

Transition Elements (Chapter 19)

November 25-Nov 29 (Chapter 19 in Open Access TextBook)

Concept Video 34:

Properties of Transition Elements

Concept Video 35:

Coordination Compounds

Concept Video 36

Bonding and Properties of Complexes

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Chapter 19: Transition metals used in many materials!



Batteries: cadmium, nickel, cobalt



Musical instruments: copper, silver, nickel, cobalt, iron



Circuitry: gold, copper, silver, zinc



Hybrid car components: dysprosium, lanthanum, neodymium, samarium



New! screens: cadmium nanoparticles



Sun protection: zinc



Cosmetics and jewellery: gold, silver, platinum, iron, zinc, titanium



Surgical instruments: iron, chromium



Electricity: uranium



Vehicles: copper, zinc

Transition Metal (TM) Elements

Period

1	1																18
2		2															
3																	
4																	
5																	
6																	
7																	

TRANSITION ELEMENTS
d block

3	4	5	6	7	8	9	10	11	12
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

INNER TRANSITION ELEMENTS
f block

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- all metals
- many coloured
- many paramagnetic

Properties of their compounds related to electron configuration of the transition metal (TM)

Review: Electron Configurations of TM Elements

General Atomic Configurations

Period 4 & 5 $[\text{noble gas}] ns^2 (n-1)d^x$

Period 6 & 7 $[\text{noble gas}] ns^2 (n-2)f^{14} (n-1)d^x$

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TABLE 24.1 Orbital Occupancy of the Period 4 Transition Metals

Element	Partial Orbital Diagram	Unpaired Electrons
Sc	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1</div> <div>4p</div> <div></div>	1
Ti	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	2
V	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	3
Cr	<div>4s</div> <div>1</div> <div>3d</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	6
Mn	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	5
Fe	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	4
Co	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	3
Ni	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>4p</div> <div></div>	2
Cu	<div>4s</div> <div>1</div> <div>3d</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>4p</div> <div></div>	1
Zn	<div>4s</div> <div>1↓</div> <div>3d</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>4p</div> <div></div>	0

Chromium (Cr) and Copper (Cu) exceptions to achieve half-filled/filled subshells

Review: Electron Configurations of TM Elements

General Cationic Configurations

Period 4 & 5 [noble gas](n-1)d^x

Period 6 & 7 [noble gas](n-2)f¹⁴(n-1)d^x

* TM elements lose 's' electrons before 'd' electrons

* TM cations with same configurations have similar properties

	Atomic Configuration	Cationic Configuration
Ti ²⁺	[Ar] 4s ² 3d ²	[Ar]3d ²
Fe ²⁺	[Ar] 4s ² 3d ⁶	[Ar]3d ⁶
Fe ³⁺	[Ar] 4s ² 3d 6	[Ar]3d ⁵
Cu ⁺	[Ar] 4s ¹ 3d ¹⁰	[Ar]3d ¹⁰

Periodic Trend in Transition Metals

Atomic Size/Radius: **Across a period**

Size decreases across TM, but less than main group

- Many 'd' electrons to *inner* energy level, which shield *outer* 's' electrons efficiently
- Z_{eff} does not change much across TM elements ('s' electrons not pulled in closer)

Think of a big classroom like this one



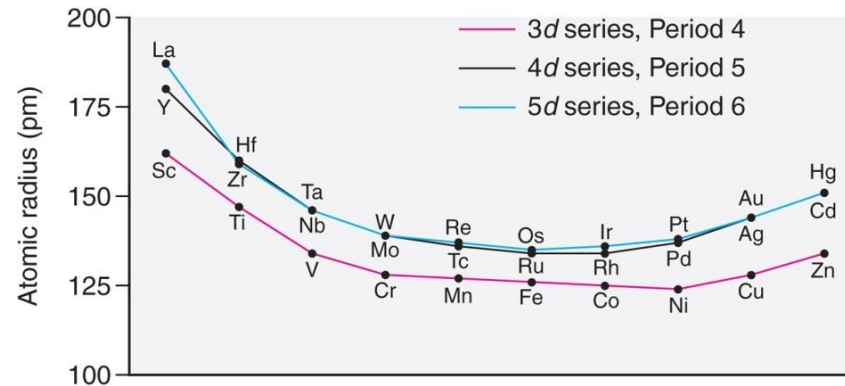
Students and their notebooks at The Missouri School of Journalism

If you are in a row at the back, you see less of the speaker at the front because of the rows in front of you “shielding” you.

Periodic Trend in Transition Metals

Atomic Size/Radius: **Down a group**

There is not a significant size change between period 5 and 6 transition metals.



There are two opposing effects:

- 1) adding an extra shell = bigger size
- 2) *Lanthanide contraction* (i.e. an extra 14 protons from f block = shrinkage)

Therefore, overall size does not change much

A periodic table diagram showing the periodic trend in atomic size. The table is color-coded: orange for main group elements, blue for transition elements (d-block), and light blue for inner transition elements (f-block). The d-block is labeled 'TRANSITION ELEMENTS d block' and the f-block is labeled 'INNER TRANSITION ELEMENTS f block'. The table shows the periodic trend in atomic size, with the size generally increasing from top-left to bottom-right.

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H	He																
2	Li	Be	B	C	N	O	F	Ne										
3	Na	Mg	Al	Si	P	S	Cl	Ar										
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Periodic Trend in Transition Metals

Ionization Energy: **Across a period**

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
419	590	631	658	650	653	717	759	758	757	745	906	579	761	947	941	1143	1351

C First ionization energy (kJ/mol)

Ionization Energy increases for period 4 transition elements.

The trend is not regular for period 5/6 transition elements

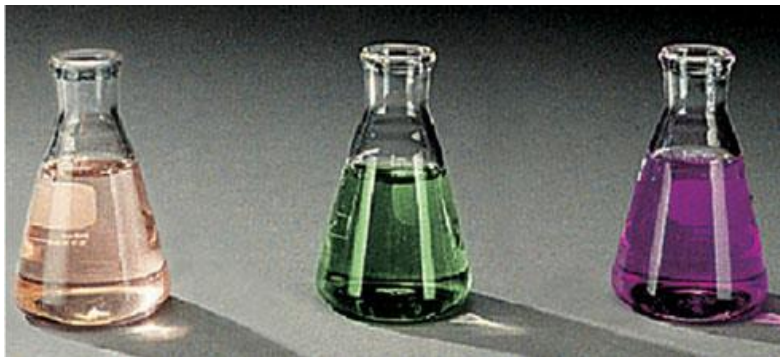
Note: Period 4 - Ga has a low ionization energy – as it is easier to remove the only 4p orbital electron as compared to the paired 4s orbital electrons.

Chemical Properties of TM Elements

+2
 Mn^{2+}

+6
 MnO_4^{2-}

+7
 MnO_4^-



Many possible oxidation states
(different oxidation numbers).

+5
 VO_4^{3-}

+6
 $\text{Cr}_2\text{O}_7^{2-}$

+7
 MnO_4^-



Oxidation Number

O.N. of an Atom – charge that the atom would have if the electrons were transferred completely to/from bonded atoms

General Rules for Assigning an Oxidation Number

1. An atom in its elemental form (Na, O₂, etc) O.N. = 0
2. A monatomic ion: O.N. = ion charge (sign BEFORE numeral)
3. Sum of O.N. values of atoms in a molecule = 0. Sum of O.N. values of atoms in a polyatomic ion = charge of the ion.

Specific Atoms/Groups

Group 1 = +1

Group 2 = +2

Hydrogen: +1 when combined with nonmetals; -1 when combined with metals or boron.

Oxygen = -2 in most cases

Group 17 = -1 in most cases

Assigning oxidation number

Is the molecule/complex neutral or charged?

Then use the overall charge and the charge you know to figure out the oxidation number of the species remaining:

Most Common: Grp1 (+1), Grp2 (+2), H (+1), O (-2), Grp17 (-1)

e.g., ZnBr_2

Assigning oxidation number

Is the molecule/complex neutral or charged?

Then use the overall charge and the charge you know to figure out the oxidation number of the species remaining:

Most Common: Grp1 (+1), Grp2 (+2), H (+1), O (-2), Grp17 (-1)

e.g., ZnBr_2

This is a molecule (not a polyatomic ion since I did not indicate a charge)

Br is group 17 so usually -1

So Zn must be +2

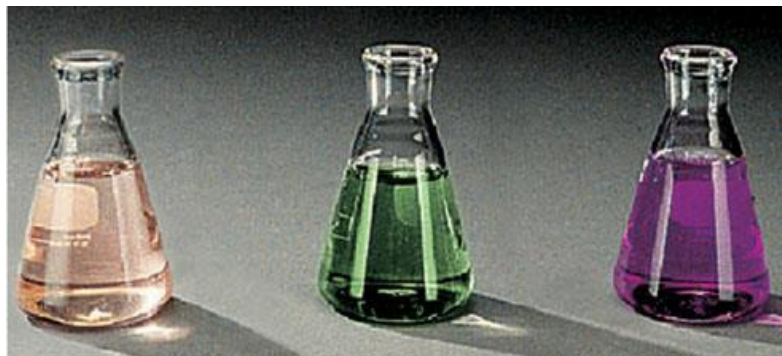
So we say Zn here has an oxidation number of +2

Chemical Properties of TM Elements

+2
 Mn^{2+}

+6
 MnO_4^{2-}

+7
 MnO_4^-



Many possible oxidation states (different oxidation numbers).

