

# CHEM 4A: GENERAL CHEMISTRY FOR MAJORS I



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# UC Davis: Chem 2AH Honors General Chemistry I

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## Licensing

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### 1: The Atom in Modern Chemistry

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### 3.3: Ionization Energies and the Shell Model of the Atom

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### 3.5: Forces and Potential Energy in Molecules: Formation of Chemical Bonds

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## 4.1: Preliminaries: Wave Motion and Light

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7.7: Pesticides and Pharmaceuticals

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## 7.1: Petroleum Refining and the Hydrocarbons

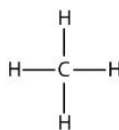
### Learning Objectives

- To get an overview of hydrocarbons molecules and their four primary classifications

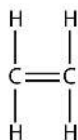
Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

1. Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon species. They are composed entirely of single bonds and are saturated with hydrogen. The general formula for saturated hydrocarbons is  $C_nH_{2n+2}$  (assuming non-cyclic structures). Saturated hydrocarbons are the basis of petroleum fuels and are found as either linear or branched species. The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:



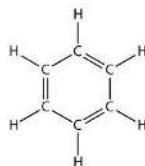
2. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes and those with one double bond have the formula  $C_nH_{2n}$  (assuming non-cyclic structures). Those containing triple bonds are called alkynes, with general formula  $C_nH_{2n-2}$ . The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:



The smallest alkyne is ethyne, which is also known as acetylene:



3. Cycloalkanes are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is  $C_nH_{2n}$ .
4. Aromatic hydrocarbons, also known as arenes, are hydrocarbons that have at least one aromatic ring. Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



Because of differences in molecular structure, the empirical formula remains different between hydrocarbons; in linear, or "straight-run" alkanes, alkenes and alkynes, the amount of bonded hydrogen lessens in alkenes and alkynes due to the "self-bonding" or catenation of carbon preventing entire saturation of the hydrocarbon by the formation of double or triple bonds.

The inherent ability of hydrocarbons to bond to themselves is known as catenation, and allows hydrocarbon to form more complex molecules, such as cyclohexane, and in rarer cases, arenes such as benzene. This ability comes from the fact that the bond character between carbon atoms is entirely non-polar, in that the distribution of electrons between the two elements is somewhat even due to the same electronegativity values of the elements (~0.30).

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## 7.2: The Alkanes

### Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and propane (C<sub>3</sub>H<sub>8</sub>) and they are shown again in Figure 7.2.1.

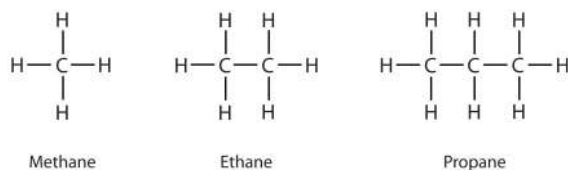


Figure 7.2.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 7.2.2).

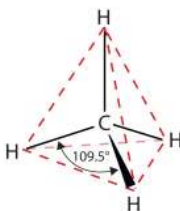


Figure 7.2.2: The Tetrahedral Methane Molecule

Methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and propane (C<sub>3</sub>H<sub>8</sub>) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH<sub>2</sub> unit. The first 10 members of this series are given in Table 7.2.1.

Table 7.2.1: The First 10 Straight-Chain Alkanes

| Name    | Molecular Formula (C <sub>n</sub> H <sub>2n + 2</sub> ) | Condensed Structural Formula                                                    | Number of Possible Isomers |
|---------|---------------------------------------------------------|---------------------------------------------------------------------------------|----------------------------|
| methane | CH <sub>4</sub>                                         | CH <sub>4</sub>                                                                 | —                          |
| ethane  | C <sub>2</sub> H <sub>6</sub>                           | CH <sub>3</sub> CH <sub>3</sub>                                                 | —                          |
| propane | C <sub>3</sub> H <sub>8</sub>                           | CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>                                 | —                          |
| butane  | C <sub>4</sub> H <sub>10</sub>                          | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>                 | 2                          |
| pentane | C <sub>5</sub> H <sub>12</sub>                          | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> | 3                          |

| Name    | Molecular Formula ( $C_nH_{2n+2}$ ) | Condensed Structural Formula               | Number of Possible Isomers |
|---------|-------------------------------------|--------------------------------------------|----------------------------|
| hexane  | $C_6H_{14}$                         | $CH_3CH_2CH_2CH_2CH_2CH_3$                 | 5                          |
| heptane | $C_7H_{16}$                         | $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$             | 9                          |
| octane  | $C_8H_{18}$                         | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$         | 18                         |
| nonane  | $C_9H_{20}$                         | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$     | 35                         |
| decane  | $C_{10}H_{22}$                      | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | 75                         |

Consider the series in Figure 7.2.3. The sequence starts with  $C_3H_8$ , and a  $CH_2$  unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a  $CH_2$  group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

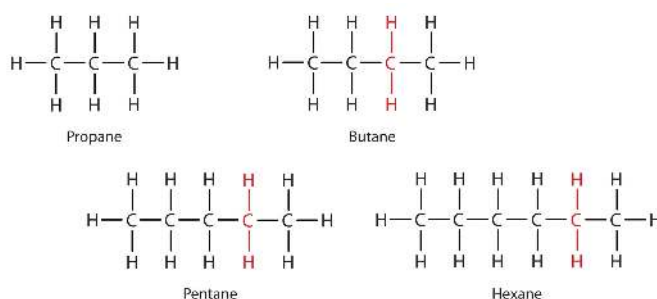


Figure 7.2.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes:  $C_nH_{2n+2}$ . Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula  $C_8H_{(2 \times 8) + 2} = C_8H_{18}$ .

### Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a  $CH_2$  unit.

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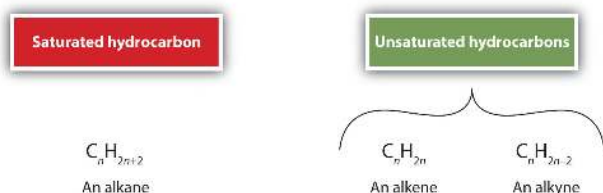
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## 7.3: The Alkenes and Alkynes

### Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ( $R_2C=CR_2$ ) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ( $R-C\equiv C-R$ ). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

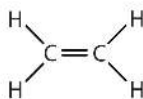


Some representative alkenes—their names, structures, and physical properties—are given in Table 7.3.1.

