的几种可能的配位方式

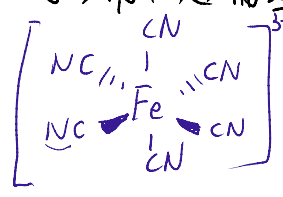
(a) 双齿, 对称 (C_{2v}) (b) 双齿, 不对称 (C_2) (c) 单齿 (C_{3v})
 (d) 单齿 (C_3) (e) 双齿, 桥式 (C_{2v}) (f) 双齿, 桥式 (C_2)
 (g) 单齿, 桥式 (C_{2v}) (h) 单齿, 桥式 (C_2) (i) 叁齿 (C_{3v})

2. 碳、氮及拟卤离子配体 (CN^- , SCN^- , N_3^- , CO , NH_3 等)

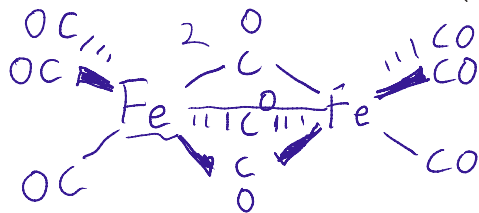
只有一对孤对电子, 常做端基配体 (例外: CO 可做桥联接配体)



$\text{Fe}^{2+} 6e + \text{CN}^- 2e \times 6 = 18e$

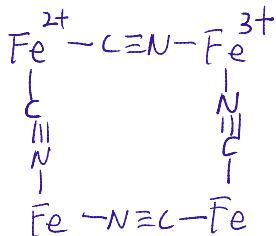


$\text{Fe}^{3+} 5e + \text{CN}^- 2e \times 6 = 17e$

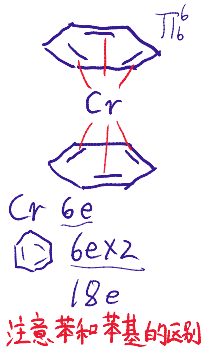
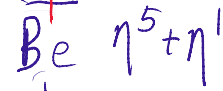
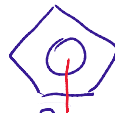


$\text{Fe } 8e + 3 \times 2e + 3 \times 1e = 17e$

若要满足EAN规则, 则有一根 Fe-Fe 键



3、多电子配体 $C_5H_5^-$ 、 C_6H_6 等



$Fe^{2+} \quad 8-2=6e$

$C_5H_5^- \quad 6e \times 2$
18e
or

Fe: 8e

$C_5H_5 \quad 5e \times 2$

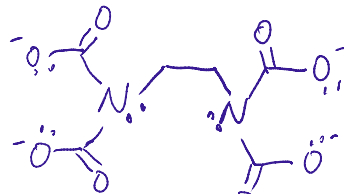
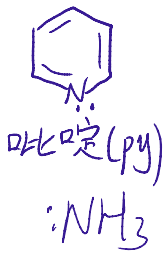
$Be^{2+} \quad 0e$

$C_5H_5^- \quad 6e \times 2$
~~12e?~~

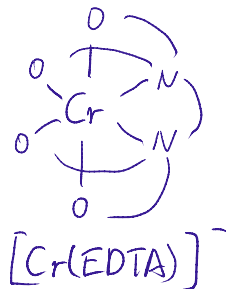
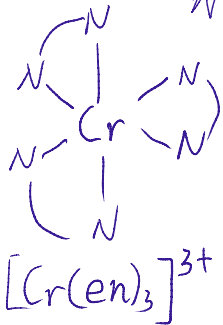
第二周期元素, 只能容纳8个电子

(习惯上将环戊二烯基看作中性5e配体, 有 η^1 、 η^3 、 η^5 三种配位方式)

4、有机配体(胺、羧酸等)



乙二胺四乙酸根(EDTA)



二、立体异构

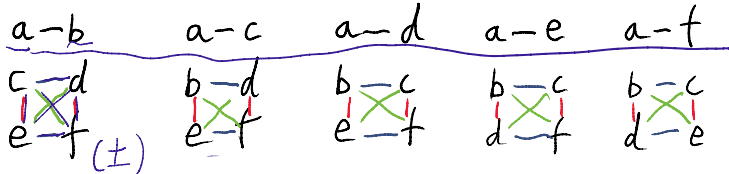
以六配位正八面体配合物为例

对配合物 $Mabcdef$, 如何准确无误画出所有立体异构体?