Since **(n-1)d** and **ns** electrons very close in energy, so many options for cations.

Transition metal ions are often highly coloured and/or paramagnetic due to **unfilled d-subshells**.

TABLE 24.1 Orbital Occupancy of the Period 4 Transition Metals				
Element	Partial Orbital Diagram			Unpaired Electrons
	4s	3d	4p	
Sc	↑↓	↑		1
Ti	↑↓	↑ ↑		2
V	↑↓	↑ ↑ ↑		3
Cr	↑	↑ ↑ ↑ ↑ ↑		6
Mn	↑↓	↑ ↑ ↑ ↑ ↑		5
Fe	↑↓	↑↓ ↑ ↑ ↑ ↑		4
Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑		3
Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑		2
Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		1
Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		0

+5
 VO_4^{3-}

+6
 $\text{Cr}_2\text{O}_7^{2-}$

+7
 MnO_4^-



Chemical Properties of TM Elements

Oxidation State	3 Sc	4 Ti	5 V	6 Cr	7 Mn	8 Fe	9 Co	10 Ni	11 Cu	12 Zn
0	d^1	d^2	d^3	d^5	d^5	d^6	d^7	d^8	d^{10}	d^{10}
+1			d^3	d^5	d^5	d^6	d^7	d^8	d^{10}	
+2		d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
+3	d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	
+4		d^0	d^1	d^2	d^3	d^4	d^5	d^6		
+5			d^0	d^1	d^2		d^4			
+6				d^0	d^1	d^4				
+7					d^0					

The most common orbital occupancies are in red

Low oxidation states are more metallic/ionic

Higher oxidation states are more covalent

Transition Elements (Chapter 19)

Concept Video 35: Coordination Compounds

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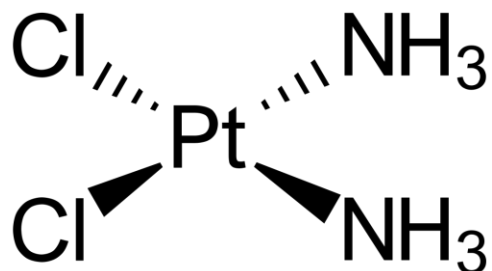
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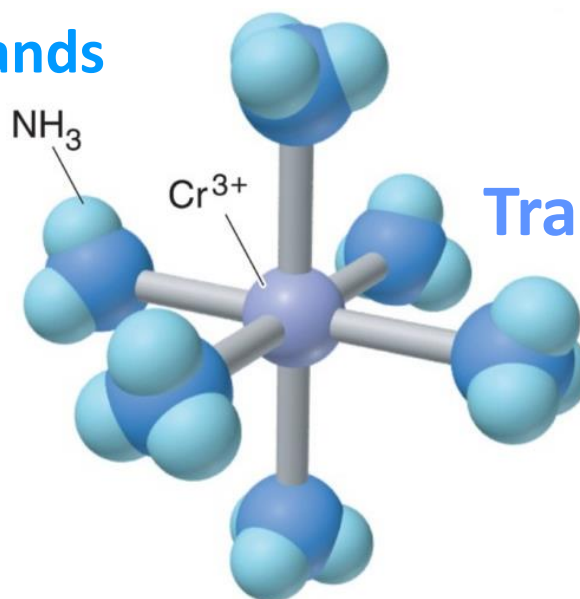
Transition metals as drugs

A Periodic Table of Medicines



What is a coordination compound?

neutral or anionic ligands



Transition Metal Center

Coordination compound is $[\text{Cr}(\text{NH}_3)_6]^{3+}$

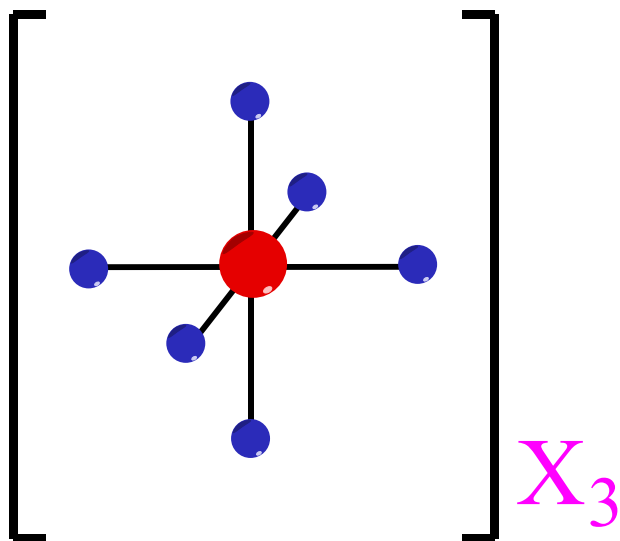
- Coordinator compounds behave like **covalent** polyatomic ions in solution (ligands remain attached)
- Coordinator compound ions associated with counterions to achieve neutrality
- Note – the coordination compound is written inside SQUARE brackets
- Counter ions written outside bracket



What is a ligand?

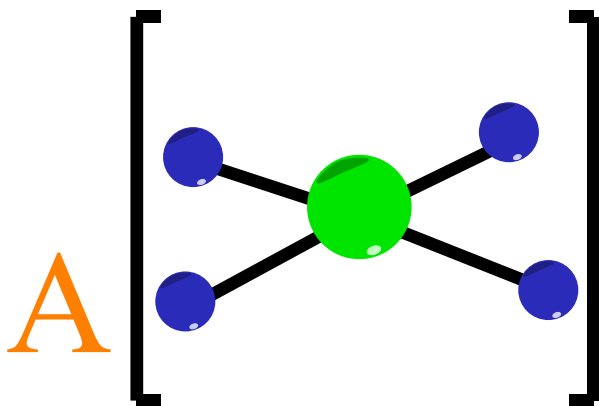
Molecules or anions with one or more donor atoms – each donor atom **donates a pair of electron** to the metal ion (to form a coordinate bond)



Can be neutral or anionic

What is a coordination compound?



-  Ligand
-  Central metal ion
- X^- Counter anion

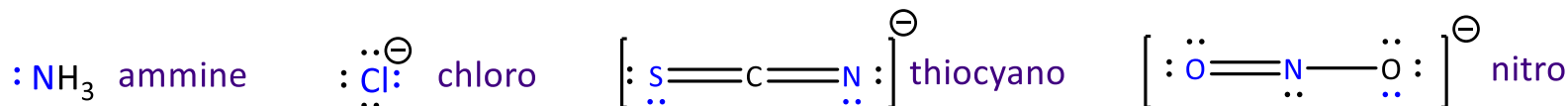
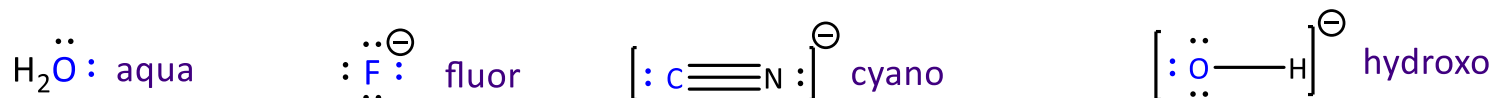


-  Ligand
-  Central metal ion
- A^+ Counter cation

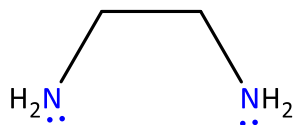
What is a ligand?

