

Coordination Chemistry
Transition Metals
Metal Complexes
Ligands / Nomenclature

Color / Isomerism

Crystal Field Theory / MO Theory



Atomic Orbitals of Period 4 Metals					
Element	Partial Orbital Diagram	Unpaired Electrons			
Sc		1			
Ti		2			
V		3			
Cr		6			
Mn		5			



# **QUESTION**

Of the following, which is the correct electron configuration for the ground state chromium atom?

A.[Ar]  $3d^6$ B.[Ar]  $4s^13d^5$ C.[Ar]  $4s^23d^4$ D.[Ar]  $4s^13d^44p^1$ 











True or false: Transition metals show great similarities both within a given period and within a given vertical group.

# ANSWER

True

The transition metals were left out of earlier periodic trends because of the close similarities they have with one another.





**ANSWER** 

D

Fe with a +6 charge in the compound, which is the same as the oxidation number of Cr in  $Cr_2O_7^{2-}$ . Although not common, Fe can be prepared in the +6 state making it an unusually good oxidizing agent. In K<sub>2</sub>FeO<sub>4</sub> the 2K provides a total +2 charge. The oxygen total charge is -8, which leaves a + 6 for Fe.



Oxidation States and <i>d</i> -Orbital Occupancy of the Period 4 Transition Metals										
	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B
Oxidation	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
State	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0	0	0	0	0	0	0	0	0	0	0
	$(d^1)$	$(d^2)$	$(d^3)$	(d <sup>5</sup> )	(d <sup>5</sup> )	$(d^{6})$	$(d^7)$	$(d^{8})$	$(d^{10})$	$(d^{10})$
+1			+1	+1	+1		+1	+1	+1	
			(d <sup>3</sup> )	(d <sup>5</sup> )	(d <sup>5</sup> )		( <b>d</b> <sup>7</sup> )	( <b>d</b> <sup>8</sup> )	$(d^{10})$	
+2		+2	+2	+2	+2	+2	+2	+2	+2	+2
		$(d^2)$	$(d^3)$	$(d^4)$	(d <sup>5</sup> )	( <b>d</b> <sup>6</sup> )	$(d^7)$	$(d^{8})$	$(d^{9})$	$(d^{10})$
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	
	$(d^0)$	$(d^1)$	$(d^2)$	$(d^3)$	$(d^4)$	(d <sup>5</sup> )	(d <sup>6</sup> )	(d7)	$(d^8)$	
+4		+4	+4	+4	+4	+4	+4	+4		
		$(d^0)$	$(d^1)$	$(d^2)$	$(d^3)$	$(d^4)$	$(d^{5})$	( <b>d</b> <sup>6</sup> )		
+5			+5	+5	+5		+5			
			$(d^0)$	( <i>d</i> <sup>1</sup> )	$(d^2)$		$(d^4)$			
+6				+6	+6	+6				
				$(d^0)$	$(d^1)$	$(d^2)$				
+7				. ,	+7 (	$d^0$				







Electronic Configurations of Transition Metal Ions

• Electronic configuration of Fe<sup>3+</sup>

Electronic Configurations of Transition Metal Ions

• Electronic configuration of  $Fe^{3+}$  $Fe - 3e^{-} \rightarrow Fe^{3+}$ 

Electronic Configurations of Transition Metal Ions

• Electronic configuration of Fe<sup>3+</sup> Fe - 3e<sup>-</sup>  $\rightarrow$  Fe<sup>3+</sup> [Ar]3d<sup>6</sup>4s<sup>2</sup>

> valence (n)  $\mathbf{s}^{\text{electrons}}$ removed first, then (n-1)  $\mathbf{d}^{\text{electrons}}$

Electronic Configurations of Transition Metal Ions

• Electronic configuration of  $Fe^{3+}$   $Fe^{-}3e^{-} \rightarrow Fe^{3+}$  $[Ar]3d^{64s^2}$   $[Ar]3d^5$ 

> valence (*n*)  $\mathbf{s}^{\text{electrons}}$ removed first, then (*n*-1)  $\mathbf{d}^{\text{electrons}}$



Electronic Configurations of Transition Metal Ions

• Electronic configuration of  $Co^{3+}$  $Co - 3e^{-} \rightarrow Co^{3+}$ 

Electronic Configurations of Transition Metal Ions

- Electronic configuration of  $Co^{3+}$   $Co - 3e^{-} \rightarrow Co^{3+}$   $[Ar]3d^{74s^{2}}$ 
  - valence (n)  $\mathbf{s}^{\text{electrons}}$ removed first, then (n-1)  $\mathbf{d}^{\text{electrons}}$

