9.配位化学与络合滴定Coordination Chemistry and Complexation Titration

- 矿物质Minerals
  - 大多数金属，包括过渡金属，都存在于被称为矿物的固体无机化合物中Most metals, including transition metals, are found in solid inorganic compounds known as minerals.
  - 矿物是用俗称命名的，而不是化学名称Minerals are named by common, not chemical names.
  - 大多数过渡金属在矿物中的氧化态为+1到+4 Most transition metals range from +1 to +4 oxidation state in minerals.
  -

    Table 23.1 Principal Mineral Sources of Some Transition Metals

Metal	Mineral	Mineral Composition
Chromium	Chromite	$FeCr_2O_4$
Cobalt	Cobaltite	CoAsS
Copper	Chalcocite	Cu_2S
	Chalcopyrite	$CuFeS_2$
	Malachite	$Cu_2CO_3(OH)_2$
Iron	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
Manganese	Pyrolusite	MnO_2
Mercury	Cinnabar	HgS
Molybdenum	Molybdenite	MoS_2
Titanium	Rutile	TiO_2
	Ilmenite	$FeTiO_3$
Zinc	Sphalerite	ZnS

- 冶金Metallurgy
  - 从自然资源中提取金属并使其用于实际用途的科学和技术The science and technology of extracting metals from their natural sources and preparing them for practical use.
  - 步骤Steps
    - 1)采矿Mining
    - 2)精矿Concentrating the ore
    - 3)将矿石还原为游离金属Reducing the ore to free metal
    - 4)净化金属Purifying the metal
    - 5)将其与其他元素混合以改变其性能(制成合金-固体混合物)Mixing it with other elements to modify its properties (making an alloy—a solid mixture)
- 过渡金属Transition Metals
  - 第一行过渡金属的性质Properties of the First Row Transition Metals
    - 第一行过渡金属指第四周期“First row” means period 4
    - 周期5和周期6具有相似的趋势特性Periods 5 and 6 have similar trendsin properties
    - 一些基本性质

Table 23.2 Properties of the Period 4 Transition Metals

Group	3B	4B	5B	6B	7B		8B		1B	2B
Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ground state electron configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
First ionization energy (kJ/mol)	631	658	650	653	717	759	758	737	745	906
Metallic radius (Å)	1.64	1.47	1.35	1.29	1.37	1.26	1.25	1.25	1.28	1.37
Density (g/cm³)	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420
Crystal structure*	hcp	hcp	bcc	bcc	**	bcc	hcp	fcc	fcc	hcp

*Abbreviations for crystal structures are hcp = hexagonal close packed, fcc = face centered cubic, bcc = body centered cubic.
晶体结构的缩写是hcp=六边形紧密排列，fcc=面心立方，bcc =体心立方

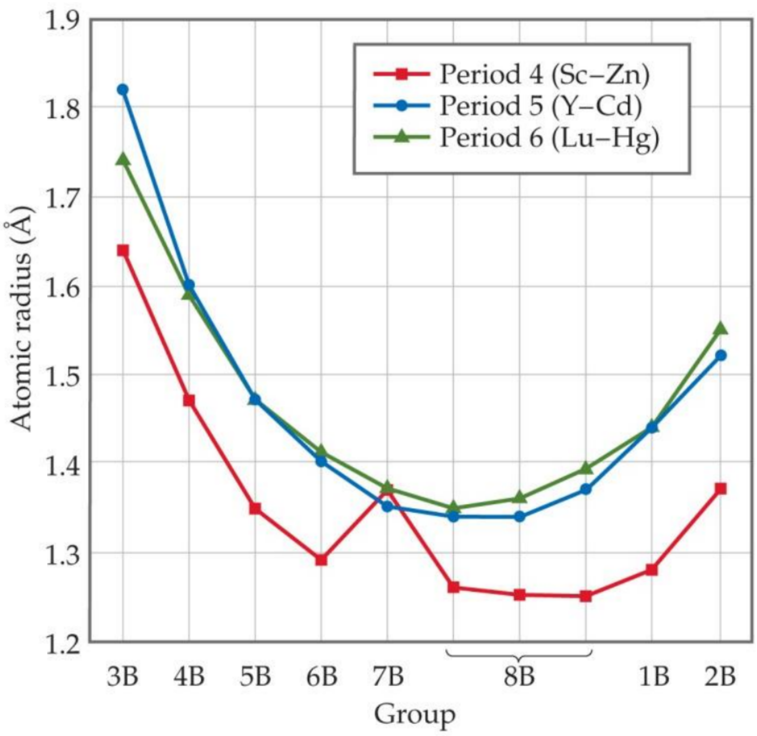
**Manganese has a more complex crystal structure.
锰的晶体结构更为复杂

- 轨道

Orbital Occupancy of the Period 4 Transition Metals

Element	Partial Orbital Diagram: 4s	3d	4p	Unpaired Electrons
Sc	[↑↓]	[↑][ ][ ][ ][ ]	[ ][ ][ ]	1
Ti	[↑↓]	[↑][↑][ ][ ][ ]	[ ][ ][ ]	2
V	[↑↓]	[↑][↑][↑][ ][ ]	[ ][ ][ ]	3
Cr	[↑]	[↑][↑][↑][↑][↑]	[ ][ ][ ]	6
Mn	[↑↓]	[↑][↑][↑][↑][↑]	[ ][ ][ ]	5
Fe	[↑↓]	[↑↓][↑][↑][↑][↑]	[ ][ ][ ]	4
Co	[↑↓]	[↑↓][↑↓][↑][↑][↑]	[ ][ ][ ]	3
Ni	[↑↓]	[↑↓][↑↓][↑↓][↑][↑]	[ ][ ][ ]	2
Cu	[↑]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[ ][ ][ ]	1
Zn	[↑↓]	[↑↓][↑↓][↑↓][↑↓][↑↓]	[ ][ ][ ]	0

- 原子半径Atomic Radius
  - 从左到右，过渡金属的半径先减小后增大As one goes from left to right, a decrease, then an increase, is seen in the radius of transition metals.
  - 一方面，增加有效核电荷会使原子变小On the one hand, increasing effective nuclear charge tends to make atoms smaller.
  - 另一方面，最强的(因此也是最短的)金属键位于过渡金属的中心On the other hand, the strongest (and, therefore, shortest) metallic bonds are found in the center of the transition metals.
  - 第5和第6周期的大小大致相同，这是由于镧系收缩——即4f电子对有效核电荷的影响Periods 5 and 6 are about the same size due to the **lanthanide contraction**—the effect of 4f electrons on effective nuclear charge.