Can have more than one binding site

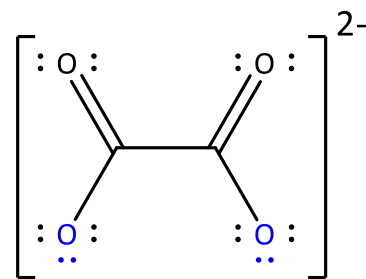
Monodentate



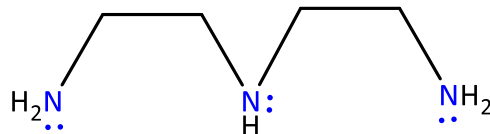
Bidentate



ethylenediamine (en)



oxalato

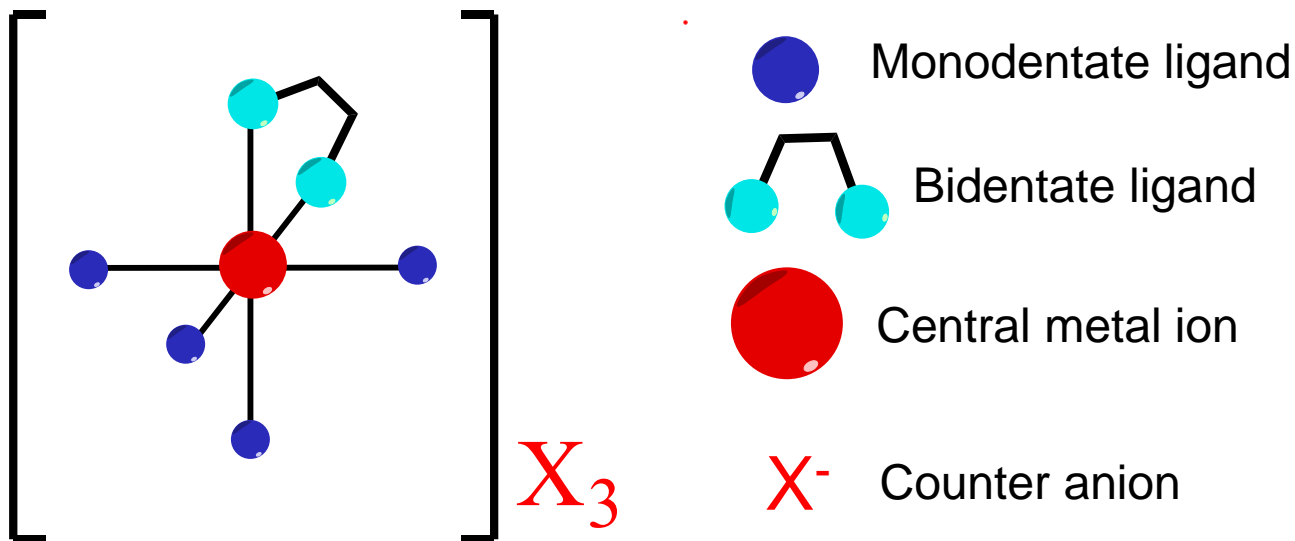


diethylenetriamine

Dentate comes from *dentis*: Latin for tooth

Coordination compounds with bi or polydentate ligands are sometimes referred to as “chelates”

What is a coordination number?




Bidentate ligands: 2 donor atoms (of the same molecule) simultaneously donating electrons to the central metal ion

Coordination number: total coordination bonds formed between the central metal ion and all the ligands.

This one here is 6! (i.e. 2 from the bidentate + 4 monodentate)

Geometry from coordination number

Why do we bother with coordination number? To figure out geometry!

TABLE 24.5		Coordination Numbers and Shapes of Some Complex Ions	
Coordination Number	Shape		Examples
2	Linear		$[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$
d^8	4	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$
d^{10}	4	Tetrahedral	$[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
	6	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$

*In some cases d^5 : like Mn^{2+}

*In some cases d^5 : like Mn^{2+}

Determining geometry: How many “d” electrons?

What is the coordination number? $[\text{PdCl}_4]^{2-}$

- Pd is coordinated with FOUR chloro groups
- chloro is MONO dentate (i.e. 1 coordination bond each)
- so $4 \times 1 =$ the coordination number is 4
- can be square planar or tetrahedral...

What is the oxidation number? (i.e. how do we know how many “electrons” to remove from the electron configuration of neutral Pd)

- overall charge of the bracket is 2- (put this on one side of the equation)
- trying to find out Pd (Pd = x)
- what else do we know? Chloro (Cl) is a -1 charge/oxidation state
- there are 4 chloro groups (so 4×-1)

So the “algebra” is

$$-2 = x + 4(-1)$$

$$-2 = x + (-4)$$

$$-2 + 4 = x$$

$$2 = x \quad \text{So the oxidation state of Pd here is } \mathbf{+2}$$

Finally, electron configuration time!

Neutral $[\text{Kr}] 5s^2 4d^8$


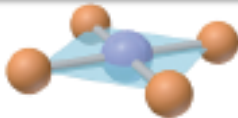
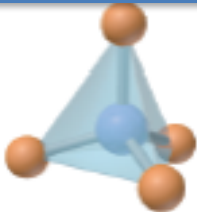
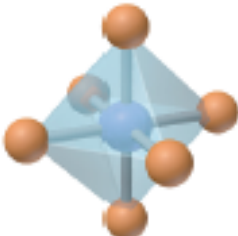
+2 oxidation $[\text{Kr}] d^8$

So there are 8 d electrons

Geometry from coordination number

TABLE 24.5

Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape		Examples
2	Linear		$[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$
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6	Octahedral		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$

*In some cases d^5 : like Mn^{2+}

Isomerism in Coordination Compound

Review! Same concept as we learned in Intro to organic!

ISOMERS – different compounds with the same molecular formula

STRUCTURAL – different connectivity

STEREISOMERS – same connectivity, different orientation in space

GEOMETRIC ISOMERS (cis, trans)

ENANTIOMERS – non-superimposable mirror image stereoisomers



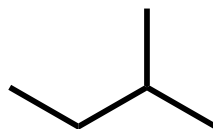
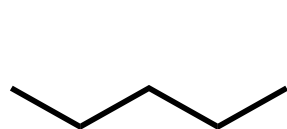
PENTANE



ISOPENTANE



NEOPENTANE



STRUCTURAL (Skeletal) ISOMERS

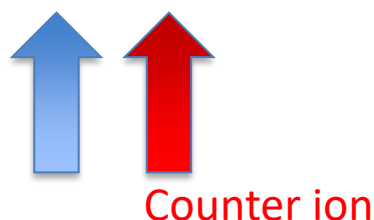
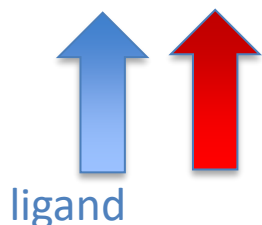
Isomerism in Coordination Compound

STRUCTURAL ISOMERS: two types for metal complexes

1: coordination isomers

2: linkage isomers

Same compound **formula** but **different composition of the complex ion** –
COORDINATION ISOMERS



Coordination means the ligands are COORDINATING with the metal. If they are isomers, it means some ARE coordinating, some are not.

So if you see some INSIDE the square brackets vs. outside – this is a hint there could be coordination isomers

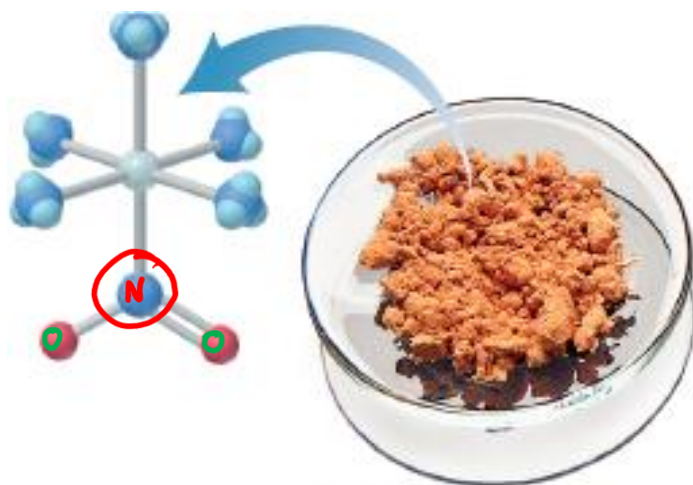
Isomerism in Coordination Compound

STRUCTURAL ISOMERS: two types for metal complexes

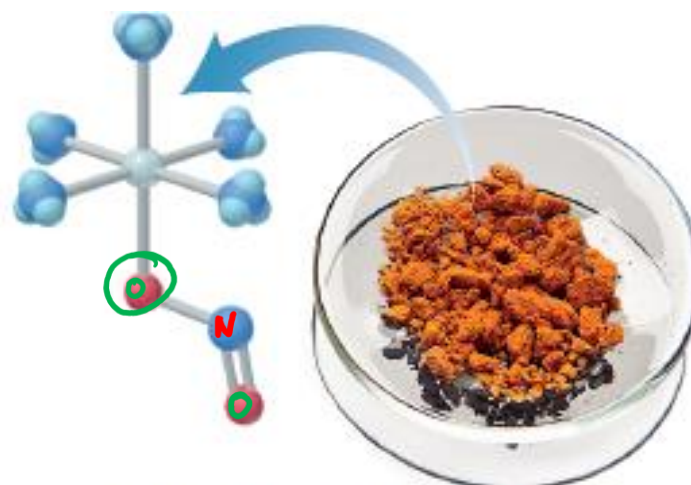
1: coordination isomers

2: linkage isomers

Same composition of the complex **but the ligand donor atom is different** –
LINKAGE ISOMERS