Electronic Configurations of Transition Metal Ions

• Electronic configuration of  $Co^{3+}$   $Co - 3e^{-} \rightarrow Co^{3+}$   $[Ar]3d^{6}$  $[Ar]3d^{6}$ 

> valence (n)  $\mathbf{s}^{\text{electrons}}$ removed first, then (n-1)  $\mathbf{d}^{\text{electrons}}$

Electronic Configurations of Transition Metal Ions

• Electronic configuration of Mn<sup>4+</sup>

Electronic Configurations of Transition Metal Ions

• Electronic configuration of  $Mn^{4+}$  $Mn - 4e^{-} \rightarrow Mn^{4+}$ 





# QUESTION

Which metal ion has a  $a^5$  electron configuration? A) Pd<sup>2+</sup> B) Ag<sup>+</sup> C) Fe<sup>3+</sup> D) Os<sup>2+</sup> E) Co<sup>2+</sup>

# ANSWER

C) Fe<sup>3+</sup>

Iron(II) ion loses two *s* electrons and one *d* electron.

# **QUESTION**

What is the electron configuration of the  $Sc^{+3}$ ion? A) [Ar] $3s^{1}4d^{0}$ B) [Ar] $4s^{1}3d^{0}$ C) [Ar] $3s^{1}3d^{0}$ D) [Ar] $4s^{2}$ E) [Ar]

# ANSWER

E) [Ar]

Standard Electrode Potentials of Period 4 M <sup>2+</sup> lons			
Half-Reaction	$E^{0}\left(\mathbf{V}\right)$		
$Ti^{2+}_{(a0)} + 2 e^{-} \longleftarrow Ti_{(s)}$	-1.63		
$V^{2+}_{(aq)} + 2 e^{-} \longleftrightarrow V^{(s)}_{(s)}$	-1.19		
$Cr^{2+}_{(aq)} + 2 e^{-} \longrightarrow Cr_{(s)}$	-0.91		
$Mn^{2+}_{(aq)} + 2 e^{-} \longrightarrow Mn_{(s)}$	-1.18		
$Fe^{2+}_{(aq)} + 2e^{-} \longrightarrow Fe_{(s)}$	-0.44		
$\operatorname{Co}^{2+}_{(aq)} + 2 e^{-} \longleftrightarrow \operatorname{Co}_{(s)}$	-0.28		
$Ni^{2+}_{(aq)} + 2 e^{-} \longrightarrow Ni_{(s)}$	-0.25		
$\operatorname{Cu}_{(aq)}^{2+} + 2 e^{-} \longrightarrow \operatorname{Cu}_{(s)}^{2+}$	0.34		
$Zn^{2+}$ $\rightarrow$ $Zn_{(a)}$	-0.76		

## **QUESTION** The reducing abilities of the first-row transition metals generally \_\_\_\_\_\_ going from left to right across the period. A) decrease B) increase C) stay the same D) none of these E) remain at 1.0 V















## Coordination Chemistry

Transition metals act as Lewis acids

• Form complexes/complex ions  $\mathrm{Fe}^{3*}(\mathrm{aq}) + 6\mathrm{CN}^{\text{-}}(\mathrm{aq}) \twoheadrightarrow \mathrm{Fe}(\mathrm{CN})_6{}^{3\text{-}}(\mathrm{aq})$ 

Lewis acid Lewis base Complex ion

$$\label{eq:Ni2+} \begin{split} Ni^{2+}(aq) + 6NH_3(aq) & \rightarrow Ni(NH_3)_6^{2+}(aq) \\ \text{Lewis acid} \quad \text{Lewis base} \qquad \text{Complex ion} \end{split}$$

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = metal = center of coordination

Lewis base = **ligand** = molecules/ions covalently bonded to metal in complex







#### Coordination Chemistry Neutral charge of coordination compound = sum of

charges on metal, ligands, and counterbalancing ions

[Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>

neutral compound

#### Coordination Chemistry Neutral charge of coordination compound = sum of

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## Coordination Complexes

- What is a coordinate covalent bond?
- A covalent bond between the transition metal and a ligand formed by a two-electron donation from the ligand to the metal, using a lone pair
- Coordination Number (CN)= number of coordinate bonds to the metal

## **Coordination Complexes**

- How does this differ from a regular covalent bond?
- In a regular covalent bond, each atom contributes 1 electron to form the bond. Here <u>the ligand is bringing both electrons</u> to form the bond!