- 过渡金属特性Transition Metal Characteristics
  - 部分占用的d层导致可能的性质Partially occupied d sublevels lead to the possibility of
    - 1)多重氧化态multiple oxidation states
    - 2)化合物的颜色colored compounds
    - 3)磁性特性magnetic properties
- 氧化态Oxidation States
  - 对于周期4的过渡元素For the period 4 transition elements
  - 当阳离子形成时，它们首先失去4s上的电子;所有(Sc除外)形成+2阳离子(具有+2氧化态)when cations are formed, they lose the 4s electrons first; all (except Sc) form a +2 cation(have a +2 oxidation state)
  - 从Sc到Mn，最大氧化态是4s和3d电子之和from Sc to Mn, the maximum oxidation state is the sum of 4s and 3d electrons
  - Mn后，最大氧化数逐渐减小，直至Zn，仅为+2 after Mn, the maximum oxidation number decreases, until Zn, which is ONLY +2
- 配合物Complexes
  - 通常，过渡金属可以有分子或离子与它们结合，称为配体Commonly, transition metals can have molecules or ions that bond to them, called ligands.
  - 这就产生了络合离子或配位化合物，在过渡金属配合物中可以观察到许多颜色These give rise to complex ions or coordination compounds. Many colors are observed in transition metal complexes.
  - 配体充当路易斯碱，提供一对电子形成配金属键Ligands act as Lewis bases, donating a pair of electrons to form the ligand–metal bond.
  - 常见的配体common ligands

- 配位化合物Coordination Compounds
  - 配位化合物通常由一个络(配)离子和一个反荷离子组成A coordination compound typically consists of a complex ion and a counter ion.
  - 络合离子包含一个与一个或多个分子或离子结合的中心金属阳离子A complex ion contains a central metal cation bonded to one or more molecules or ions.
  - 在络合离子中围绕金属的分子或离子称为配体The molecules or ions that surround the metal in a complex ion are called ligands.
  - 配体至少有一对未共用的价电子A ligand has at least one unshared pair of valence electrons.
- 阿尔弗雷德·维尔纳的过渡金属配合物理论Alfred Werner's Theory on Transition Metal Complexes
  - 存在许多由CoCl3和NH3结合而成的化合物，Alfred Werner在1893年解释了它们的性质Many compounds exist combining CoCl3 and NH3.Their nature was explained by Alfred Werner in 1893.
  - 每种化合物中金属的氧化值都是+3，然而，与金属结合的原子数是不同的。他称之为配位数The oxidation number of a metal is +3 in each compound. However, the number of atoms bonded to the metal is different. He called this the coordination number.
  - 解决这个问题的关键是溶液中每个配方单位产生的离子数量:除了一个阳离子，其余的将告诉有多少cl离子没有直接连接到金属The key to solving this problem is the number of ions produced in solution per formula unit: along with ONE cation, the rest would tell how many Cl– ions are NOT connected directly to the metal.
  - AgCl的沉淀确定了游离Cl -的数量Precipitation of AgCl confirmed amount of free Cl–.
  - 写公式:括号表示复数;反荷离子写在后面Writing the formula: the brackets show the complex; counterions are written after.

Table 23.3 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\,NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\,NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\,NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\,NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

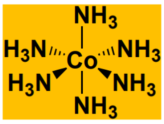
  - 配位配合物的结构:Co3+的氨配合物 Structures of Coordination Complexes: The ammonia complexes of Co3+

Composition	Ions released	Color
$CoCl_3 \cdot 6NH_3$	3 “free” Cl^- ions	Orange-Yellow
$CoCl_3 \cdot 5NH_3$	2 “free” Cl^- ions	Purple
$CoCl_3 \cdot 4NH_3$	1 “free” Cl^- ions	Green or Violet
$CoCl_3 \cdot 3NH_3$	0 “free” Cl^- ions	Green

In all of these complexes there is no free NH_3
(No reaction with acid)

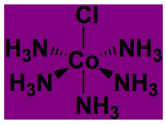
- 配合物的三维结构Coordination complexes’ three dimensional structures

$CoCl_3 \cdot 6NH_3$



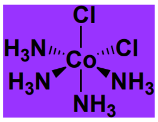
Cl^- Cl^- Cl^-

$CoCl_3 \cdot 5NH_3$

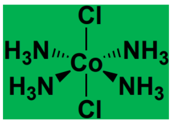


Cl^- Cl^-

$CoCl_3 \cdot 4NH_3$

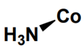


Cl^-



Cl^-

Isomers!

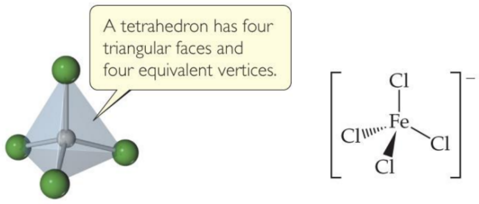


Bond toward you

Bond away from you

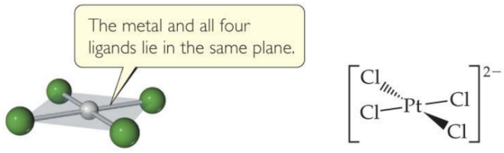
- 配位键The Metal–Ligand Bond
  - 金属和配体之间的反应是路易斯酸(金属)和路易斯碱(配体)之间的反应The reaction between a metal and a ligand is are action between a Lewis acid (the metal) and a Lewis base (the ligand).
  - 新的配合物具有独特的物理和化学性质(例如，颜色、还原电位)The new complex has distinct physical and chemical properties (e.g., color, reduction potential)
- 配位数Coordination Numbers
  - 金属的配位数取决于金属的大小和配体的大小The coordination number of a metal depends upon the size of the metal and the size of the ligands.
  - 铁(III)可以与6个氟化物结合，但只能与4个氯化物(更大)结合Iron(III) can bind to 6 fluorides but only 4 chlorides (larger).
  - 最常见的配位数是4和6。它们对应于常见的几何形状:四面体或正方形平面;八面体The most common coordination numbers are4 and 6. They correspond to common geometries: tetrahedral or square planar; octahedral.

四面体有四个三角形
面和四个相等的顶点



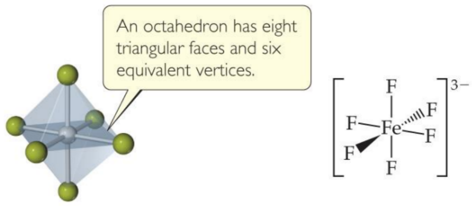
Tetrahedral geometry
四面体

金属和所有四个配
体在同一平面上

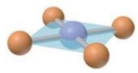
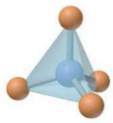
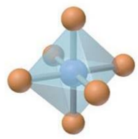