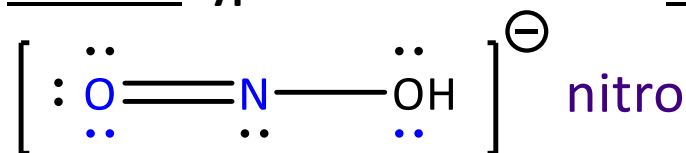
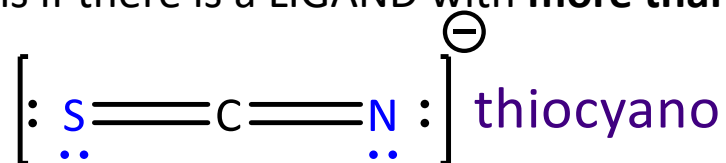


Nitro Isomer, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$



Nitrito Isomer, $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$

Clue is if there is a LIGAND with **more than one different type of atom that has a lone pair**



Isomerism in Coordination Compound

Same concept as we learned in intro to organic

ISOMERS – different compounds with the same molecular formula

STEREISOMERS – same connectivity, different orientation in space

GEOMETRIC ISOMERS (cis, trans)


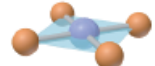
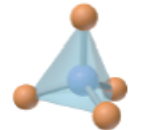
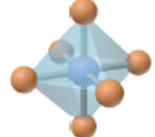
ENANTIOMERS – non-superimposable mirror image stereoisomers

Linear has no isomers

Square planar can have geometric isomers

Tetrahedral can have enantiomers

Octahedral can have enantiomers, but we will NOT cover this.

TABLE 24.5		Coordination Numbers and Shapes of Some Complex Ions	
Coordination Number	Shape		Examples
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4	Tetrahedral		$[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
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Isomerism in Coordination Compound

Same concept as we learned in intro to organic

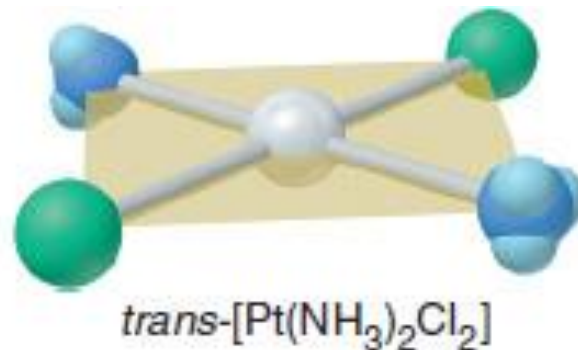
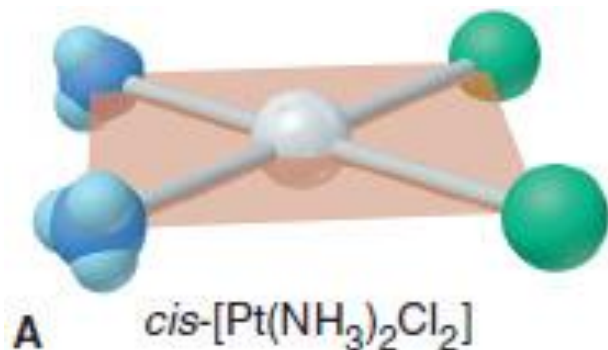
ISOMERS – different compounds with the same molecular formula

STRUCTURAL – different connectivity

STEREISOMERS – same connectivity, different orientation in space

***GEOMETRIC ISOMERS (cis, trans)**

ENANTIOMERS – non-superimposable mirror image stereoisomers



We will only see this for square planar in this class

Isomerism in Coordination Compound

Same concept as we learned in intro to organic

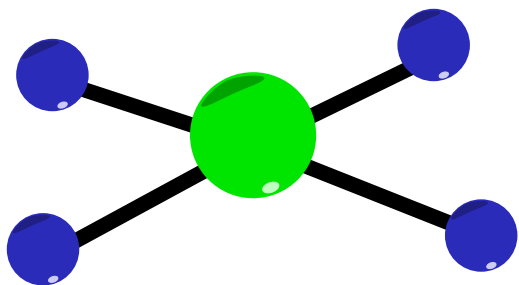
ISOMERS – different compounds with the same molecular formula

STRUCTURAL – different connectivity

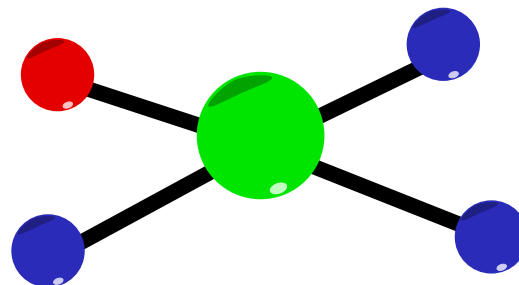
STEREISOMERS – same connectivity, different orientation in space

***GEOMETRIC ISOMERS (cis, trans)**

ENANTIOMERS – non-superimposable mirror image stereoisomers



No geometric isomers



No geometric isomers

Isomerism in Coordination Compound

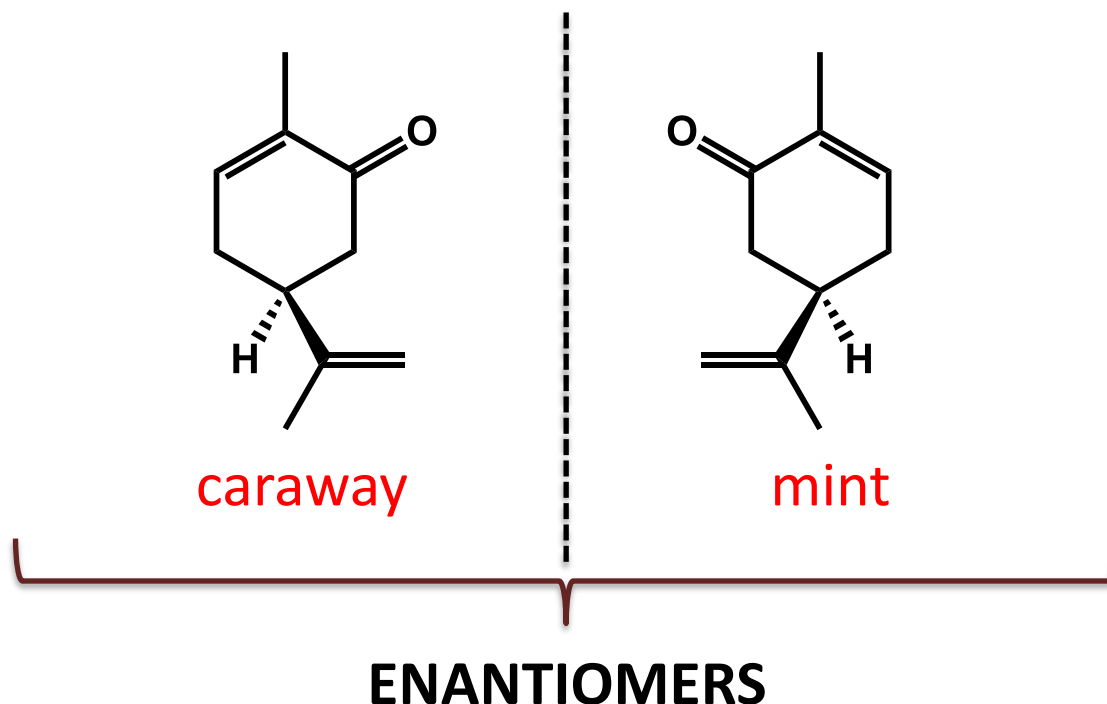
ISOMERS – different compounds with the same molecular formula

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GEOMETRIC ISOMERS (cis, trans)

ENANTIOMERS – non-superimposable mirror image stereoisomers

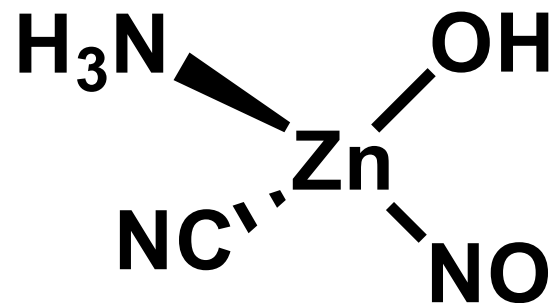
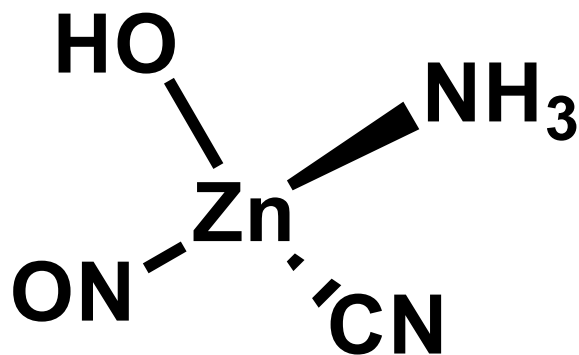


Isomerism in Coordination Compound

Nonsuperimposable mirror images– ENANTIOMERS

If you have a coordination number 4 with only monodentate ligands, same rule applies that we learned in chapter 20!