Table 7.3.1: Physical Properties of Some Selected Alkenes

| IUPAC Name | Molecular Formula | Condensed Structural Formula | Melting Point (°C) | Boiling Point (°C) |
|------------|-------------------|------------------------------|--------------------|--------------------|
| ethene     | $C_2H_4$          | $CH_2=CH_2$                  | −169               | −104               |
| propene    | $C_3H_6$          | $CH_2=CHCH_3$                | −185               | −47                |
| 1-butene   | $C_4H_8$          | $CH_2=CHCH_2CH_3$            | −185               | −6                 |
| 1-pentene  | $C_5H_{10}$       | $CH_2=CH(CH_2)_2CH_3$        | −138               | 30                 |
| 1-hexene   | $C_6H_{12}$       | $CH_2=CH(CH_2)_3CH_3$        | −140               | 63                 |
| 1-heptene  | $C_7H_{14}$       | $CH_2=CH(CH_2)_4CH_3$        | −119               | 94                 |
| 1-octene   | $C_8H_{16}$       | $CH_2=CH(CH_2)_5CH_3$        | −102               | 121                |

We used only condensed structural formulas in Table 7.3.1. Thus,  $CH_2=CH_2$  stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is  $C_2H_4$ , whereas that for ethane is  $C_2H_6$ .

The first two alkenes in Table 7.3.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 7.3.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

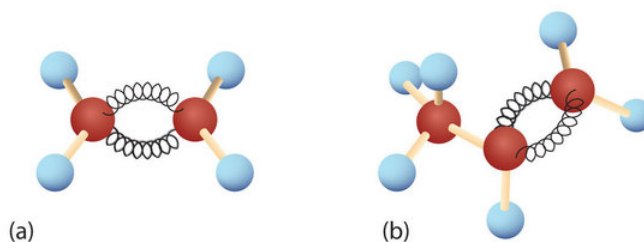
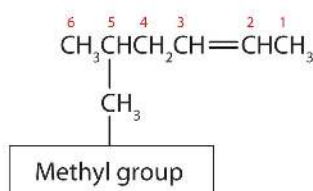


Figure 7.3.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula  $C_2H_4$  (ethene) and only one with the formula  $C_3H_6$  (propene), there are several alkenes with the formula  $C_4H_8$ .

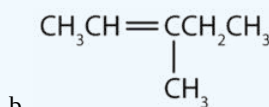
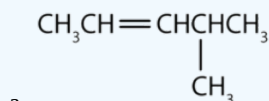
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound  $CH_2=CHCH_3$  is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbon atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers. The compound  $CH_3CH=CHCH_2CH_3$ , for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



### ✓ Example 7.3.1

Name each compound.

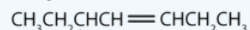
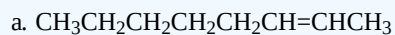


### Solution

- The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
- The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

### ? Exercise 7.3.1

Name each compound.



### Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

### ✓ Example 7.3.2

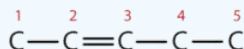
Draw the structure for each compound.

- 3-methyl-2-pentene
- cyclohexene

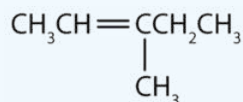
### Solution

a.

First write the parent chain of five carbon atoms:  $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$ . Then add the double bond between the second and third carbon atoms:

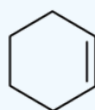


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



### ? Exercise 7.3.2

Draw the structure for each compound.

- 2-ethyl-1-hexene
- cyclopentene

### Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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## 7.4: Aromatic Hydrocarbons

### Learning Objectives

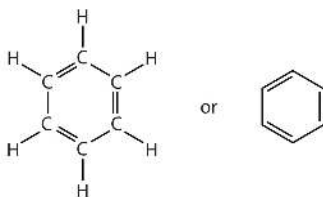
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene ( $C_6H_6$ ) is of great commercial importance, but it also has noteworthy health effects.

The formula  $C_6H_6$  seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula  $C_6H_{14}$ —eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at  $80^\circ C$ , and freezes at  $5.5^\circ C$ . It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

### To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or

heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

### Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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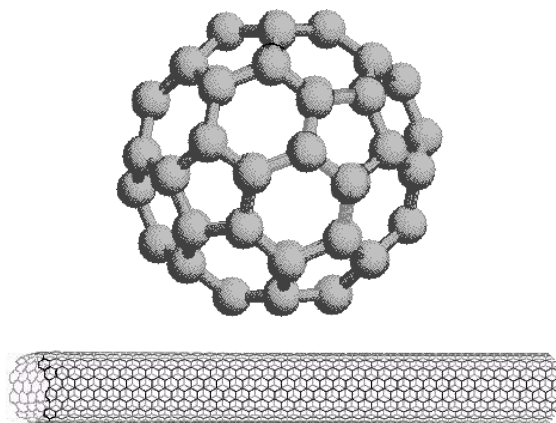
## 7.5: Fullerenes

If we extend the structure of corannulene by adding similar cycles of five benzene rings, the curvature of the resulting molecule should increase, and eventually close into a sphere of carbon atoms. The archetypical compound of this kind ( $C_{60}$ ) has been named **buckminsterfullerene** because of its resemblance to the geodesic structures created by Buckminster Fuller. It is a member of a family of similar carbon structures that are called **fullerenes**. These materials represent a third class of carbon allotropes. Alternating views of the  $C_{60}$  fullerene structure are shown on the right, together with a soccer ball-like representation of the 12 five and 20 six-membered rings composing its surface. Precise measurement by Atomic Force Microscopy (AFM) has shown that the C-C bond lengths of the six-membered rings are not all equal, and depend on whether the ring is fused to a five or six-membered neighbor. [By clicking on this graphic, a model of  \$C\_{60}\$  will be displayed.](#)

Although  $C_{60}$  is composed of fused benzene rings its chemical reactivity resembles that of the cycloalkenes more than benzene. Indeed, exposure to light and oxygen slowly degrade fullerenes to cage opened products. Most of the reactions thus far reported for  $C_{60}$  involve addition to, rather than substitution of, the core structure. These reactions include hydrogenation, bromination and hydroxylation. Strain introduced by the curvature of the surface may be responsible for the enhanced reactivity of  $C_{60}$ .

Larger fullerenes, such as  $C_{70}$ ,  $C_{76}$ ,  $C_{82}$  &  $C_{84}$  have ellipsoidal or distorted spherical structures, and fullerene-like assemblies up to  $C_{240}$  have been detected. A fascinating aspect of these structures is that the space within the carbon cage may hold atoms, ions or small molecules. Such species are called **endohedral fullerenes**. The cavity of  $C_{60}$  is relatively small, but encapsulated helium, lithium and atomic nitrogen compounds have been observed. Larger fullerenes are found to encapsulate lanthanide metal atoms.

Interest in the fullerenes has led to the discovery of a related group of carbon structures referred to as nanotubes. As shown in the following illustration, nanotubes may be viewed as rolled up segments of graphite. The chief structural components are six-membered rings, but changes in tube diameter, branching into side tubes and the capping of tube ends is accomplished by fusion with five and seven-membered rings.