Square planar geometry
正方形平面

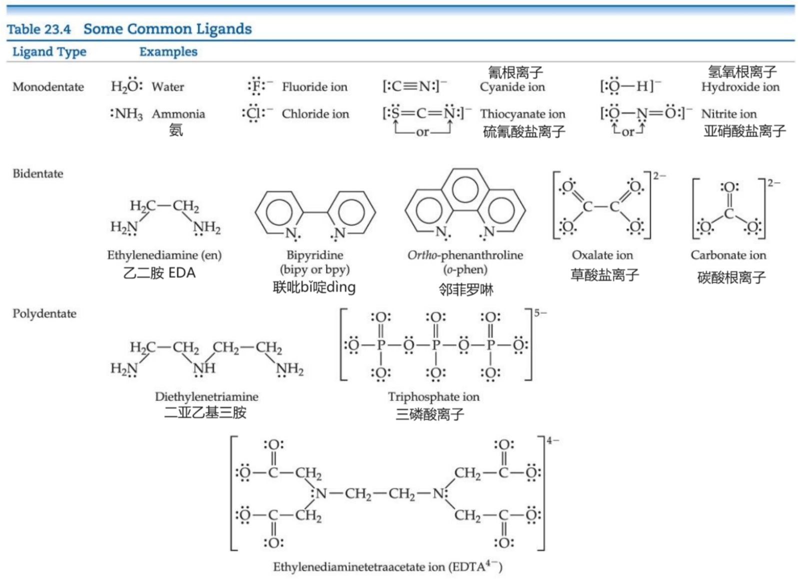
一个八面体有八
个三角形面和六
个相等的顶点



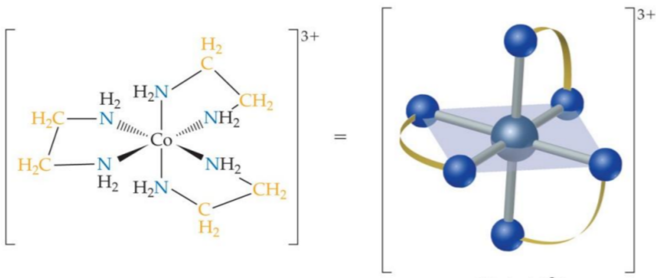
Octahedral geometry
八面体

Coordination Number	Shape		Examples
2	Linear		$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square planar		$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4	Tetrahedral		$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6	Octahedral		$[Ti(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cr(NH_3)_4Cl_2]^+$, $[Mn(H_2O)_6]^{2+}$, $[FeCl_6]^{3-}$, $[Co(en)_3]^{3+}$

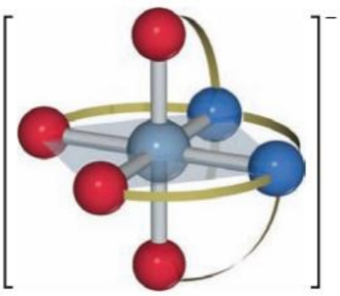
- 常见的配体Common Ligands
  - 所示的表格包含了一些在配合物中常见的配体The table shown contains some ligands commonly found in complexes.
  - 单齿配体与金属上的一个位点相协调，双齿配体与两个位点相协调Monodentate ligands coordinate to one site on the metal, bidentate to two sites
  -



- 螯合物Chelates
  - 双齿和多齿配体也称为螯合剂Bidentate and polydentate ligands are also called chelating agents.
  - 有许多过渡金属对人类生命至关重要There are many transition metals that are vital to human life.
  - 其中一些与螯合剂结合Several of these are bound to chelating agents.
  -



$[Co(en)_3]^{3+}$

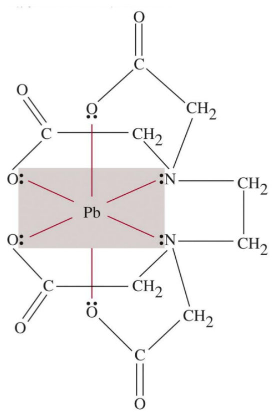


【Co(EDTA)】$^-$

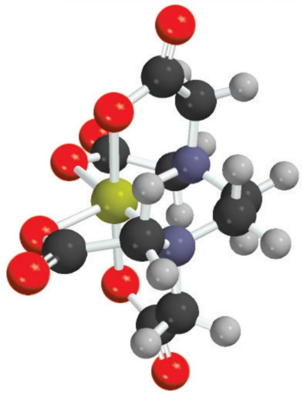
-

多齿的配体

polydentate ligand
(EDTA)



$[PbEDTA]^{2-}$



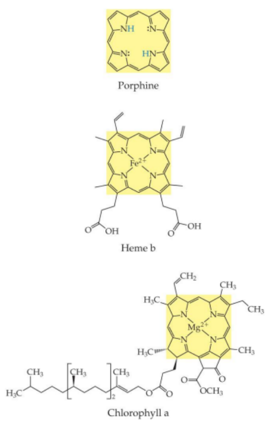
Bidentate and polydentate ligands are called ***chelating agents***

双齿和多齿配体称为螯合剂

-

Chelates in Biological Systems

- The porphine（卟吩）molecule is the basis for many important biological metal chelates, becoming a porphyrin（卟啉）ring.
- The iron in hemoglobin（血红蛋白）carries O_2 and CO_2 through the blood. It contains heme（血红素）units.
- Chlorophylls (叶绿素) also have metals bound to porphine units.

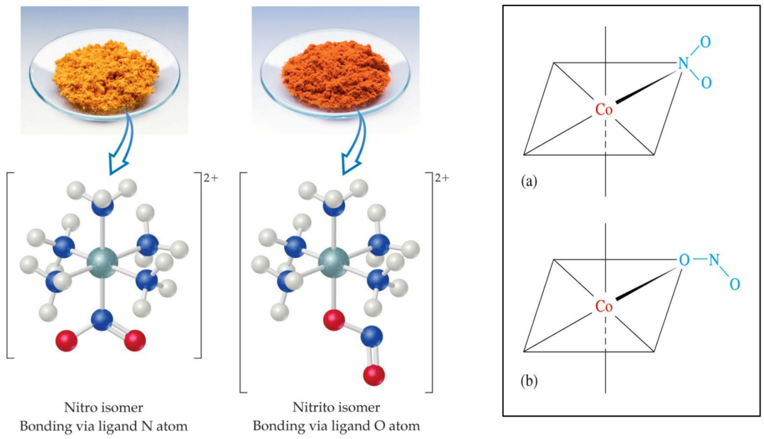


- 同分异构体Isomers
  - 同分异构体分子式相同，但原子排列不同Isomers have the same molecular formula but a different arrangement of atoms.
  - 两种同分异构体
    - 结构异构体structural isomers
      - 分子式相同但原子连接方式不同same molecular formula but different connections of atoms
      - 配位异构Coordination sphere isomers
        - 络合离子的组成多种多样Composition of the complex ion varies
        - 配位异构的不同之处在于与金属结合的配体在配位球之外的配体Coordination sphere isomers differ in what ligands are bound to the metal and which fall outside the coordination sphere
        -

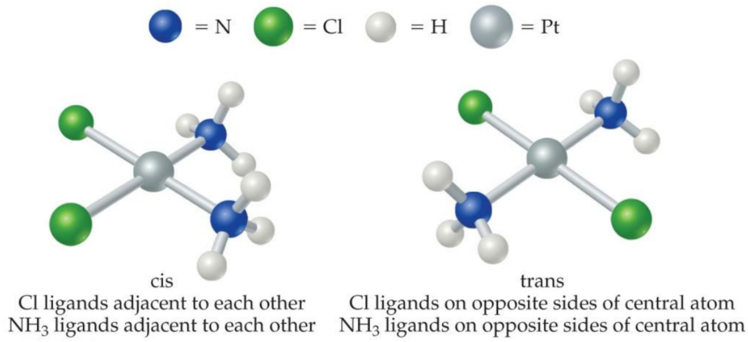
For example, $CrCl_3(H_2O)_6$ exists as $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, or $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$.