“4 different groups” can be chiral, and thus there is a possibility of enantiomers



Naming a coordination compound

When writing out the formula of a coordination compound, the coordination compound is in the brackets as follows:

-Metal first (most important)

-ligands next



If there are counter ions, they go OUTSIDE square brackets. Cations go first; anions second.



Naming a coordination compound

1. Name the **ligands first** and then the metal atom or metal ion.

Here are the names of common ligands (when in complex with the transition metal ion):

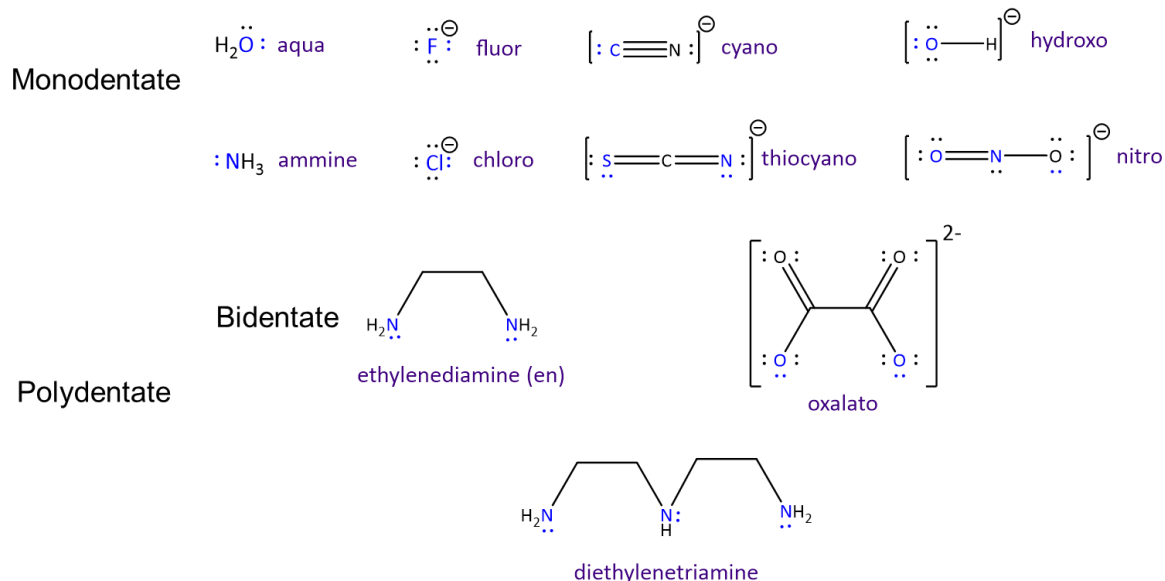
Neutral Ligand	Name
NH_3	ammine
H_2O	aqua
NO	Nitrosyl
en	Ethylene diamine
CO	carbonyl

Anionic Ligand	Name
$\text{Cl}^-/\text{I}^-/\text{F}^-$ Br^-	Chloro/iodo/fluoro/ bromo
NO_2^-	Nitro/nitrito
CN^-	cyano
OH^-	hydroxo
$\text{C}_2\text{O}_4^{2-}$	Oxalato

Naming a coordination compound

2. *Greek prefixes* indicate the number of each type of ligand in the complex ion: 2 di-, 3 tri-, 4 tetra-....

If ligand already contains a Greek prefix (as in ethylenediamine) or if it is **bi/polydentate** then use : 2:bis-, 3:tris-, 4:tetrakis-, 5:pentakis-...



Example: $[\text{Co}(\text{en})_3]^{3+}$ is : **tris(ethylenediamine)**cobalt(III) ion

Naming a coordination compound

3. Ligands are named in alphabetical order, **ignoring** the Greek prefix that indicates the number of each one present.

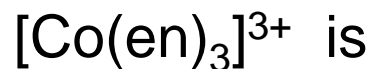
Example: $[\text{FeCl}(\text{H}_2\text{O})_5]^+$ is : **pentaaquachloro**iron(II) ion

Naming a coordination compound

4. A Roman numeral denotes the oxidation number of the central metal ion:



tetraamminedichlorochromium(III) ion



tris(ethylenediamine)cobalt(III) ion

Naming a coordination compound

5. If the complex has an overall **negative** charge (an *anionic* complex), the suffix -ate is *added to the* metal's name.

$[\text{Ni}(\text{CN})_4]^-$ tetracyano**nickelate** (III) ion

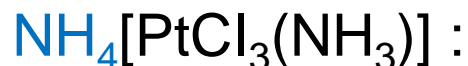
The symbol for iron is Fe, from the Latin ferrum. Therefore, any **anionic** complex of iron ends with -ferrate followed by the oxidation number of the metal in Roman numerals:

$[\text{Fe}(\text{CN})_6]^{4-}$ hexacyano**ferrate** (II) ion

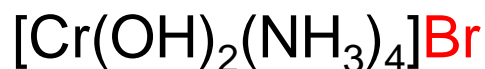
In contrast, if it has an overall positive charge, you just write the metal as normal, i.e. nickel, chromium, etc...

Naming a coordination compound

6. Cation is always written before the anion.



ammonium amminetrichloroplatinate(II)



tetraamminedihydroxochromium(III) bromide

Also note: when writing the molecular formula, the coordination complex is designated with square brackets – any counter cation/anion are written outside the brackets

Transition Elements (Chapter 19)

Concept Video 36

Bonding and Properties of Complexes

Prof. Maureen McKeague

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Department of Chemistry

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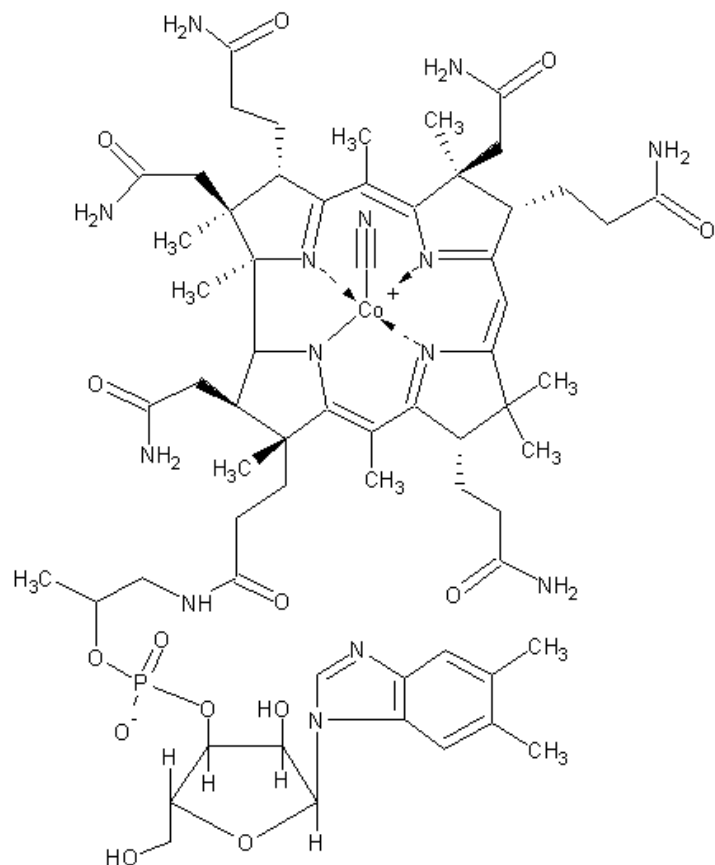
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Transition metals are essential for life

H																He	
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						

- Blue = essential in large quantities
- Pink = essential in ultratrace quantities

Transition metals are essential for life



Vitamin B₁₂ - Cobalamin



Valence Bond Theory

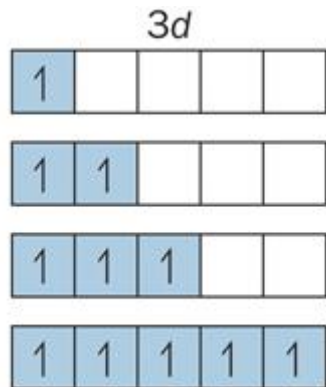
What we learned previously (valence bond theory) is used for metal complexes, but it does not explain why these compounds are colored and it cannot help us predict magnetic properties.