#### **Coordination Complexes**

- How do ligands bond to a transition metal?
- Coordinate complexes received their namesake due to the <u>coordinate covalent</u> <u>bonds</u> they form with empty d-orbitals of the metal.

## **Coordination Chemistry**

#### ♦Ligands

▲ Are classified according to the number of donor atoms

- ▲ Examples
  - \* monodentate = 1
  - \* bidentate = 2
  - \*tetradentate = 4
  - \*hexadentate = 6
- \* polydentate = 2 or more donor atoms



## QUESTION

500.0 mL of 0.020 M Mn(NO<sub>3</sub>)<sub>2</sub> are mixed with 1.0 L of 1.0 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The oxalate ion, C<sub>2</sub>O<sub>4</sub><sup>2</sup>, acts as a ligand to form a complex ion with the Mn<sup>2+</sup> ion with a coordination number of two.

 $\begin{array}{l} \mathrm{Mn}^{2+} + \mathrm{C_2O_4}^{2-} & & \mathrm{MnC_2O_4} \\ [\mathrm{Mn}(\mathrm{C_2O_4})_2]^{2-} & & \mathrm{MnC_2O_4} + \mathrm{C_2O_4}^{2-} \end{array}$ 

 $K_1 = 7.9 \ge 10^3$  $K_2 = 1.26 \ge 10^{-2}$ 

 $_{2}O_{4} + C_{2}O_{4}^{2-}$   $K_{2} = 1.26 \text{ x } 1$ 

What is the equilibrium constant for the following formation?  $Mn^{2+} + 2C_2O_4^{2-} \rightarrow [Mn(C_2O_4)_2]^{2-}$ 

A) 1.0
B) 3.7 x 10<sup>2</sup>
C) 2.1 x 10<sup>-1</sup>
D) 6.3 x 10<sup>5</sup>

## **ANSWER** 500.0 mL of 0.020 *M* Mn(NO<sub>3</sub>)<sub>2</sub> are mixed with 1.0 L of 1.0 *M* Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The oxalate ion, C<sub>2</sub>O<sub>4</sub><sup>2</sup>, acts as a ligand to form a complex ion with the Mn<sup>2+</sup> ion with a coordination number of two. Mn<sup>2+</sup> + C<sub>2</sub>O<sub>4</sub><sup>2-</sup> $\longrightarrow$ MnC<sub>2</sub>O<sub>4</sub> $K_1 = 7.9 \times 10^3$ [Mn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> $\implies$ MnC<sub>2</sub>O<sub>4</sub> + C<sub>2</sub>O<sub>4</sub><sup>2-</sup> $K_2 = 1.26 \times 10^{-2}$ What is the equilibrium constant for the following formation? Mn<sup>2+</sup> + C<sub>2</sub>O<sub>4</sub><sup>2-</sup> $\implies$ [Mn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> A) 1.0 B) 3.7 × 10<sup>2</sup> C) 2.1 × 10<sup>-1</sup> D) 6.3 × 10<sup>5</sup>

















#### **Coordination Compound Summary**

- Lewis acids are electron pair acceptors.
- Coordination compounds are metal compounds formed by Lewis acid-base interactions.
- Complexes: Have a metal ion (can be zero oxidation state) bonded to a number of ligands. Complex ions are charged. Example, [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.
- Ligands are Lewis bases.
- Coordination number: the number of ligands attached to the metal.

#### **Coordination Numbers and Geometry**

- The most common coordination numbers are 4 and 6.
- Some metal ions have a constant coordination number (e.g. Cr<sup>3+</sup> and Co<sup>3+</sup> have a coordination number of 6).
- The size of the ligand affects the coordination number (e.g. [FeF<sub>6</sub>]<sup>3</sup> forms but only [FeCl<sub>4</sub>]<sup>-</sup> is stable).
- The amount of charge transferred from ligand to metal affects coordination number (e.g.  $[Ni(NH_3)_6]^{2+}$  is stable but only  $[Ni(CN)_4]^{2-}$  is stable).
- Four coordinate complexes are either tetrahedral or square planar (commonly seen for *d*<sup>8</sup> metal ions).
- Six coordinate complexes are octahedral.