$[Cr(NH_3)_5SO_4]Br$ and $[Cr(NH_3)_5Br]SO_4$

- 键连异构Linkage isomers
    - 在链式异构体中，配体通过不同的原子与金属结合In linkage isomers the ligand is bound to the metal by a different atom.
    - 例如，亚硝酸盐可以通过N或O键结合For example, nitrite can bind via the N or via an O

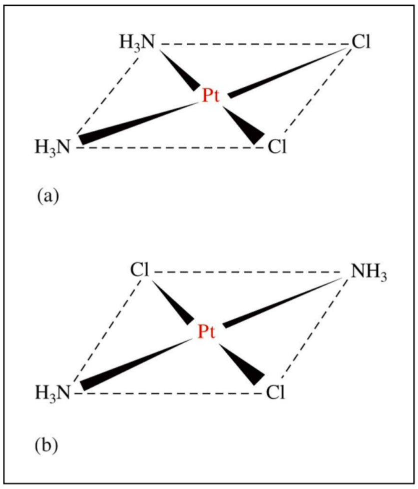


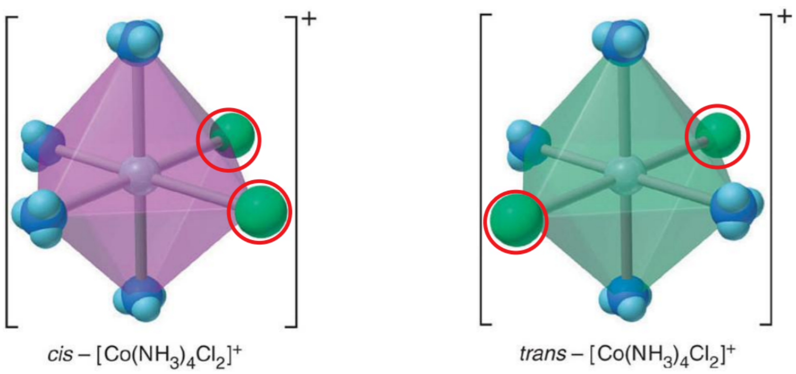
- 立体异构体stereoisomers
    - 相同的原子连接，但不同的三维方向same connections of atoms, but different three-dimensional orientations
    - 几何异构体Geometric isomers
        - 在几何异构体中，原子的排列是不同的，但在络合物上存在相同的键In geometric isomers, the arrangement of the atoms is different, but the same bonds exist on the complex.
        - 例如，氯原子可以相邻(顺式)或相反(反式);存在于方形平面或八面体复合体中，而不是四面体For example, chlorine atoms can be adjacent to each other (cis) or opposite each other (trans); found in square planar or octahedral complexes, not tetrahedral.
        - 它们具有不同的物理性质，并且通常具有不同的化学反应性They have different physical properties and, often, different chemical reactivity
        - 顺反异构



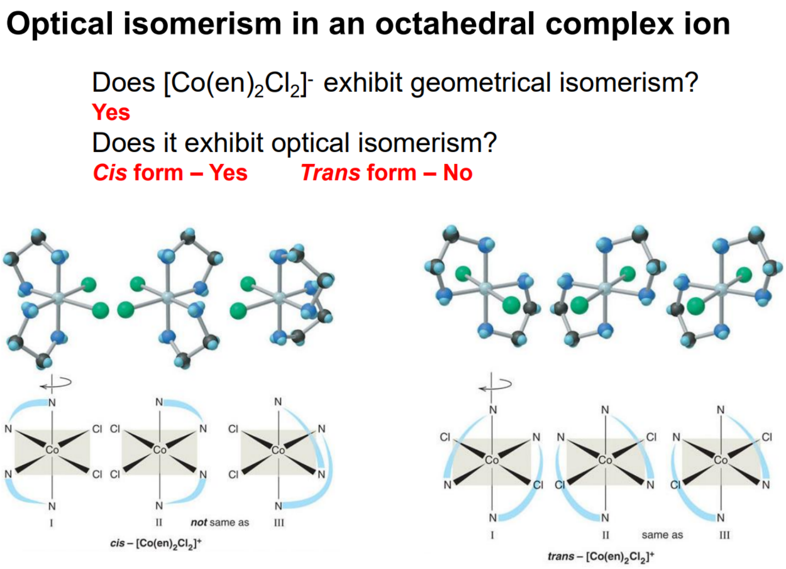
Geometric (*cis-trans*) isomers for a square planar compound

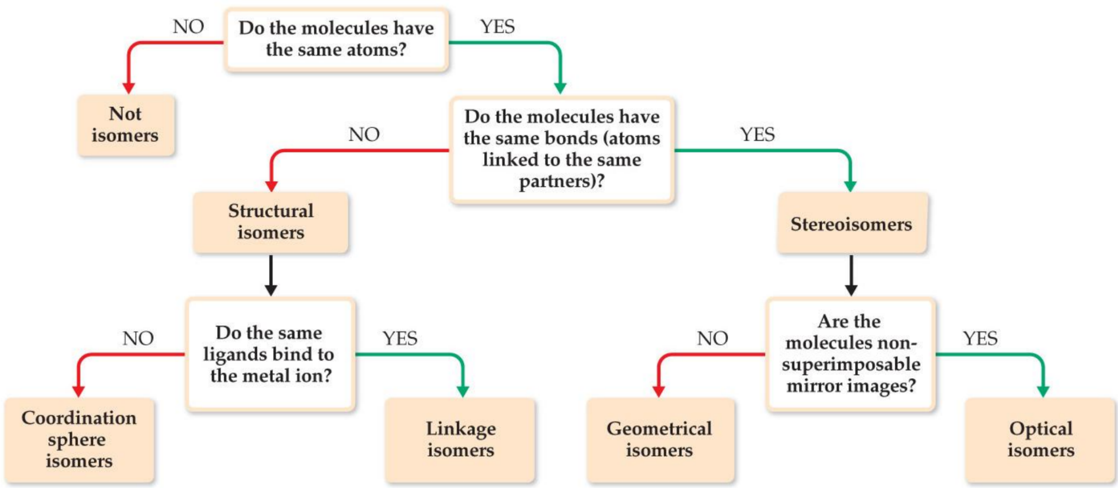
(a) *cis* isomer (b) *trans* isomer





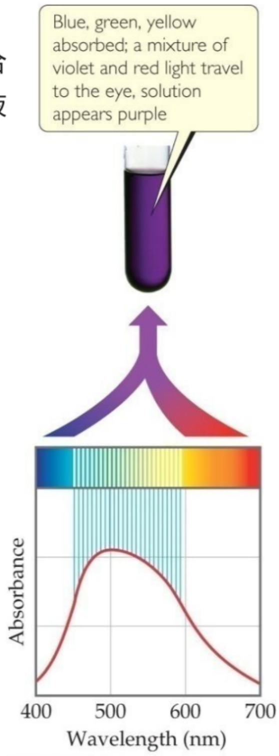
- 旋光异构体(手性)Optical isomers
  - 光学异构体，或对映体，是彼此的镜像，彼此不重叠Optical isomers, or enantiomers, are mirror images of one another that don’t superimpose on each other.
  - 我们说这是手性的They are said to be chiral.
  - 它们的性质只有在与其他手性物质接触时才有所不同Their properties differ from each other only when in contact with other chiral substances
-