So, we introduce a new theory!

Applies differently to tetrahedral and octahedral complexes but we will focus on octahedral

Crystal Field Theory (CFT)

d orbitals of an atom are degenerate (all five d orbitals are the same energy)

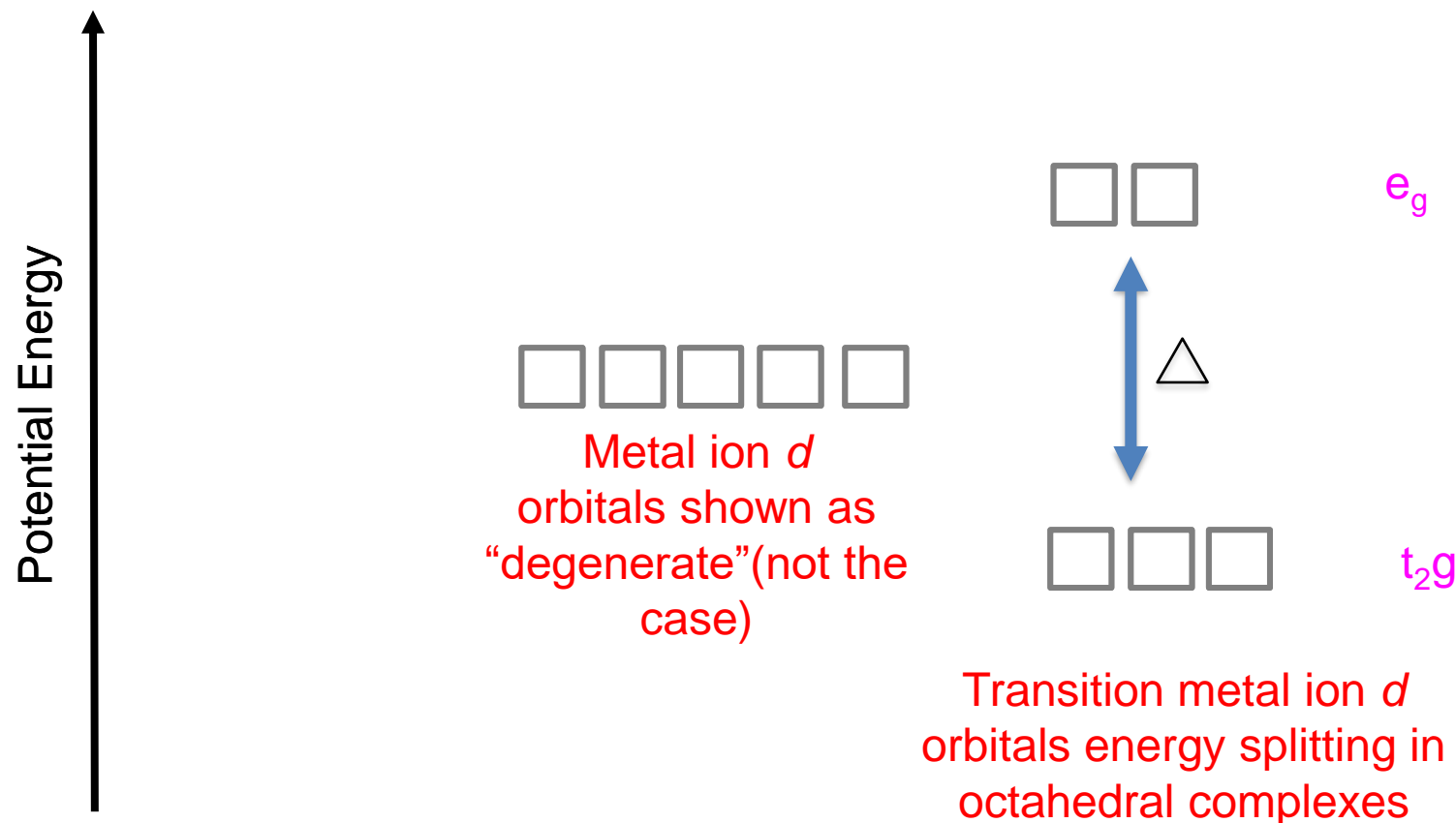


but in coordination compounds according to CFT

as ligands begin to align themselves, the d orbitals do not remain degenerate

Degenerate means = same energy

Crystal Field Theory: Octahedral Complex

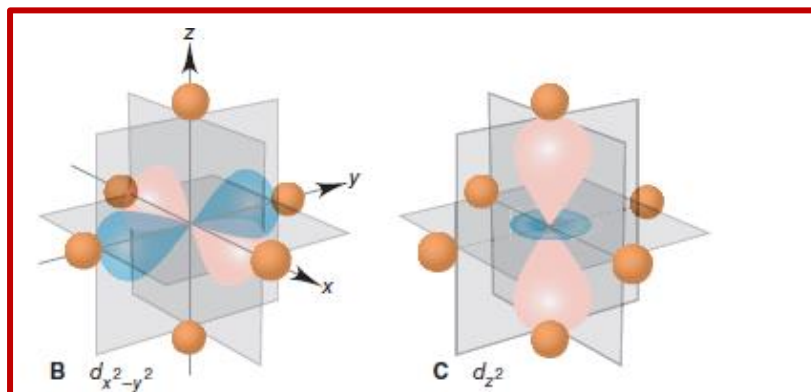
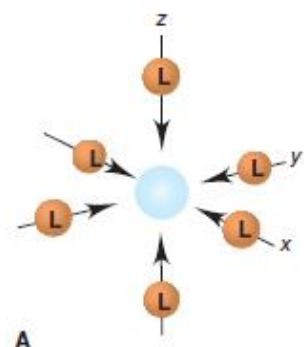


This splitting of orbitals is CRYSTAL FIELD EFFECT

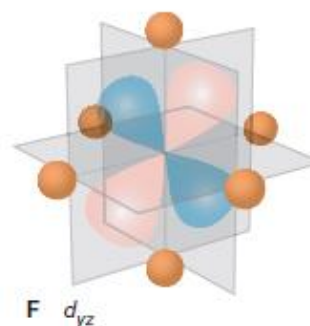
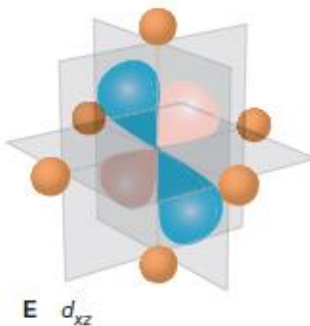
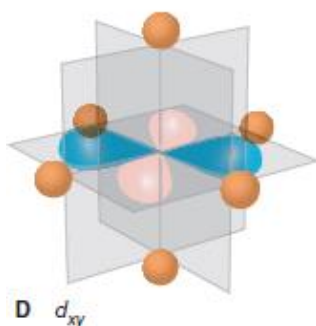
The energy difference between the orbitals is crystal field splitting energy or ligand field splitting energy also denoted as Δ (Δ_o for octahedral complexes)

Crystal Field Theory: Octahedral Complex

Ligands pointing at d_z^2 and $d_{x^2-y^2}$ orbitals – higher in energy



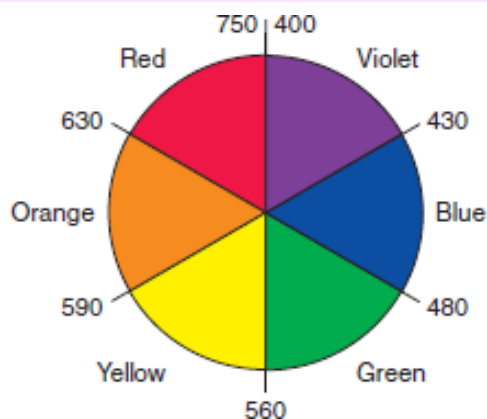
Closest to ligands, so repel the most (e_g orbitals)



2 sets of orbitals - t_{2g} orbitals and e_g orbitals

- as ligands approach, their donor electrons repel d-electrons of TM center
- d-electrons repelled unequally due to different orbital orientations
- e_g and t_{2g} are symmetry group names

Crystal Field Theory: Color!