第一步: 将配体两两分组, 同组配体处于对位

有以下分组方式:

$5 \times 3 = 15$ 种

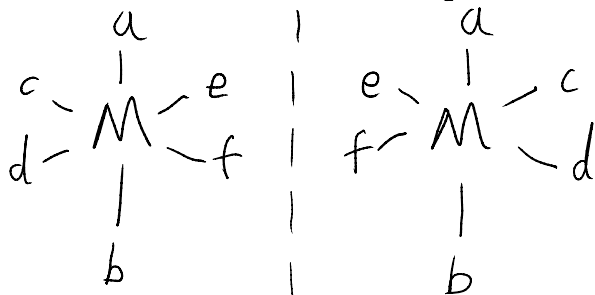


第二步: 含 a 的一组配体位于竖直方向, 另外四个位于水平方向

将所有配体画出

以 a-b c-f d-e 组合为例

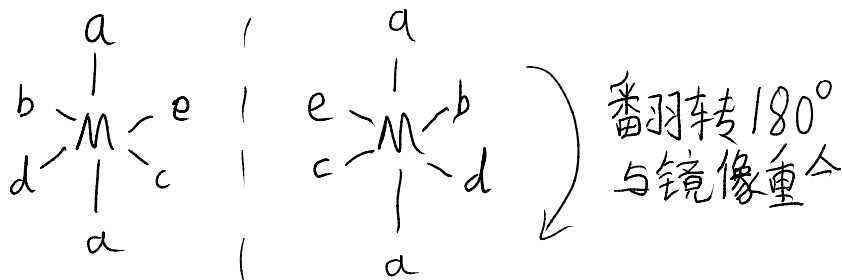
有且仅有 2 种结构



互为对映体 (无对称面)

若有相同配体位于对位, 则该配合物有镜面, 无对映体

如:



Formula	Total number	Pairs of enantiomers	Formula	Total number	Pairs of enantiomers
Ma_3d_3	2	0	$\text{M}(\widehat{\text{AA}})(\widehat{\text{BC}})\text{ef}$	10	5
Ma_3def	5	1	$\text{M}(\widehat{\text{AB}})_2\text{ef}$	11	5
<u>Ma_2cdef</u>	<u>15</u>	6	$\text{M}(\widehat{\text{AB}})(\widehat{\text{CD}})\text{ef}$	20	10
Mabcedf	30	15	$\text{M}(\widehat{\text{AB}})_3$	4	2
$\text{Ma}_2\text{c}_2\text{e}_2$	6	1	$\text{M}(\widehat{\text{ABA}})\text{def}$	9	3
$\text{Ma}_2\text{c}_2\text{ef}$	8	2	$\text{M}(\widehat{\text{ABC}})_2$	11	5
$\text{Ma}_3\text{d}_2\text{f}$	3	0	$\text{M}(\widehat{\text{ABBA}})\text{ef}$	7	3
			$\text{M}(\widehat{\text{ABCBA}})\text{f}$	7	3

三、价键理论

强场配体和弱场配体

配位性强, 把电子“往里挤”

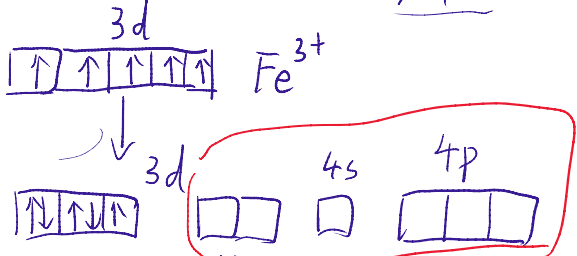
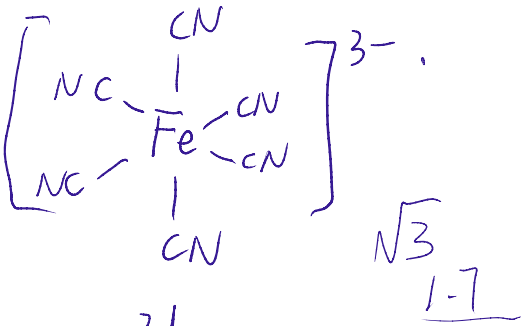
电子易成对, 低自旋, 内轨型

轨道易分裂

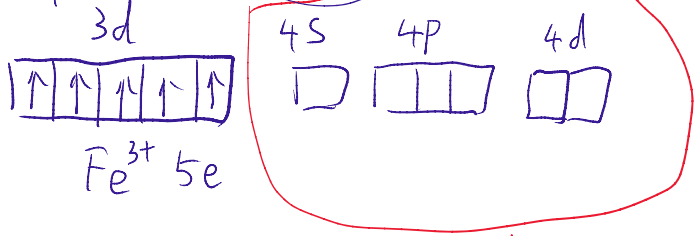
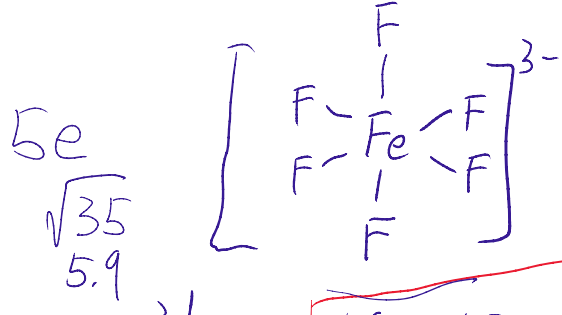
电负性大, 把电子“往外拉”