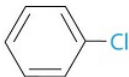
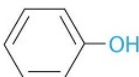
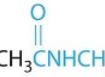
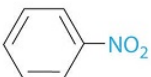
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## 7.6: Functional Groups and Organic Reactions

### Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as  $\text{CO}_2\text{H}$ ). The major families of organic compounds are characterized by their functional groups. Figure 7.6.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

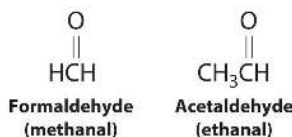
| Class                                | General Formula         | Example                                                                             | Common Name (Systematic Name)     | Common Suffix/Prefix (Systematic) |
|--------------------------------------|-------------------------|-------------------------------------------------------------------------------------|-----------------------------------|-----------------------------------|
| <b>Hydrocarbons</b>                  |                         |                                                                                     |                                   |                                   |
| Alkanes                              | $RH$                    | $CH_3CH_3$                                                                          | ethane                            | -ane                              |
| Alkenes                              | $RR'C=CR''R'''$         | $H_2C=CH_2$                                                                         | ethylene (ethene)                 | -ene                              |
| Alkynes                              | $RC\equiv CR'$          | $HC\equiv CH$                                                                       | acetylene (ethyne)                | (-yne)                            |
| Arenes                               | $ArH^a$                 |    | benzene                           | -ene                              |
| <b>Halogen-Containing Compounds</b>  |                         |                                                                                     |                                   |                                   |
| Alkyl halides                        | $RX$                    | $CH_3CH_2Cl$                                                                        | ethyl chloride (chloroethane)     | halide (halo-)                    |
| Aryl halides                         | $ArX^a$                 |    | chlorobenzene                     | halo-                             |
| <b>Oxygen-Containing Compounds</b>   |                         |                                                                                     |                                   |                                   |
| Alcohols                             | $ROH^a$                 | $CH_3CH_2OH$                                                                        | ethyl alcohol (ethanol)           | -ol                               |
| Phenols                              | $ArOH^b$                |    | phenol                            | -ol                               |
| Ethers                               | $ROR'$                  | $H_3CH_2COCH_2CH_3$                                                                 | diethyl ether                     | ether                             |
| Aldehydes                            | $RCHO$                  |  | acetaldehyde (ethanal)            | -aldehyde (-al)                   |
| Ketones                              | $RR'C=O$                |  | acetone (2-propanone)             | -one                              |
| Carboxylic acids                     | $RCO_2H$                |  | acetic acid (ethanoic acid)       | -ic acid (-oic acid)              |
| <b>Carboxylic Acid Derivatives</b>   |                         |                                                                                     |                                   |                                   |
| Esters                               | $RCO_2R'$               |  | methyl acetate (methyl ethanoate) | -ate (-oate)                      |
| Amides                               | $RCONHR'$               |  | N-methylacetamide                 | -amide                            |
| <b>Nitrogen-Containing Compounds</b> |                         |                                                                                     |                                   |                                   |
| Amines                               | $RNH_2, RNHR', RNR'R''$ | $CH_3CH_2NH_2$                                                                      | ethylamine                        | -amine                            |
| Nitriles                             | $RC\equiv N$            | $H_3C\equiv N$                                                                      | acetonitrile                      | -nitrile                          |
| Nitro compounds                      | $ArNO_2^a$              |  | nitrobenzene                      | nitro-                            |

<sup>a</sup>R indicates an alkyl group <sup>b</sup>Ar indicates an aryl group.

Figure 7.6.1: Major Classes of Organic Compounds

The first family listed in Figure 7.6.1 is the hydrocarbons. These include alkanes, with the general molecular formula  $C_nH_{2n+2}$  where  $n$  is an integer; alkenes, represented by  $C_nH_{2n}$ ; alkynes, represented by  $C_nH_{2n-2}$ ; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the  $-CO_2H$  functional group is replaced by either an alkoxy ( $-OR$ ) group, producing an ester, or by an amido ( $-NRR'$ , where  $R$  and  $R'$  can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a  $C\equiv N$  bond; and nitro compounds, which contain the  $-NO_2$  group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone,  $(CH_3)_2C=O$ ]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first  $CH_3$  group in dimethyl benzene is indicated with a 1, but the second  $CH_3$  group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 7.6.2). In common nomenclature, in contrast, the prefixes *ortho*-, *meta*-, and *para*- are used to describe the relative positions of groups attached to an aromatic ring. If the  $CH_3$  groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called *ortho*-xylene, abbreviated *o*-xylene. If they are across from each other on the ring, the compound is commonly called *para*-xylene or *p*-xylene. When the arrangement is intermediate between those of *ortho*- and *para*- compounds, the name is *meta*-xylene or *m*-xylene.

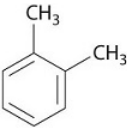
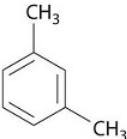
| Prefix         | Positions of Methyl Groups | Example                                                                             | Common Name (Systematic Name)          |
|----------------|----------------------------|-------------------------------------------------------------------------------------|----------------------------------------|
| <i>ortho</i> - | 1,2                        |  | <i>o</i> -xylene (1,2-dimethylbenzene) |
| <i>meta</i> -  | 1,3                        |  | <i>m</i> -xylene (1,3-dimethylbenzene) |
| <i>para</i> -  | 1,4                        |  | <i>p</i> -xylene (1,4-dimethylbenzene) |

Figure 7.6.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

## Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

## Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

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## 7.7: Pesticides and Pharmaceuticals

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## CHAPTER OVERVIEW

### 8: Bonding in Transition Metal Compounds and Coordination Complexes

#### Topic hierarchy

- 8.1: Chemistry of the Transition Metals
- 8.2: Bonding in Simple Molecules That Contain Transition Metals
- 8.3: Introduction to Coordination Chemistry
- 8.4: Structures of Coordination Complexes
- 8.5: Crystal Field Theory: Optical and Magnetic Properties
- 8.6: Optical Properties and the Spectrochemical Series
- 8.7: Bonding in Coordination Complexes

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## 8.1: Chemistry of the Transition Metals

This page explains what a transition metal is in terms of its electronic structure, and then goes on to look at the general features of transition metal chemistry. These include variable oxidation state (oxidation number), complex ion formation, colored ions, and catalytic activity.

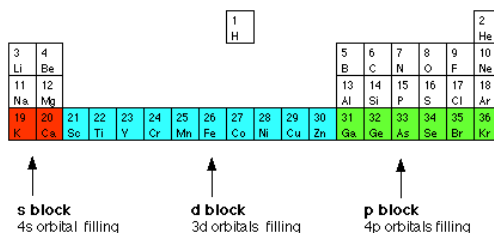
### What is a transition metal?

The terms transition metal (or element) and d block element are sometimes used as if they mean the same thing. They don't - there's a subtle difference between the two terms. We'll explore d block elements first:

#### d-block elements

You will remember that when you are building the [Periodic Table](#) and working out where to put the electrons using the [Aufbau Principle](#), something odd happens after argon.