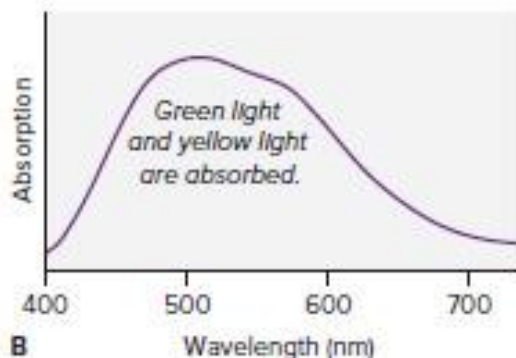
An object reflects light of the color we observe

An object absorbs light of the complementary color

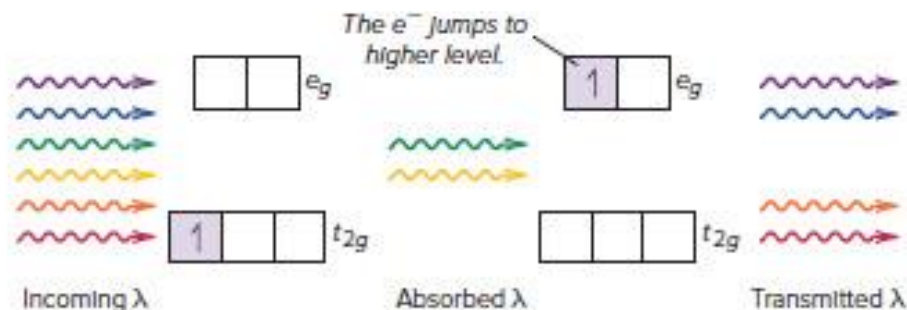
This reflection and absorption we observe depend upon the wavelength (frequency)/energy of the light



A



B

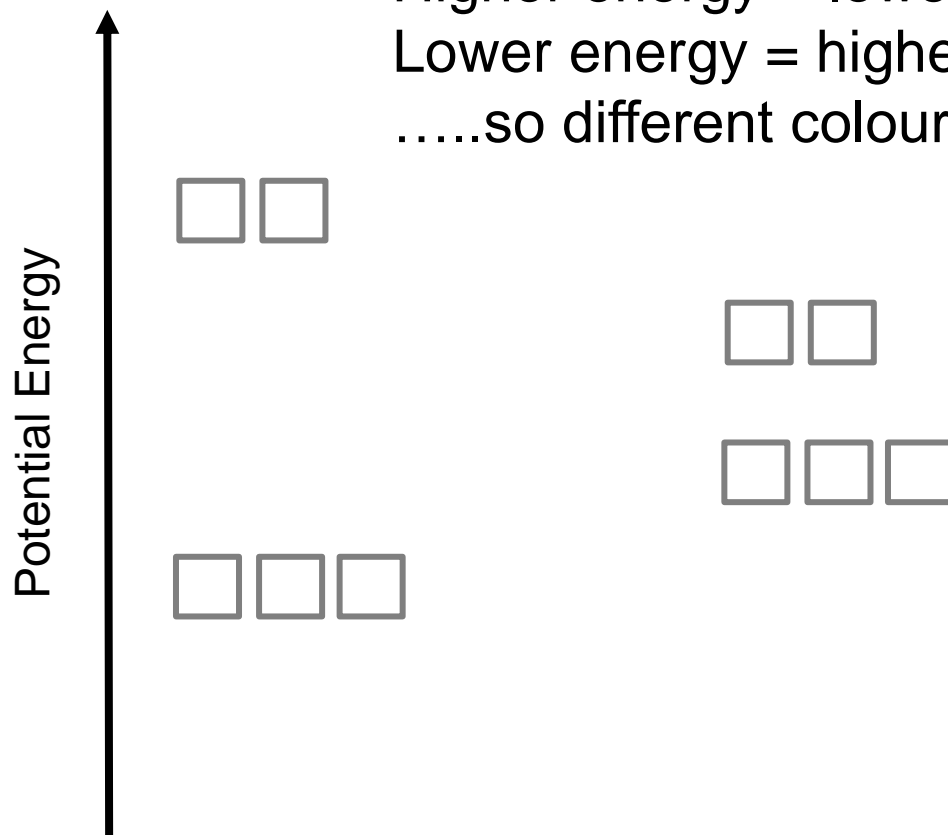


C

Crystal Field Theory

When scientists measured the spectra of different complexes (**same metal**), they found that the difference in this energy was not always the same! So the ligands are changing the energy of the d orbitals!!!

Higher energy = lower wavelength
Lower energy = higher wavelength
.....so different colours



What affects the energy difference (Δ)

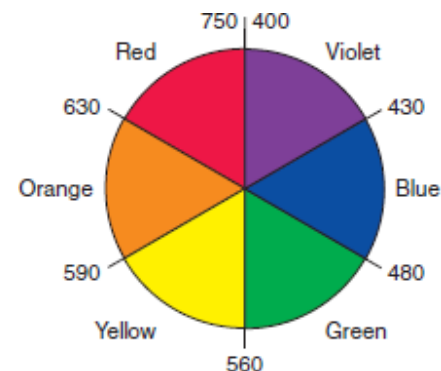
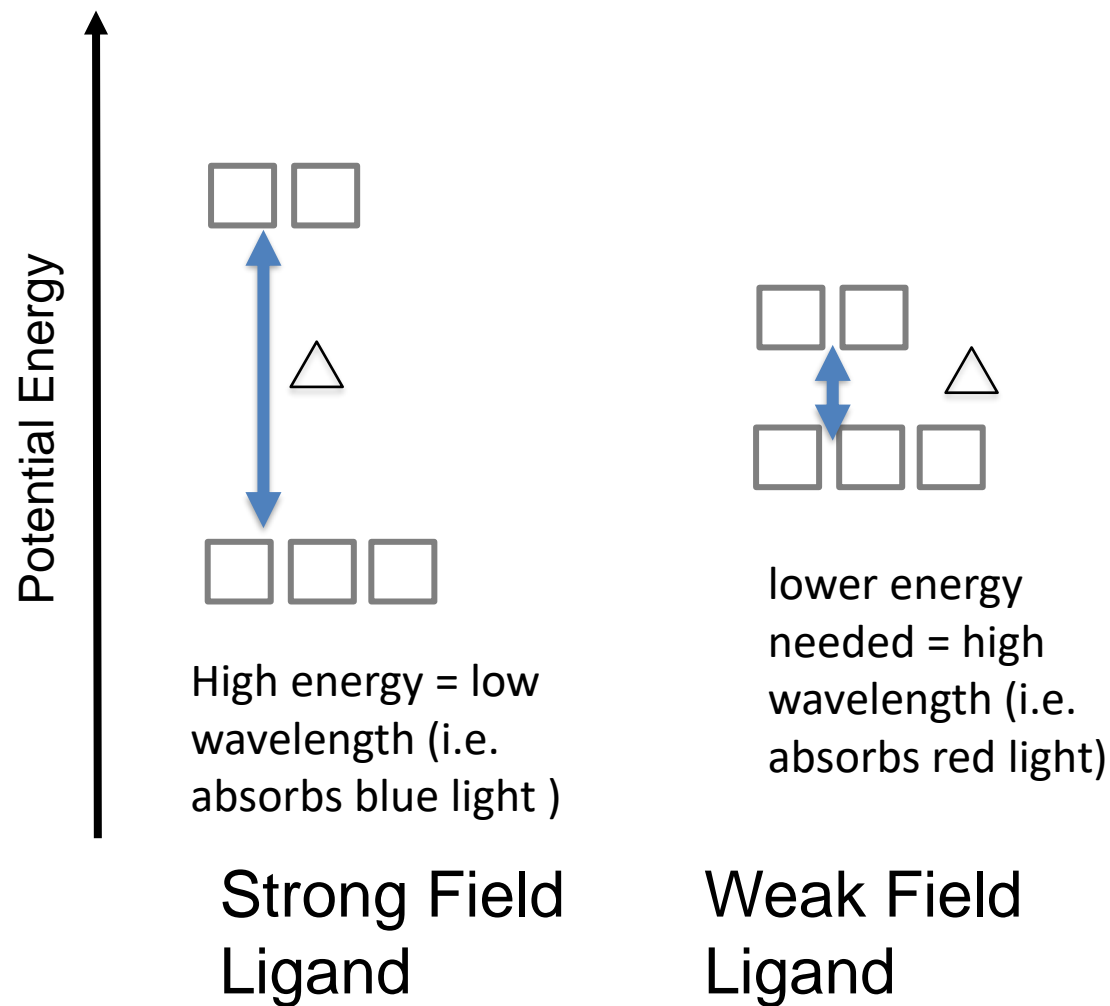
The Spectrochemical Series

Organizes the ligands as
strong field or weak-field

Strong field ligands (more electron density) – more repulsion of the particular d orbitals.

This cause a larger difference in the energy of t_{2g} and e_g orbitals, so a higher Δ_o as compared to “weak field” ligands

What affects the energy difference (Δ)



SIDE NOTE: so if a metal complex absorbs blue light, it will LOOK orange in colour!

if a metal complex absorbs red light, it will LOOK green in colour!