电子易成单, 外轨型

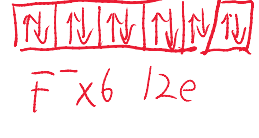
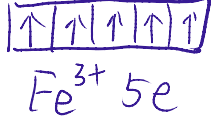
轨道不易分裂



$d^2 \quad \downarrow d^2 sp^3 \quad (n-1)dns \quad np$



$\downarrow sp^3 d^2 \quad nsnpnd$

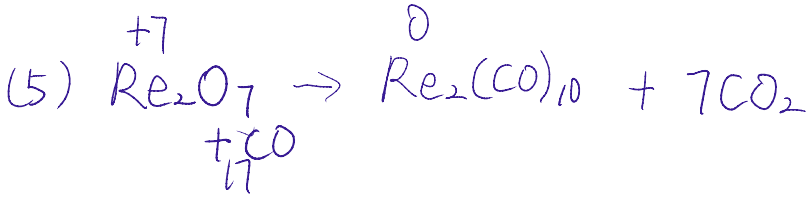
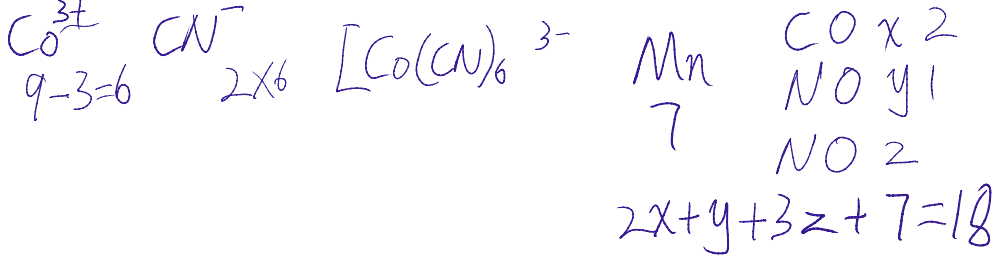
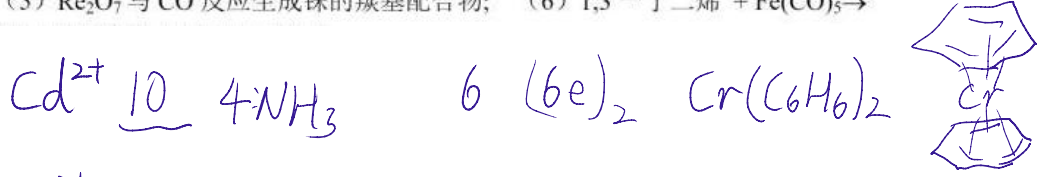


3. 在下列各配离子中，哪些符合 EAN 规则，哪些不符合 EAN 规则？

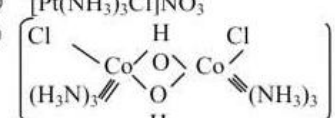
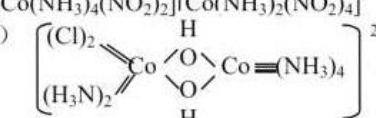
- | | |
|---|---|
| (1) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$ | (2) $[\text{HgCl}_4]^{2-}$ |
| (3) $[\text{Fe}(\text{CN})_6]^{4-}$ | (4) $[\text{Cu}(\text{CN})_2]^-$ |
| (5) $\text{Mn}(\text{CO})_6$ | (6) $\text{Fe}(\text{CO})_4\text{Cl}_2$ |
| (7) $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_4$ | (8) $\text{Cr}(\text{CO})_5$ |

4. 用 EAN 规则预言下列各分子或离子所形成的分子式、离子式或者化学反应方程式：

- | | | |
|--|--|---------------------------|
| (1) Cd^{2+} 的氨配合物； | (2) Cr^0 与苯； | \rightarrow 可提供 1e 或 3e |
| (3) Co^{3+} 与 CN^- ； | (4) Mn 与 CO 、 NO 形成配合物； | |
| (5) Re_2O_7 与 CO 反应生成铼的羰基配合物； | (6) 1,3-丁二烯 + $\text{Fe}(\text{CO})_5 \rightarrow$ | |