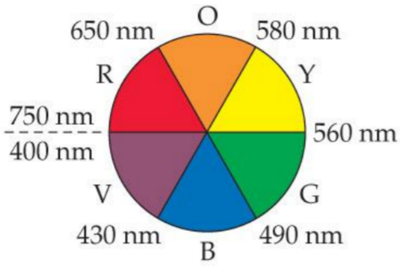


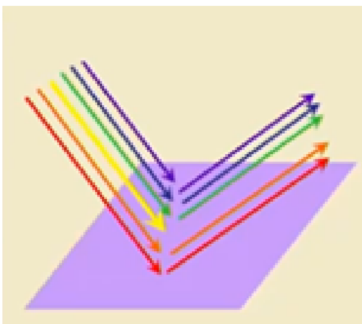


- 颜色color
  - 颜色取决于金属和配体Color depends on the metal and the ligands.
  - 我们在络合物中看到颜色的两种方式Two ways we see color in a complex
    - 物体反射那种颜色的光Object reflects that color of light.
    - 物体能透射除互补色以外的所有颜色(如在吸收光谱中所见)Object transmits all colors except the complementary color(as is seen in an absorption spectrum)

吸收蓝、绿、黄紫色和红色的混合光进入眼睛，溶液呈现紫色





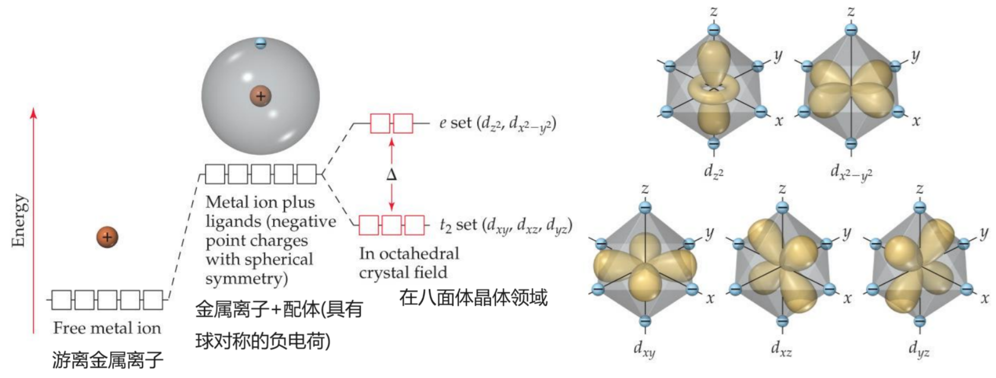


Relation Between Absorbed and Observed Colors

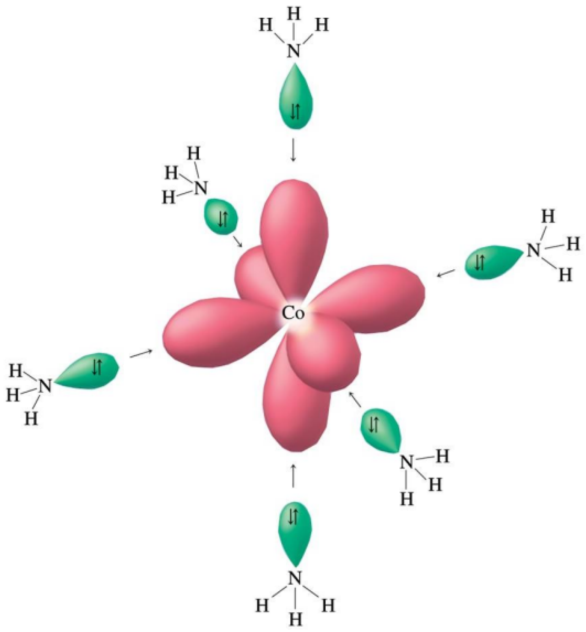
Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

- 晶体场理论Crystal-Field Theory
  - 如前所述，配体是被路易斯酸(金属)吸引的路易斯碱As was mentioned earlier, ligands are Lewis bases that are attracted to a Lewis acid (the metal).
  - 但是金属上d层的电子会排斥配体But d electrons on the metal would repel the ligand.
  - 在晶体场理论中，接近的配体被认为是被金属d轨道上的电子排斥的点电荷In crystal-field theory, the approaching ligand is considered to be a point charge repelled by the electrons in a metal’s d-orbitals
  - 因此，配合物中金属的d轨道不会简并Therefore, the d orbitals on a metal in a complex would not be degenerate.

- 那些指向配体的能量会比那些不指向配体的能量高Those that point toward ligands would be higher in energy than those that do not.



- Co3+上的杂化轨道可以接受来自每个NH3配体的电子对Hybrid Orbitals on Co3+ Can Accept an Electron Pair from Each NH3 Ligand



- 八面体构型配合物的电子分布Octahedral Complexes

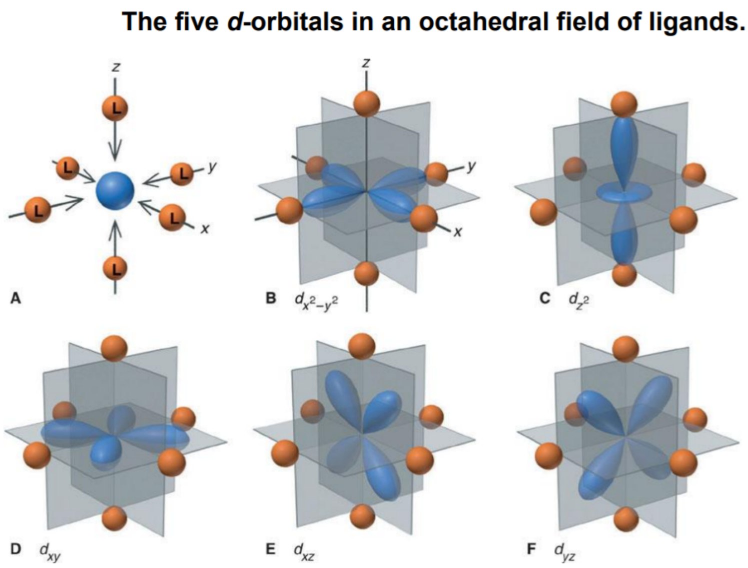
d_{z^2} and $d_{x^2-y^2}$ point their lobes *directly* at the point-charge ligands.

d_{z^2} and $d_{x^2-y^2}$ 将他们的叶片指向被看作点电荷的配体

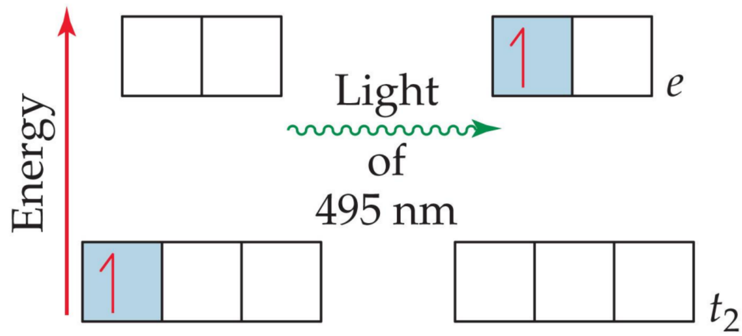
d_{xz}, d_{yz}, and d_{xy} point their lobes *between* the point charges.