	Num	bers, Sh	napes
	Coordination N	umbers and	Shapes of Some
Coordinati Number	Shape		Examples
2	Linear		[CuCl <sub>2</sub> ] <sup>-</sup> , [Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> , [AuCl <sub>2</sub> ] <sup>-</sup>
4	Square planar	-	$[Ni(CN)_4]^{2-}$ , $[PdCI_4]^{2-}$ , $[Pt(NH_3)_4]^{2+}$ , $[Cu(NH_3)_4]^2$
4	Tetrahedral	4	[Cu(CN) <sub>4</sub> ] <sup>3-</sup> , [Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> [CdCl <sub>4</sub> ] <sup>2-</sup> , [MnCl <sub>4</sub> ] <sup>2-</sup>
6	Octahedral	-	$\begin{array}{l} [\text{Ti}(\text{H}_2\text{O})_6]^{3+}, [\text{V}(\text{CN})_6]^{4-}, \\ [\text{Cr}(\text{NH}_3)_4\text{CL}_2]^+, \\ [\text{Mn}(\text{H}_2\text{O})_6]^{2+}, [\text{FeCl}_6]^{3-}, \\ [\text{Co}(\text{en})_3]^{3+} \end{array}$







#### Ligands

• Monodentate ligands bind through one donor atom only.

Therefore they occupy only one coordination site.

- Polydentate ligands (or chelating agents) bind through more than one donor atom per ligand. Example, ethylenediamine (en), H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>.
- The octahedral [Co(en)<sub>3</sub>]<sup>3+</sup> is a typical en complex.
- Chelate effect: More stable complexes are formed with chelating agents than with the equivalent number of monodentate ligands.





## ANSWER

E) six

Species found outside of the brackets are not directly bonded to the metal ion.

## **QUESTION**

The following compound has two atoms of Pt with two different oxidation states. What are the two states, respectively, for Pt in the compound  $[Pt(NH_3)_4I_2][PtI_4]$ ?

A.+2; +4 B.+4; +2 C.+6; +2 D.+4; 0

## **ANSWER**

В

The charge on the cation equals the charge on the anion. If Pt = +4, the charge on the cation would be +2. In the anion, Pt's charge of +2 would allow a -2 anion, which would bond to the +2 cation in a 1:1 ratio as shown in the compound.

#### Nomenclature

- Rules:
  - ♦ For salts, name the cation before the anion. Example in [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> we name [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> before Cl<sup>-</sup>.
  - Within a complex ion, the ligands are named (in alphabetical order) before the metal. Example [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> is pentamminechlorocobalt(III). Note the penta portion is an indication of the number of NH<sub>3</sub> groups and is therefore not considered in the alphabetizing of the ligands.
  - Anionic ligands end in -o and neutral ligands are simply the name of the molecule. Exceptions: H<sub>2</sub>O (aqua) and NH<sub>3</sub> (ammine).

## Nomenclature

#### • Rules:

- Greek prefixes are used to indicate number of ligands (di-, tri-, tetra-, penta-, and hexa-). Exception: if the ligand name has a Greek prefix already. Then enclose the ligand name in parentheses and use bis-, tris-, tetrakis-, pentakis-, and hexakis.
  - $\label{eq:constraint} & \& Example \ [Co(en)_3]Cl_3 \ is \ tris(ethylenediamine)cobalt(III) \\ chloride. \end{cases}$
- $\bigstar$  If the complex is an anion, the name ends in -ate.
- Oxidation state of the metal is given in Roman numerals in parenthesis at the end of the complex name.

## Names of Some Neutral and Anionic Ligands

Name	Formula	
A. Neutral		
Aqua	H <sub>2</sub> O	
Ammine	NH <sub>3</sub>	
Carbonyl	CO	
Nitrosyl	NO	
B. Anionic		
Fluoro	F -	
Chloro	Cl-	
Bromo	Br	
Iodo	I-	
Hydroxo	OH-	
Cyano	CN-	

Na	Names of Some Metal lons in Complex Anions				
	Metal (Cation)	Name in Anion			
	Lead	Plumbate			
	Silver	Argentate			
	Gold	Aurate			
	Tin	Stannate			

Transition Metal	Name if in Cationic Complex	Name if in Anionic Complex
Sc	Scandium	Scandate
Ti	titanium	titanate
V	vanadium	vanadate
Cr	chromium	chromate
Mn	manganese	manganate
Fe	iron	ferrate
Со	cobalt	cobaltate
Ni	nickel	nickelate
Cu	Copper	cuprate
Zn	Zinc	zincate

# QUESTION

What is the formula of tris(ethylenediamine)manganese(II)nitrate?