What impacts the energy difference (Δ)

Crystal Field Splitting Energy (Δ):

energy difference between t_{2g} and e_g

- different ligands have different strength crystal fields (different Δ)

Strong Field Ligands = larger Δ

Weak Field Ligands = smaller Δ

Spectrochemical Series (of Ligands)

I^- , Cl^- , F^- , HO^- , H_2O , SCN^- , NH_3 , en, NO_2^- , NC^- , CO

Increasing Field Strength

SUMMARY

halogens < oxygen < nitrogen < carbon
(anions weaker field than neutral of same element)

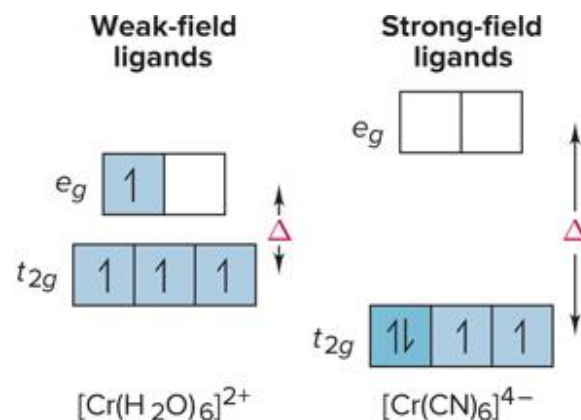
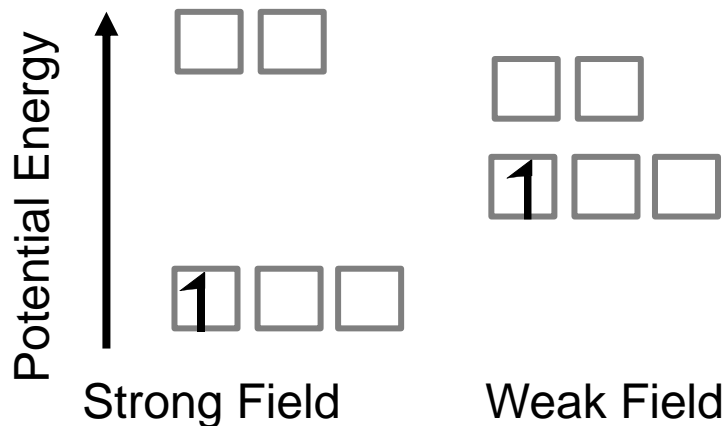


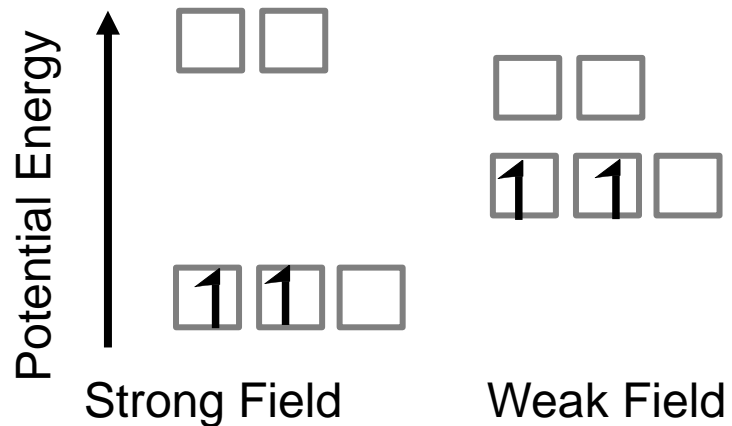
FIGURE 24.18 The effect of ligands and splitting energy on orbital occupancy

Note these are RELATIVE not absolute. i.e. we are only going to compare ligands in chem 110!

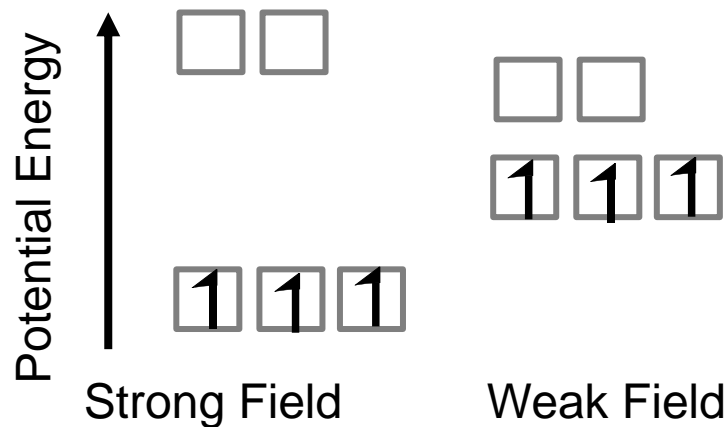
Magnetic Properties of Coordination Compounds



d^1



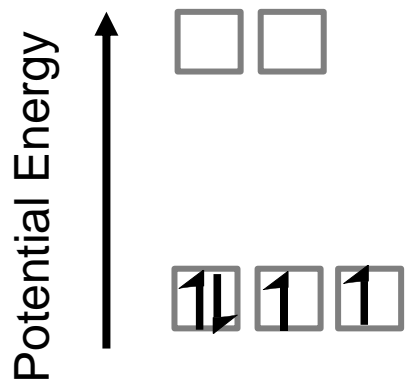
d^2



d^3

From d^1 to d^3 : Same number of unpaired electrons for strong field or weak field

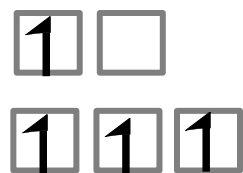
Magnetic Properties of Coordination Compounds



Strong Field

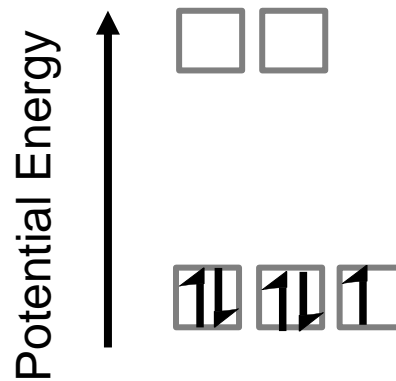
2 unpaired e^-

d^4



Weak Field

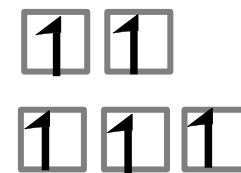
4 unpaired e^-



Strong Field

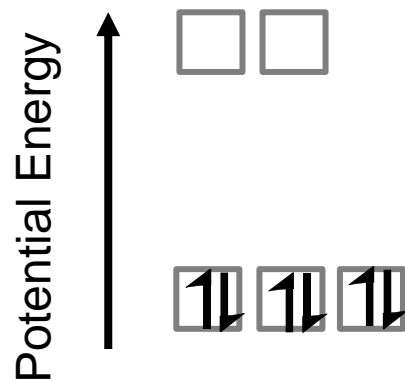
1 unpaired e^-

d^5



Weak Field

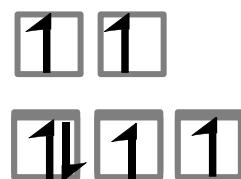
5 unpaired e^-



Strong Field

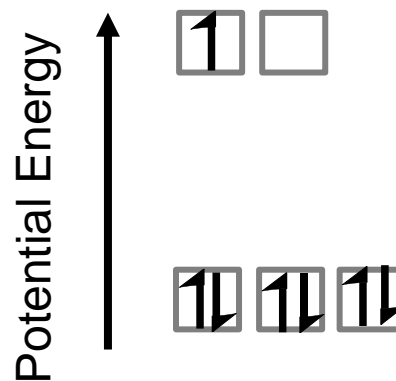
0 unpaired e^-

d^6



Weak Field

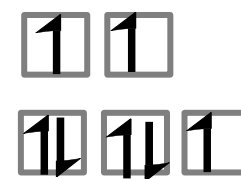
4 unpaired e^-



Strong Field

1 unpaired e^-

d^7



Weak Field

3 unpaired e^-

Magnetic Properties of Coordination Compounds

TABLE 9D.1 The Electron Configurations of d^N Complexes

Number of d-electrons, d^N	Configuration	
	Octahedral complexes	
d^1	t_{2g}^1	
d^2	t_{2g}^2	
d^3	t_{2g}^3	
	low spin	high spin
d^4	t_{2g}^4	$t_{2g}^3 e_g^1$
d^5	t_{2g}^5	$t_{2g}^3 e_g^2$
d^6	t_{2g}^6	$t_{2g}^4 e_g^2$
d^7	$t_{2g}^6 e_g^1$	$t_{2g}^5 e_g^2$
d^8	$t_{2g}^6 e_g^2$	
d^9	$t_{2g}^6 e_g^3$	
d^{10}	$t_{2g}^6 e_g^4$	

Anything with
unpaired
electrons is
magnetic.

But few unpaired
electrons (i.e. low
spin) is only
weakly magnetic