d_{xz}, d_{yz}, and d_{xy} 将他们的叶片指向点电荷之间

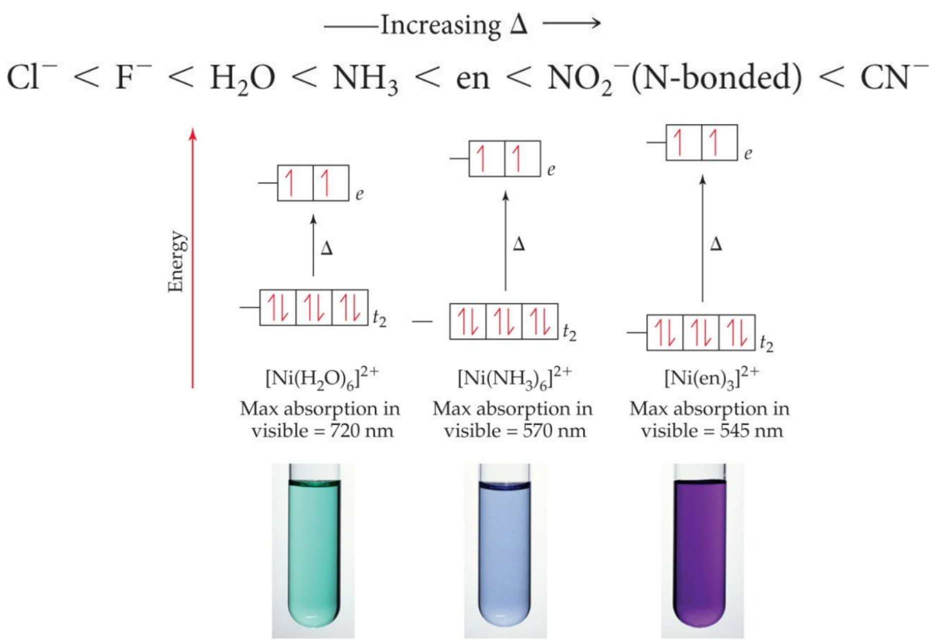
- 因为带负电荷的配体排斥带负电荷的电子，电子首先会填入离配体最远的d轨道，以使排斥最小化Because the negative point-charge ligands repel negatively charged electrons, the electrons will first fill the d orbitals farthest from the ligands to minimize repulsions.



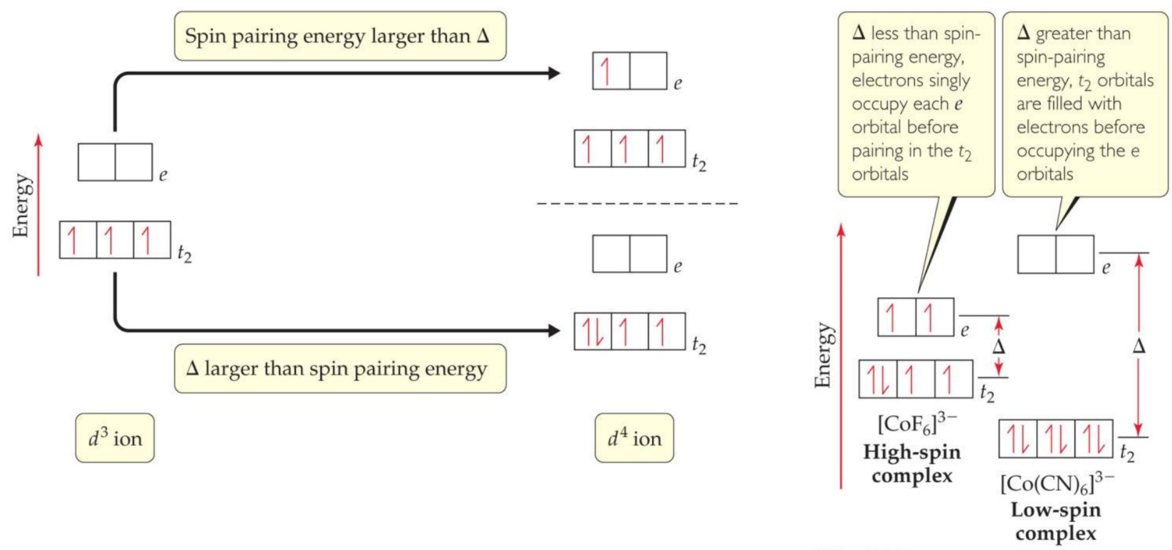
- 分裂能splitting energy
    - 轨道之间的能量差称为晶体场分裂能The energy difference between the orbitals is called the crystal-field splitting energy
    - d轨道之间的能隙对应于作为光子发射或吸收的能量This energy gap between d orbitals corresponds to the energy emitted or absorbed as a photon



    - 光谱化学序列根据它们增加d轨道间能量间隙的能力对配体进行排序(这是一种被称为晶体场理论的变体)The spectrochemical series ranks ligands in order of their ability to increase the energy gap between d orbitals. (This is a variation known as ligand-field theory.)



- 磁性特性Magnetic Properties
  - 强场(低自旋)Strong–field (low–spin)
    - 产生最小数量的未成对电子Yields the minimum number of unpaired electrons.
  - 弱场(高自旋)Weak–field (high–spin)
    - 产生最大数量的未成对电子Yields the maximum number of unpaired electrons.
  - 洪特规则依然适用Hund’s rule still applies
  - 未配对电子的数目取决于轨道被填满的顺序Numbers of unpaired electrons can differ depending upon the order in which orbitals are filled.
    - 更强的配体场导致更大的轨道分裂;这是一个“高场”但“低旋转”的案例Stronger ligand fields result in greater splitting of orbitals; this is a “high-field” but “low-spin” case.
    - 较弱的配体场导致较低的轨道分裂;这是一个“低场”但“高自旋”的案例Weaker ligand fields result in lower splitting of orbitals; this is a “low-field” but “high-spin” case
    - spin pairing energy 电子成对能