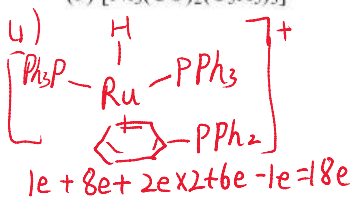


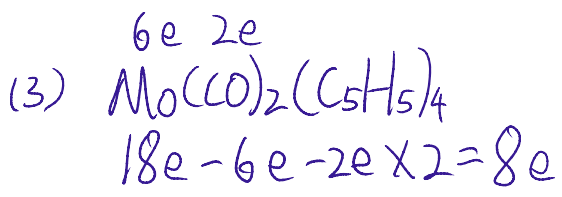
8. 指出下列配合物中，哪些互为异构体，并写出各类异构体的名称及其特点。

- | | |
|---|---|
| (1) $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ | (2) $[\text{Co}(\text{NH}_3)_3\text{Co}(\text{NO}_2)_3]$ |
| (3) $[\text{Pt}(\text{NH}_3)_3(\text{ONO}_2)]\text{Cl}$ | (4) $[\text{PtCl}_4(\text{en})] \cdot 2\text{py}$ |
| (5) $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$ | (6) $[\text{PtCl}_2(\text{en})(\text{py})_2]\text{Cl}_2$ |
| (7) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$ | (8) $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ |
| (9)  | (10)  |

9. 用 EAN 规则画出下列各分子的结构式

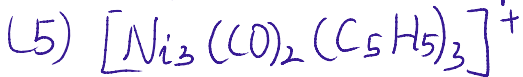
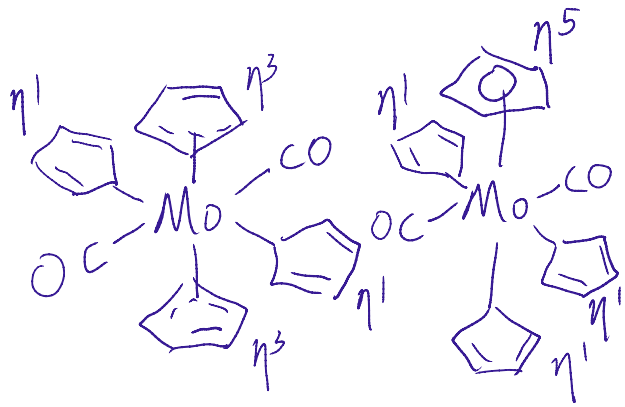
- | | |
|--|---|
| (1) $[\text{HRu}(\text{PPh}_3)_3]$ <small>带正电少 1e</small> | (2) $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$ |
| (3) $\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)_4$ | (4) $\text{H}_4\text{Co}_4(\text{C}_5\text{H}_5)_4$ |
| (5) $[\text{Ni}_3(\text{CO})_2(\text{C}_5\text{H}_5)_3]^+$ | (6) $\text{Re}(\text{CH}_3)_2(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_5\text{CH}_3)$ |





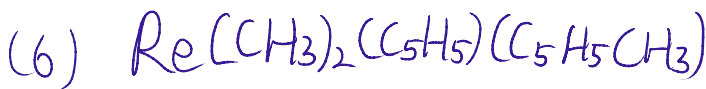
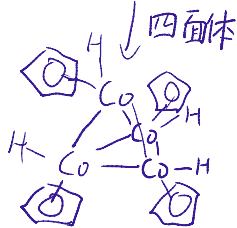
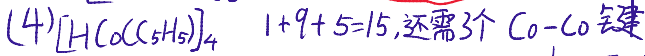
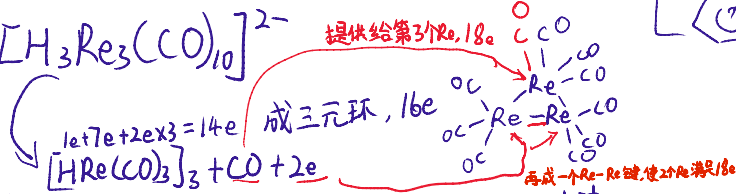
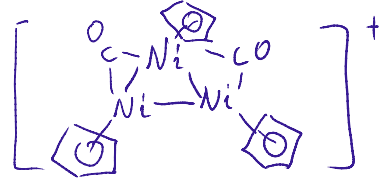
4个 C_5H_5 提供 8e
 C_5H_5 可作 η^1, η^3, η^5 配体
 $8 = 5 + 3 \times 1 = 3 \times 2 + 1 \times 1$

通常尽可能多以 η^5 配位



$10e \times 3 + 2e \times 2 + 5e \times 3 - 1e = 48e$

满足 EAN 需 $18e \times 3 = 54e$, 差 6e, 需 3 个 Ni-Ni 键



$7 + 1 \times 2 + 5 + 4 = 18$