At argon, the 3s and 3p levels are full, but rather than fill up the 3d levels next, the 4s level fills instead to give potassium and then calcium. Only after that do the 3d levels fill. The elements in the Periodic Table which correspond to the d levels filling are called **d block elements**. The first row of these is shown in the shortened form of the Periodic Table below.



The electronic structures of the d block elements shown are:

|    |                            |
|----|----------------------------|
| Sc | $[\text{Ar}] 3d^1 4s^2$    |
| Ti | $[\text{Ar}] 3d^2 4s^2$    |
| V  | $[\text{Ar}] 3d^3 4s^2$    |
| Cr | $[\text{Ar}] 3d^5 4s^1$    |
| Mn | $[\text{Ar}] 3d^5 4s^2$    |
| Fe | $[\text{Ar}] 3d^6 4s^2$    |
| Co | $[\text{Ar}] 3d^7 4s^2$    |
| Ni | $[\text{Ar}] 3d^8 4s^2$    |
| Cu | $[\text{Ar}] 3d^{10} 4s^1$ |
| Zn | $[\text{Ar}] 3d^{10} 4s^2$ |

You will notice that the pattern of filling is not entirely tidy! It is broken at both chromium and copper.

#### Transition metals

Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:

*The official IUPAC definition:*

**A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.**

*The older definition:*

**A transition metal is one which forms one or more stable ions which have *incompletely* filled d orbitals.**

Notice how similar these two definitions are. The only difference is that the IUPAC definition allows for the atom itself having incompletely filled d levels as well as the ions.

The problem lies only at the extreme left-hand end of the d block with, for example, scandium: Scandium has the electronic structure  $[\text{Ar}] 3d^1 4s^2$ . When it forms ions, it always loses the 3 outer electrons and ends up with an argon structure. The  $\text{Sc}^{3+}$  ion has **no d electrons** and so does not meet the second (older) definition.

Zinc has the electronic structure  $[\text{Ar}] 3d^{10} 4s^2$ . When it forms ions, it always loses the two 4s electrons to give a  $2+$  ion with the electronic structure  $[\text{Ar}] 3d^{10}$ . The zinc ion has **full d levels** and does not meet either definition.

By contrast, copper,  $[\text{Ar}] 3d^{10} 4s^1$ , forms two ions. In the  $\text{Cu}^+$  ion the electronic structure is  $[\text{Ar}] 3d^{10}$ . However, the more common  $\text{Cu}^{2+}$  ion has the structure  $[\text{Ar}] 3d^9$ . Copper is definitely a transition metal because the  $\text{Cu}^{2+}$  ion has an incomplete d level.

### Transition metal ions

Here you are faced with one of the most irritating facts in chemistry at this level! When you work out the electronic structures of the first transition series (from scandium to zinc) using the [Aufbau Principle](#), you do it on the basis that the 3d orbitals have higher energies than the 4s orbitals.

That means that you work on the assumption that the 3d electrons are added after the 4s ones. However, in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.

It is important to note that when d block elements form ions, the 4s electrons are always lost first.

To write the electronic structure for  $\text{Co}^{2+}$ :

|                  |  |                         |
|------------------|--|-------------------------|
| Co               |  | $[\text{Ar}] 3d^7 4s^2$ |
| $\text{Co}^{2+}$ |  | $[\text{Ar}] 3d^7$      |

The  $2+$  ion is formed by the loss of the two 4s electrons.

To write the electronic structure for  $\text{V}^{3+}$ :

|                 |  |                         |
|-----------------|--|-------------------------|
| V               |  | $[\text{Ar}] 3d^3 4s^2$ |
| $\text{V}^{3+}$ |  | $[\text{Ar}] 3d^2$      |

The 4s electrons are lost first followed by one of the 3d electrons.

### Variable oxidation state (number)

One of the key features of transition metal chemistry is the wide range of [oxidation states](#) (oxidation numbers) that the metals can show. It would be wrong, though, to give the impression that only transition metals can have variable oxidation states. For example, elements like Sulfur or nitrogen or chlorine have a very wide range of oxidation states in their compounds - and these obviously aren't transition metals. However, this variability is less common in metals apart from the transition elements. Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.

### Examples of variable oxidation states in the transition metals

- Iron:** Iron has two common oxidation states (+2 and +3) in, for example,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . It also has a less common +6 oxidation state in the ferrate(VI) ion,  $\text{FeO}_4^{2-}$ .
- Manganese:** Manganese has a very wide range of oxidation states in its compounds. For example:

|    |                     |
|----|---------------------|
| +2 | in $\text{Mn}^{2+}$ |
|----|---------------------|

|    |                            |
|----|----------------------------|
| +3 | in $\text{Mn}_2\text{O}_3$ |
| +4 | in $\text{MnO}_2$          |
| +6 | in $\text{MnO}_4^{2-}$     |
| +7 | in $\text{MnO}_4^-$        |

You will find the above examples and others looked at in detail if you explore the chemistry of individual metals from the transition metal menu. There is a link to this menu at the bottom of the page.

## Explaining the variable oxidation states in the transition metals

We'll look at the formation of simple ions like  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process. On the whole, the compound formed is the one in which most energy is released. The more energy released, the more stable the compound. There are several energy terms to think about, but the key ones are:

- The amount of energy needed to ionize the metal (the sum of the various ionization energies)
- The amount of energy released when the compound forms. This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

The more highly charged the ion, the more electrons you have to remove and the more ionization energy you will have to provide. But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

### Thinking about a typical non-transition metal (calcium)

The formula for Calcium chloride is  $\text{CaCl}_2$ . Why is that? If you tried to make  $\text{CaCl}$ , (containing a  $\text{Ca}^+$  ion), the overall process is slightly exothermic. By making a  $\text{Ca}^{2+}$  ion instead, you have to supply more ionization energy, but you get out lots more lattice energy. There is much more attraction between chloride ions and  $\text{Ca}^{2+}$  ions than there is if you only have a  $1+$  ion. The overall process is very exothermic. Because the formation of  $\text{CaCl}_2$  releases much more energy than making  $\text{CaCl}$ , then  $\text{CaCl}_2$  is more stable - and so forms instead.

What about  $\text{CaCl}_3$ ? This time you have to remove yet another electron from calcium. The first two come from the 4s level. The third one comes from the 3p. That is much closer to the nucleus and therefore much more difficult to remove. There is a large jump in ionization energy between the second and third electron removed. Although there will be a gain in lattice enthalpy, it is not anything like enough to compensate for the extra ionization energy, and the overall process is very endothermic. It definitely is not energetically sensible to make  $\text{CaCl}_3$ !

### Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the  $2+$  or the  $3+$  ion.

|                  |  |                         |
|------------------|--|-------------------------|
| Fe               |  | $[\text{Ar}] 3d^6 4s^2$ |
| $\text{Fe}^{2+}$ |  | $[\text{Ar}] 3d^6$      |
| $\text{Fe}^{3+}$ |  | $[\text{Ar}] 3d^5$      |

The 4s orbital and the 3d orbitals have very similar energies. There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second. The figures for the first three ionization energies (in  $\text{kJ mol}^{-1}$ ) for iron compared with those of calcium are:

| metal | 1st IE | 2nd IE | 3rd IE |
|-------|--------|--------|--------|
| Ca    | 590    | 1150   | 4940   |
| Fe    | 762    | 1560   | 2960   |

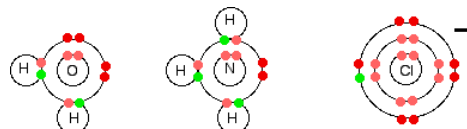
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

In the iron case, the extra ionization energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made. The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say,  $\text{FeCl}_2$  or  $\text{FeCl}_3$ . That means that it is not too difficult to convert between the two compounds.

## The formation of complex ions

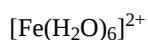
### What is a complex ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion.

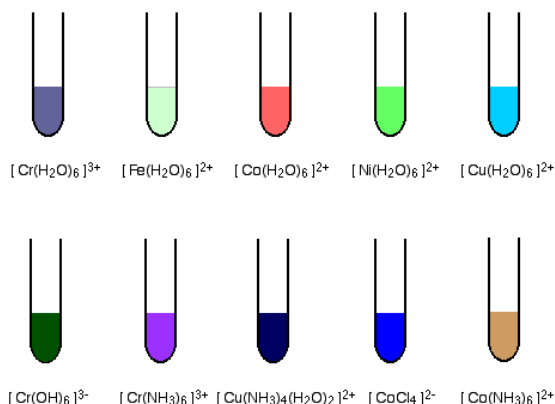
### Some examples of complex ions formed by transition metals



Other metals also form complex ions - it is not something that only transition metals do. Transition metals do, however, form a very wide range of complex ions.

## The formation of colored compounds

The diagrams show approximate colors for some common transition metal complex ions.



You will find these and others discussed if you follow links to individual metals from the transition metal menu (link at the bottom of the page). Alternatively, you could explore the complex ions menu (follow the link in the help box which has just disappeared off the top of the screen).

### The origin of color in the transition metal ions

When white light passes through a solution of one of these ions, or is reflected off it, some colors in the light are absorbed. The color you see is how your eye perceives what is left. Attaching ligands to a metal ion has an effect on the energies of the d orbitals.

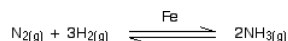
Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

## Catalytic Activity

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

### Iron in the Haber Process

The [Haber Process](#) combines hydrogen and nitrogen to make ammonia using an iron catalyst.



### Nickel in the hydrogenation of C=C bonds

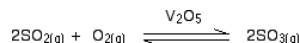
This reaction is at the heart of the manufacture of [margarine](#) from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.



## Transition metal compounds as catalysts

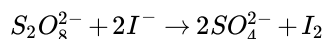
### Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.



### Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions),  $\text{S}_2\text{O}_8^{2-}$ , are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.



## Contributors and Attributions

- Jim Clark ([Chemguide.co.uk](http://Chemguide.co.uk))

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## 8.2: Bonding in Simple Molecules That Contain Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the [transition metals](#) have multiple oxidation states experimentally observed.

### Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on [atomic orbitals](#).

Table 8.2.1

| s Orbital              | p Orbitals                                            | d Orbitals                                                                            |
|------------------------|-------------------------------------------------------|---------------------------------------------------------------------------------------|
| 1 orbital, 2 electrons | 3 orbitals: $p_x$ , $p_y$ , $p_z$ ; 6 electrons       | 5 orbitals: $d_{x^2-y^2}$ , $d_{z^2}$ , $d_{xy}$ , $d_{yz}$ , $d_{xz}$ ; 10 electrons |
|                        | Highest energy orbital for a given quantum number $n$ | Degenerate with s-orbital of quantum number $n+1$                                     |

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

### Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the [Periodic Table](#).

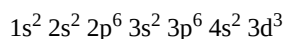
1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on [electron configuration](#).

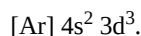
Figure 8.2.1: Periodic Table (Public Domain; PubChem)

Figure 8.2.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.



OR



The neutral atom configurations of the fourth period transition metals are in Table 8.2.2.

Table 8.2.2

| Sc                                      | Ti                                      | V                                       | Cr                                      | Mn                                      | Fe                                      | Co                                      | Ni                                   | Cu                                       | Zn                                       |
|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|--------------------------------------|------------------------------------------|------------------------------------------|
| [Ar]<br>4s <sup>2</sup> 3d <sup>1</sup> | [Ar]<br>4s <sup>2</sup> 3d <sup>2</sup> | [Ar]<br>4s <sup>2</sup> 3d <sup>3</sup> | [Ar]<br>4s <sup>2</sup> 3d <sup>4</sup> | [Ar]<br>4s <sup>2</sup> 3d <sup>5</sup> | [Ar]<br>4s <sup>2</sup> 3d <sup>6</sup> | [Ar]<br>4s <sup>2</sup> 3d <sup>7</sup> | [Ar] 4s <sup>2</sup> 3d <sup>8</sup> | [Ar] 4s <sup>2</sup> 3d <sup>9</sup>     | [Ar]<br>4s <sup>2</sup> 3d <sup>10</sup> |
|                                         |                                         |                                         | [Ar]<br>4s <sup>1</sup> 3d <sup>5</sup> |                                         |                                         |                                         |                                      | [Ar]<br>4s <sup>1</sup> 3d <sup>10</sup> |                                          |

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 8.2.1). The electronic configuration for chromium is not [Ar] 4s<sup>2</sup>3d<sup>4</sup> but instead it is [Ar] 4s<sup>1</sup>3d<sup>5</sup>. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 8.2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

## Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose its s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see [formation of coordination complexes](#).

## ✓ Example 8.2.1

Write the electronic configurations of:

- neutral iron,
- iron(II) ion, and
- iron(III) ion.

**Answer**

The atomic number of iron is 26 so there are 26 protons in the species.

- Fe:  $[\text{Ar}] 4s^2 3d^6$
- $\text{Fe}^{2+}$ :  $[\text{Ar}] 3d^6$
- $\text{Fe}^{3+}$ :  $[\text{Ar}] 3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

## ✓ Example 8.2.2

Determine the more stable configuration between the following pair:

- $[\text{Kr}] 5s^2 4d^6$  vs.  $[\text{Kr}] 5s^1 4d^7$
- $\text{Ag}^{1+}$  vs.  $\text{Ag}^{2+}$

**Answer**

- This describes Ruthenium. There is only one 5s electron.
- Once-oxidized silver ( $[\text{Kr}] 4d^{10}$ ) is more stable than twice- ( $[\text{Kr}] 4d^9$ ).

## Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

| Element Name and Symbol | Atomic Number | Common Oxidation States | Electron Configuration                    |                                                                                                                                                                |
|-------------------------|---------------|-------------------------|-------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Scandium (Sc)           | 21            | +3                      | Sc: [Ar] 4s <sup>2</sup> 3d <sup>1</sup>  | Sc: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$                                                                                                               |
| Titanium (Ti)           | 22            | +4                      | Ti: [Ar] 4s <sup>2</sup> 3d <sup>2</sup>  | Ti: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$                                                                                                |
| Vanadium (V)            | 23            | +2, +3, +4, +5          | V: [Ar] 4s <sup>2</sup> 3d <sup>3</sup>   | V: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$                                                                                  |
| Chromium (Cr)           | 24            | +2, +3, +6              | Cr: [Ar] 4s <sup>1</sup> 3d <sup>5</sup>  | Cr: [Ar] $\frac{1}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$                                                             |
| Manganese (Mn)          | 25            | +2, +3, +4, +6, +7      | Mn: [Ar] 4s <sup>2</sup> 3d <sup>5</sup>  | Mn: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$                                                   |
| Iron (Fe)               | 26            | +2, +3                  | Fe: [Ar] 4s <sup>2</sup> 3d <sup>6</sup>  | Fe: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$                                         |
| Cobalt (Co)             | 27            | +2, +3                  | Co: [Ar] 4s <sup>2</sup> 3d <sup>7</sup>  | Co: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$                               |
| Nickel (Ni)             | 28            | +2                      | Ni: [Ar] 4s <sup>2</sup> 3d <sup>8</sup>  | Ni: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$                     |
| Copper (Cu)             | 29            | +1, +2                  | Cu: [Ar] 4s <sup>1</sup> 3d <sup>10</sup> | Cu: [Ar] $\frac{1}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$           |
| Zinc (Zn)               | 30            | +2                      | Zn: [Ar] 4s <sup>2</sup> 3d <sup>10</sup> | Zn: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ |

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

### ✓ Example 8.2.3

What makes zinc stable as Zn<sup>2+</sup>? What makes scandium stable as Sc<sup>3+</sup>?

#### Answer

Zinc has the neutral configuration [Ar]4s<sup>2</sup>3d<sup>10</sup>. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as [Ar]4s<sup>2</sup>3d<sup>1</sup>. Losing 3 electrons brings the configuration to the noble state with valence 3p<sup>6</sup>.

### ✓ Example 8.2.4

Why is iron almost always Fe<sup>2+</sup> or Fe<sup>3+</sup>?

#### Answer

Iron is written as [Ar]4s<sup>2</sup>3d<sup>6</sup>. Losing 2 electrons from the s-orbital (3d<sup>6</sup>) or 2 s- and 1 d-orbital (3d<sup>5</sup>) electron are fairly stable oxidation states.

### ✓ Example 8.2.5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

#### Answer

Although  $\text{Mn}^{+2}$  is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as  $\text{Mn}_{(s)}$ , Mn(II) as  $\text{MnO}$ , Mn(II,III) as  $\text{Mn}_3\text{O}_4$ , Mn(IV) as  $\text{MnO}_2$ , or manganese dioxide, Mn(VII) in the permanganate ion  $\text{MnO}_4^-$ , and so on.

## Oxidation State of Transition Metals in Compounds

When given an ionic compound such as  $\text{AgCl}$ , you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the **halogen** group of the periodic table, we then know that it has a charge of -1, or simply  $\text{Cl}^-$ . In addition, by seeing that there is no overall charge for  $\text{AgCl}$ , (which is determined by looking at the top right of the compound, i.e.,  $\text{AgCl}^\#$ , where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us  $\text{Ag}^+$  and  $\text{Cl}^-$ , in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

### ✓ Example 8.2.6

Determine the oxidation state of cobalt in  $\text{CoBr}_2$ .

#### Answer

Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 ( $\text{Br}^-$ ). Since there are two bromines each with a charge of -1. In addition, we know that  $\text{CoBr}_2$  has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

### ✓ Example 8.2.7

What is the oxidation state of zinc in  $\text{ZnCO}_3$ . (Note: the  $\text{CO}_3$  anion has a charge state of -2)

#### Answer

Knowing that  $\text{CO}_3$  has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us  $\text{Zn}^{2+}$  and  $\text{CO}_3^{2-}$ , in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

## Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate ( $\text{MnO}_4^-$ ) ion. Since **oxygen** has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us  $\text{Mn}^{7+}$  and  $4\text{O}^{2-}$ , which will result as  $\text{MnO}_4^-$ .

*This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.*

### 📌 Manganese: A Case Study

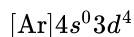
**Manganese** is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.



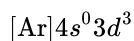
Figure 8.2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

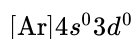
$\text{Mn}_2\text{O}_3$  is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.



$\text{MnO}_2$  is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than  $\text{Mn}^{3+}$ .



$\text{KMnO}_4$  is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.



Since the 3p orbitals are all paired, this complex is diamagnetic.

## Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the [formation of coordination complexes](#) or synthesis of other compounds.

## Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

|                                                            |                                                            |                                                          |
|------------------------------------------------------------|------------------------------------------------------------|----------------------------------------------------------|
| (A) <u>Copper</u> (I) Chloride: $\text{CuCl}$              | (B) <u>Copper</u> (II) Nitrate: $\text{Cu}(\text{NO}_3)_2$ | (C) <u>Gold</u> (V) Fluoride: $\text{AuF}_5$             |
| (D) <u>Iron</u> (II) Oxide: $\text{FeO}$                   | (E) <u>Iron</u> (III) Oxide: $\text{Fe}_2\text{O}_3$       | (F) <u>Lead</u> (II) Chloride: $\text{PbCl}_2$           |
| (G) <u>Lead</u> (II) Nitrate: $\text{Pb}(\text{NO}_3)_2$   | (H) <u>Manganese</u> (II) Chloride: $\text{MnCl}_2$        | (I) <u>Molybdenum</u> trioxide: $\text{MoO}_3$           |
| (J) <u>Nickel</u> (II) Hydroxide: $\text{Ni}(\text{OH})_2$ | (K) <u>Platinum</u> (IV) Chloride: $\text{PtCl}_4$         | (L) <u>Silver</u> Sulfide: $\text{Ag}_2\text{S}$         |
| (M) <u>Tungsten</u> (VI) Fluoride: $\text{WF}_6$           | (N) <u>Vanadium</u> (III) Nitride: $\text{VN}$             | (O) <u>Zirconium</u> Hydroxide: $\text{Zr}(\text{OH})_4$ |

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate ( $\text{MnO}_4^{2-}$ )
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?
4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

## References

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2. Audi A, Sherwood, P. *Valence-band x-ray photoelectron spectroscopic studies of manganese and its oxides interpreted by cluster and band structure calculations*; Surf. Interface Anal.; 2002; 33; 274-282.
3. Reaney S, Kwik-Urbe C, Smith D. *Manganese Oxidation State and Its Implications for Toxicity*. Chem. Res. Toxicol.; 2002; 15; 1119-1126.
4. *CRC Handbook*, 88<sup>th</sup> ed. Sct. 1, Prt. 1 *Electron Configuration and Ionization Energy of Neutral Atoms in the Ground State*; 13-14.
5. *CRC Handbook*, 88<sup>th</sup> ed. Sct. 4, Prt. 1 *Melting, Boiling, Triple, and Critical Point Temperatures of the Elements*; 133-134.