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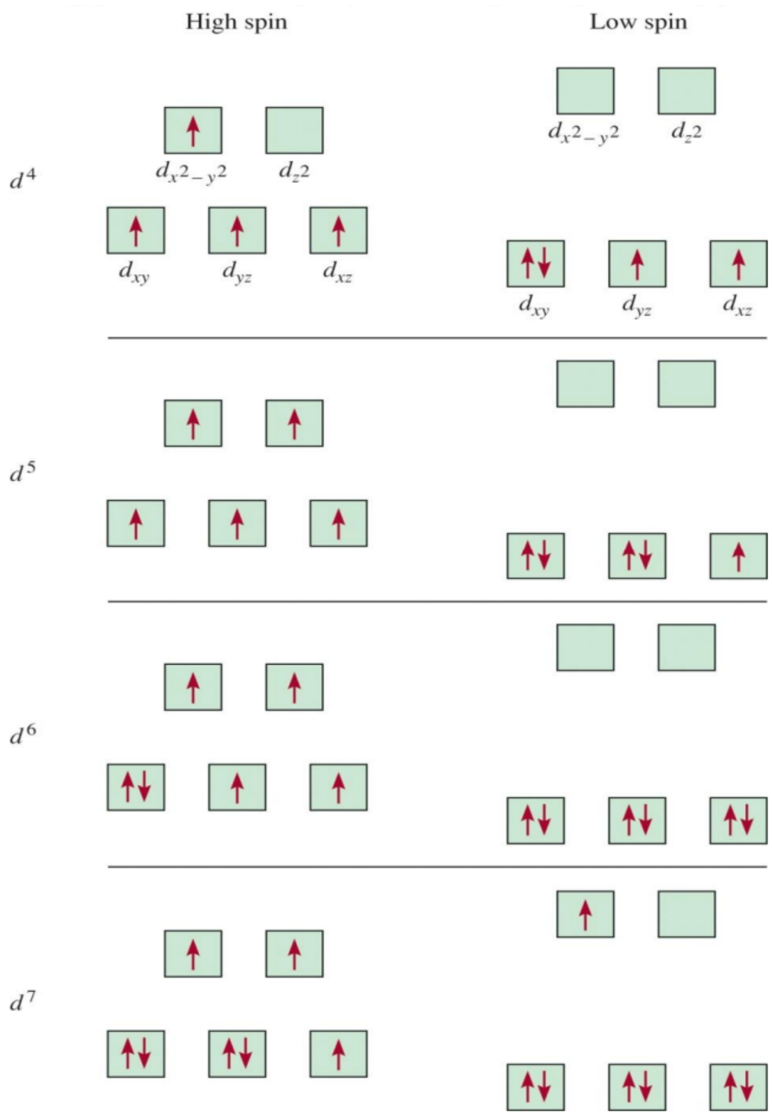
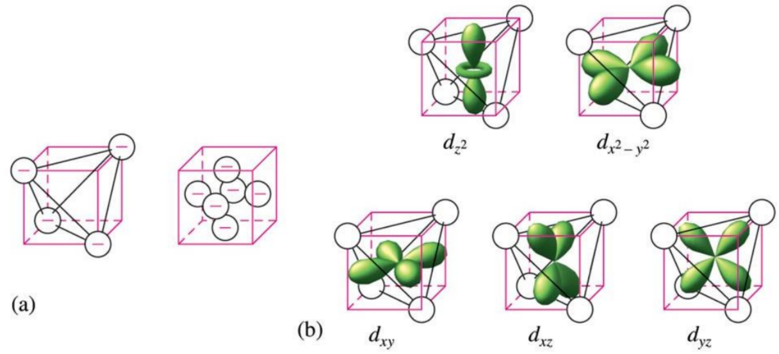
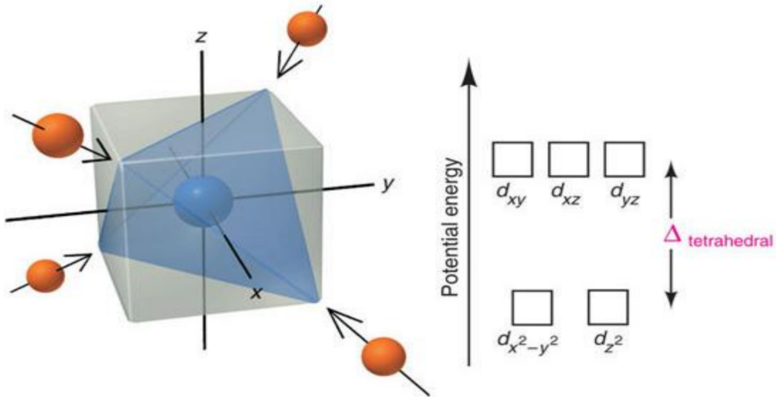


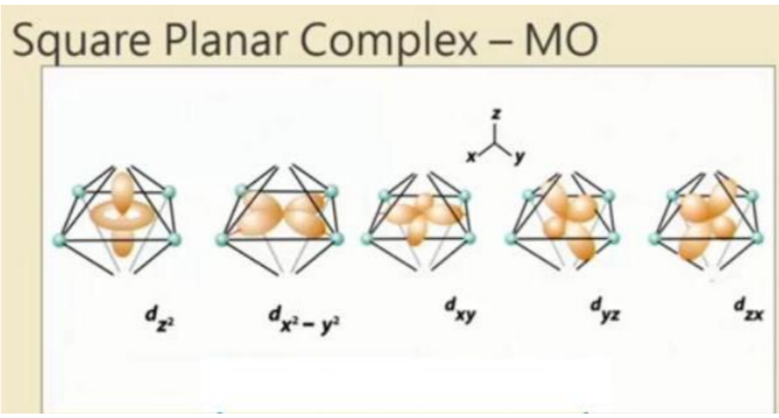
- 有单电子就是顺磁性paramagneitic
- 没有单电子就是逆磁性diamagnetic

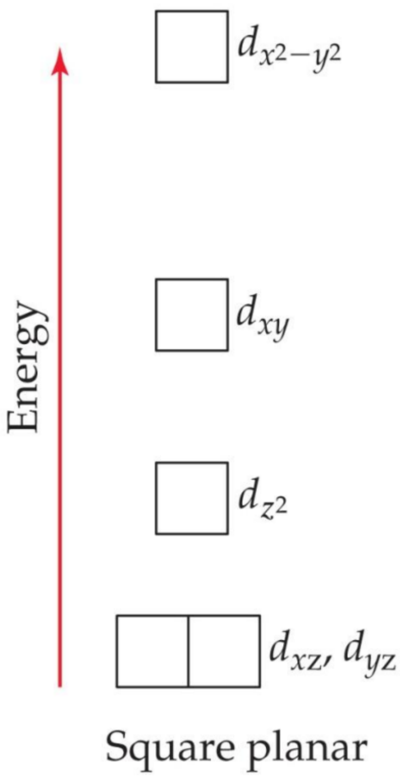
- 四面体排列Tetrahedral Arrangement
  - 没有一个三d轨道“指向配体”None of the 3d orbitals “point at the ligands”.
  - 分裂d轨道之间的能量差要小得多Difference in energy between the split d orbitals is significantly less.
  - d轨道分裂与八面体排列相反d–orbital splitting will be opposite to that for the octahedral arrangement.
  - 弱场情况(高自旋)总是适用的Weak–field case (high–spin) always applies.
  -





- 正方形平面Square Planar
  -



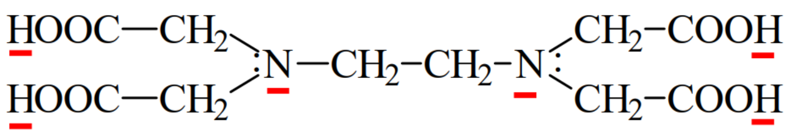


- 络合滴定Complexation Titration
  - 简单络合滴定的例子Examples of simple Complexation titration