 $\begin{array}{l} A.[Mn(en)_{3}]NO_{3}\\ B.[Mn(en)_{4}](NO_{3})_{2}\\ C.[Mn(EDTA)_{3}]NO_{3}\\ D.[Mn(en)_{3}](NO_{3})_{2} \end{array}$ 

# ANSWER

D

Note that the prefix "tris" is used when a ligand that has a prefix in its name is used three times. Since ethylenediamine is neutral and the Mn ion is +2, two NO<sub>3</sub><sup>-</sup> counter ions would be required.

# QUESTION

In the compound tetraamminechloronitritocobalt (III) chloride what is the total negative charge contributed by ligands? Also, how many chloride counterions are attached to the cation?

A.Zero; 3 B.-1; 2 C.-2; 1 D.-3; 2

# ANSWER

#### С

In the compound, there are three ligands.  $NH_3$  is neutral and therefore contributing no negative charge.  $NO_2^-$  contributes a total of -1 and  $Cl^-$  also contributes -1. Therefore, the total negative charge from ligands is -2. When this is added to the +3 charge from Co, the result is an overall +1 for the cation. This would require only 1 Cl<sup>-</sup> counterion.

Coordination Compounds of Cobalt Studied by Werner						
Traditional Formula	<u>Werner</u> Total Ions	<u>''s Data*</u> Free Cl <sup>.</sup>	Modern Formula	Charge of Complex Ion		
$CoCl_3 \cdot 6 NH_3$	4	3	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	3+		
CoCl <sub>3</sub> • 5 NH <sub>3</sub>	3	2	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	2+		
CoCl <sub>3</sub> • 4 NH <sub>3</sub>	2	1	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl	1+		
CoCl <sub>3</sub> • 3 NH <sub>3</sub>	0	0	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]			

#### Verner's Observations

- CoCl<sub>3</sub>·nNH<sub>3</sub> (n = 1 4) can exist as four different compounds with different numbers of "free" Cl<sup>-</sup> ions per formula unit.
- The NH<sub>3</sub> ligands are covalently bonded to the central  $\mathrm{Co}^{3+}$  ion.
- A maximum of six ligands can be bonded to the central cobalt atom.
- There are two isomers for the Cl ligands attached to cobalt of CoCl<sub>3</sub>·4NH<sub>3</sub>.



## **Coordination Complexes**

• Now that we've seen how coordination complexes form, let's take a look at the how the relative energy values of the d-orbitals

We'll look at the d-orbital splitting in the three most common shapes: octahedral, tetrahedral, and square planar

## Coordination Chemistry

#### • Coordination compound

- Compound that contains 1 or more complexes
- Example
  - [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>
  - [Cu(NH<sub>3</sub>)<sub>4</sub>][PtCl<sub>4</sub>]
  - [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]

# Coordination Chemistry Coordination sphere Metal and ligands bound to it Coordination number number of donor atoms bonded to the central netal atom or ion in the complex \*Most common = 4, 6 \*Determined by ligands Larger ligands and those that transfer substantial negative charge to metal favor lower coordination numbers

#### Name the following complex ions.

a. Ru(NH<sub>3</sub>)<sub>5</sub>Cl<sub>2</sub><sup>+</sup>

- b.  $Fe(CN)_6^{4-}$
- c. Mn(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub><sup>2+</sup>
- d. Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub><sup>2+</sup>

#### Name the following coordination compounds.

- a. [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>
- b.  $[Co(H_2O)_6]I_3$
- c.  $K_2$  [PtCl<sub>4</sub>]
- d. K<sub>4</sub>[PtCl<sub>6</sub>]

#### Give the formulas for the following.

- a. Hexakispyridinecobalt(III)chloride
- b. Pentaammineiodochromium(III) iodide
- c. Trisethylenediamminenickel(II)bromide
- d. Potassium tetracyanonickelate(II)
- e. Tetraamminedichloroplatinum(IV) f. Tetrachloroplatinate(II)
- Draw geometrical isomers of each of the following complex ions.
  - - a.  $[Co(C_2O_4)_2(H_2O_2)]^{-1}$ b.  $[Pt(NH_3)_4I_2]^{2+}$

    - c. [Ir(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]
  - d.  $[Cr(en(NH_3)_2I_2]^+$