## Contributors and Attributions

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## 8.3: Introduction to Coordination Chemistry

### Learning Objectives

- To introduce complex ions and the basic principles of metal-ligand bonding

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by **coordinate (dative covalent) bonds** (in some cases, the bonding is actually more complicated than that). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.

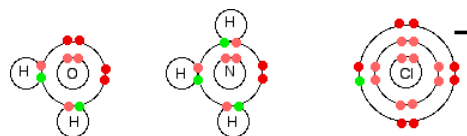


Figure 8.3.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

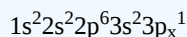
What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as **Lewis bases**.

### Bonding in Simple Complex Ions

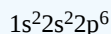
We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

#### ✓ Example 8.3.1: $\text{Al}(\text{H}_2\text{O})_6^{3+}$

Aluminum has the electronic structure

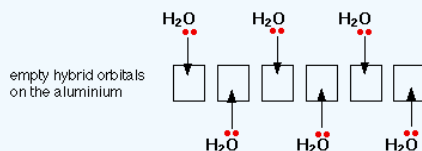


When it forms an  $\text{Al}^{3+}$  ion it loses the 3-level electrons to leave

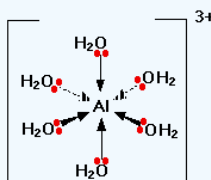


That means that all the 3-level orbitals are now empty. The aluminium uses all six of these empty 3-level orbitals to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that will fit around an aluminum ion (and most other metal ions) due to steric constraints. By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



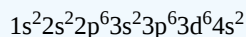
Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of

the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

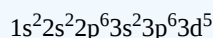
In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

### ✓ Example 8.3.2: $Fe(H_2O)_6^{3+}$

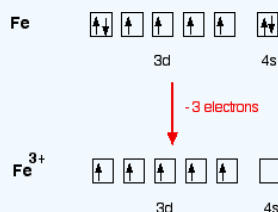
Iron has the electronic structure



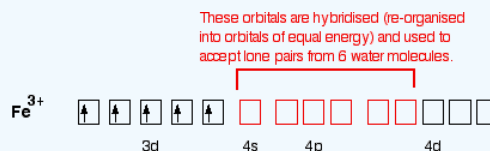
When it forms an  $Fe^{3+}$  ion it loses the 4s electrons and one of the 3d electrons to leave



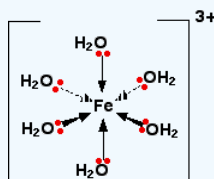
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminium ion.

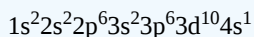


Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

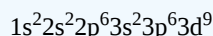
### ✓ Example 8.3.3: $CuCl_4^{2-}$

This is a simple example of the formation of a complex ion with a negative charge.

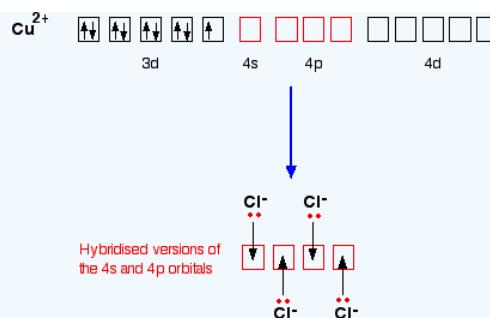
Copper has the electronic structure



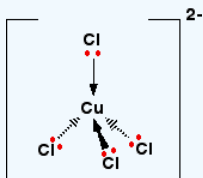
When it forms a  $Cu^{2+}$  ion it loses the 4s electron and one of the 3d electrons to leave



To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridized form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

## Contributors and Attributions

- Jim Clark ([Chemguide.co.uk](http://Chemguide.co.uk))

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## 8.4: Structures of Coordination Complexes

### Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride,  $(\text{NH}_3)_2\text{PtCl}_2$ . This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

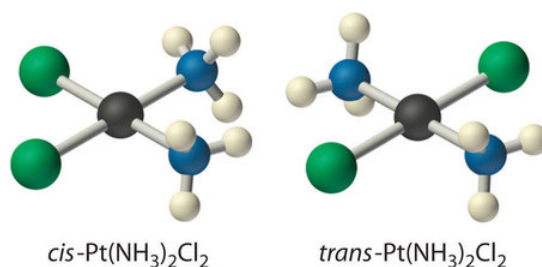


Figure 8.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of [coordination compounds](#) bond together is discussed in the chapter of [Lewis acids and bases](#). For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

### CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

### CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by [MIT](#) chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two amines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

### ? Exercise 8.4.1

Draw the cis and trans isomers of the following compounds:

- $(\text{NH}_3)_2\text{IrCl}(\text{CO})$
- $(\text{H}_3\text{P})_2\text{PtHBr}$
- $(\text{AsH}_3)_2\text{PtH}(\text{CO})$

### ? Exercise 8.4.2

Only one isomer of  $(\text{tmeda})\text{PtCl}_2$  is possible [ $\text{tmeda} = (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ ; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

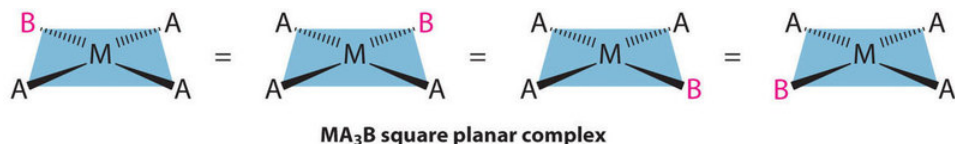
## Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

### Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called **geometrical isomers**. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar  $\text{MA}_3\text{B}$  complex; hence only a single geometrical isomer is possible in this case (and in the analogous  $\text{MAB}_3$  case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



For an  $\text{MA}_2\text{B}_2$  complex, there are two possible isomers: either the A ligands can be adjacent to one another (**cis**), in which case the B ligands must also be cis, or the A ligands can be across from one another (**trans**), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