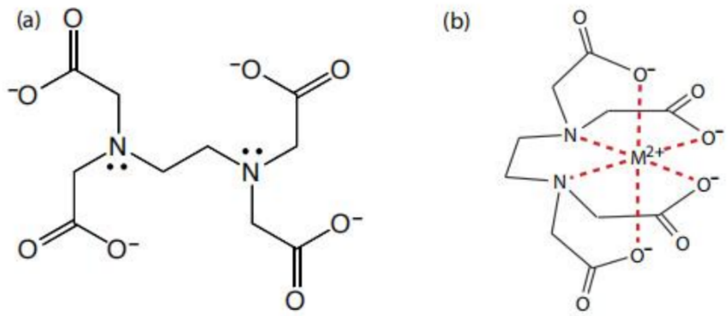
Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, thiourea	Products are neutral Hg(II) complexes, Various indicators used可使用多种指示剂
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI 滴定至AgI的第一浊度
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; Various indicators used
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Product are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

Remark:
Feasibility titration for M + L ⇆ ML $K_f = \frac{[ML]}{[M][L]} > 10^8$
可行性滴定

  - EDTA滴定 EDTA Titration
    - EDTA的化学和性质Chemistry and Properties of EDTA
      - Structure of Ethylenediaminetetraacetic acid



      - EDTA是一个六齿配体(2个N原子和4个O原子)EDTA is a hexadentate ligand (2 N atoms and 4 O atoms)
      - 所有金属- EDTA配合物的化学计量比均为1:1(金属:配体= 1:1)All metal-EDTA complexes have a 1:1 stoichiometric ratio(metal : ligand = 1 : 1)
      - 金属- EDTA六坐标结构(实际上是Y^4-金属配合物)Six-coordinate structure of metal-EDTA (indeed Y^4-complex with metal)



- 为了说明金属- EDTA络合物的形成，让我们考虑Cd2+和EDTA之间的反应To illustrate the formation of a metal–EDTA complex, let’s consider the reaction between Cd2+ and EDTA
-

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

- Y^4-是EDTA完全去质子化形式的简写where Y^4- is a shorthand notation for the fully deprotonated form of EDTA
- 反应的平衡常数Kf The reaction’s formation constant, Kf

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16}$$

- Kf'

$\alpha_{Y^{4-}}$ - Equation for Y^{4-} fraction:

$$C_{EDTA} = [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}}$$

The reaction’s formation constant, K_f:

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}} C_{EDTA}}$$

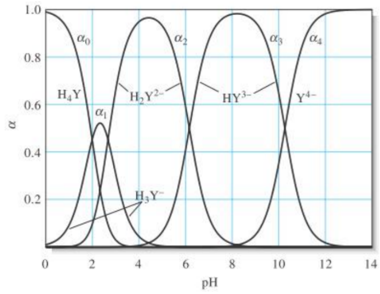
$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[CdY^{2-}]}{[Cd^{2+}] C_{EDTA}}$$

K'_f is a pH-dependent conditional formation constant

K'是一个依赖于ph的反应平衡常数

在酸性更大的ph值下，CDY^2-的Kf'常数变小，络合物变得不稳定

K'_f, the conditional formation constant for CdY^{2-} becomes smaller and the complex becomes less stable at more acidic pHs.



Values of $\alpha_{Y^{4-}}$ for Selected pH Levels

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
1	1.94×10^{-18}	8	5.68×10^{-3}
2	3.47×10^{-14}	9	5.47×10^{-2}
3	2.66×10^{-11}	10	0.367
4	3.80×10^{-9}	11	0.853
5	3.73×10^{-7}	12	0.983
6	2.37×10^{-5}	13	0.988
7	5.06×10^{-4}	14	1.00

- 小计算

Complexometric EDTA Titration Curve

Calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7.

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

- At a pH of 10, where some of the EDTA is present in forms other than Y^{4-}. To evaluate the titration curve, therefore, we need the conditional formation constant for CdY^{2-}, K'_f.

$$K'_f = K_f \times \alpha_{Y^{4-}} = 2.9 \times 10^{16} \times 0.367$$

$$= 1.1 \times 10^{16}$$

- The titration's equivalence point requires volume of EDTA:

$$V_{eq} = V_{EDTA} = \frac{M_{Cd} V_{Cd}}{M_{EDTA}} = \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{(0.0100\ \text{M})} = 25.0\ \text{mL}$$

Complexometric EDTA Titration Curve

Calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7.

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

- Before the equivalence point. For example, after adding 5.00 mL of EDTA, the total concentration of Cd^{2+} is:

$$[Cd^{2+}] = \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL}) - (0.0100\ \text{M})(5.00\ \text{mL})}{50.0\ \text{mL} + 5.00\ \text{mL}}$$

$$= 3.64 \times 10^{-3}\ \text{M}$$

$$\text{pCd} = 2.43$$

Complexometric EDTA Titration Curve

Calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7.

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

- At the equivalence point all Cd^{2+} initially in the titrand is now present as CdY^{2-}. The concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentration of CdY^{2-}.

$$[CdY^{2-}] = \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 25.00\ \text{mL}} = 3.33 \times 10^{-3}\ \text{M}$$

- Caculate the concentration of Cd^{2+} in equilibrium with CdY^{2-}

$$K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]\,C_{EDTA}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 1.1 \times 10^{16}$$

$$x = [Cd^{2+}] = 5.50 \times 10^{-10}\ \text{M} \qquad \text{pCd} = 9.26$$

Complexometric EDTA Titration Curve

Calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7.

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

- After the equivalence point, EDTA is in excess and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentrations of CdY^{2-} and of unreacted EDTA. For example, after adding 30.0 mL of EDTA.

$$[CdY^{2-}] = \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 30.00\ \text{mL}} = 3.12 \times 10^{-3}\ \text{M}$$

$$C_{EDTA} = \frac{(0.0100\ \text{M})(30.00\ \text{mL}) - (5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 30.00\ \text{mL}}$$

$$C_{EDTA} = 6.25 \times 10^{-4}\ \text{M}$$

$$K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]\,C_{EDTA}} = \frac{3.12 \times 10^{-3}\ \text{M}}{(x)(6.25 \times 10^{-4}\ \text{M})} = 1.1 \times 10^{16}$$

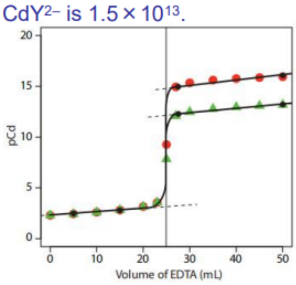
$$x = [Cd^{2+}] = 4.54 \times 10^{-16}\ \text{M} \qquad \text{pCd} = 15.34$$

Complexometric EDTA Titration Curve

Calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7.

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

The calculations at a pH of 7 are identical, except the conditional formation constant for CdY^{2-} is 1.5×10^{13}.



The points in red are the calculations for a pH of 10, and the points in green are the calculation for a pH of 7

Volume of EDTA (mL)	pCd at pH 10	pCd at pH 7
0	2.30	2.30
5.00	2.43	2.43
10.0	2.60	2.60
15.0	2.81	2.81
20.0	3.15	3.15
23.0	3.56	3.56
25.0	9.26	7.83
27.0	14.94	12.08
30.0	15.34	12.48
35.0	15.61	12.78
40.0	15.76	12.95
45.0	15.86	13.08
50.0	15.94	13.18