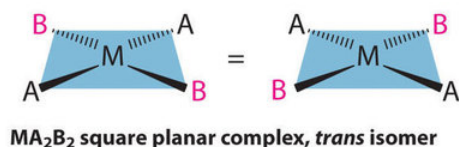
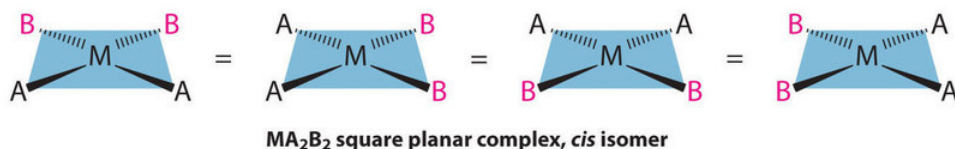
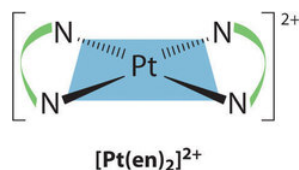


Figure 8.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed

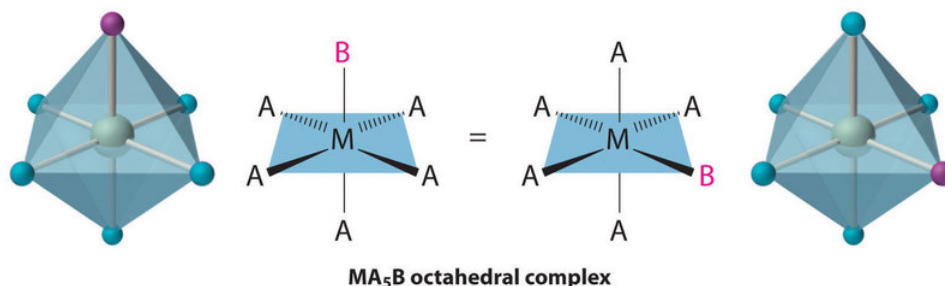
with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

Square planar complexes that contain symmetrical bidentate ligands, such as  $[\text{Pt}(\text{en})_2]^{2+}$ , have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:

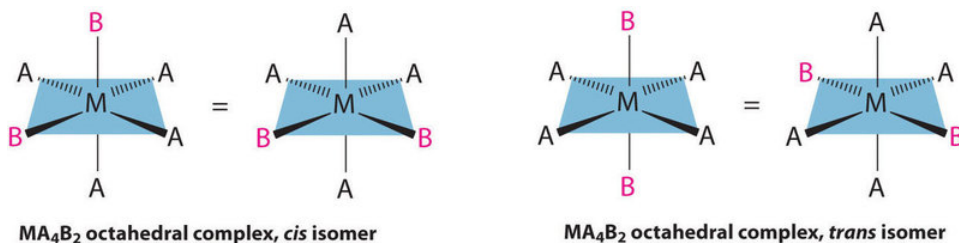


## Octahedral Isomers

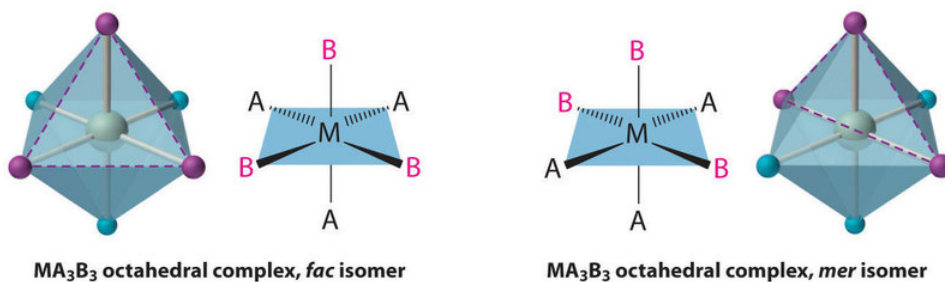
Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five ( $\text{MA}_5\text{B}$ ). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an  $\text{MA}_5\text{B}$  structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an  $\text{MA}_5\text{B}$  structure are as follows:



If two ligands in an octahedral complex are different from the other four, giving an  $\text{MA}_4\text{B}_2$  complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  are examples of this type of system:



Replacing another A ligand by B gives an  $\text{MA}_3\text{B}_3$  complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



### ✓ Example 8.4.1

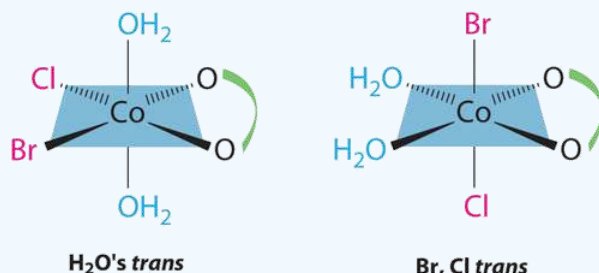
Draw all the possible geometrical isomers for the complex  $[\text{Co}(\text{H}_2\text{O})_2(\text{ox})\text{BrCl}]^-$ , where ox is  $^-\text{O}_2\text{CCO}_2^-$ , which stands for oxalate.

**Given:** formula of complex

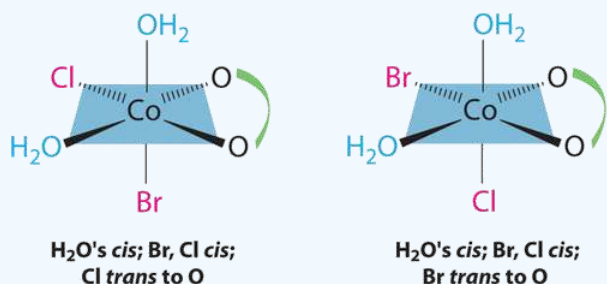
**Asked for:** structures of geometrical isomers

#### Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical ( $\text{H}_2\text{O}$ ). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



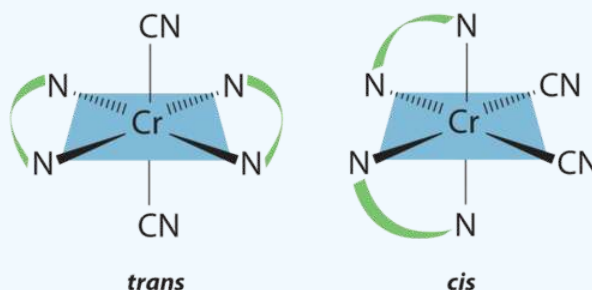
This complex can therefore exist as four different geometrical isomers.

### ? Exercise 8.4.1

Draw all the possible geometrical isomers for the complex  $[\text{Cr}(\text{en})_2(\text{CN})_2]^+$ .

#### Answer

Two geometrical isomers are possible: trans and cis.



## Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

## Contributors and Attributions

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## 8.5: Crystal Field Theory: Optical and Magnetic Properties

### Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

### d-Orbital Splittings

CFT focuses on the interaction of the five  $(n - 1)d$  orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the  $d$  orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five  $d$  orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the  $d$  orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the  $d$  orbitals (Figure 8.5.1a). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the  $d$  orbitals, but it does remove their degeneracy: the five  $d$  orbitals split into two groups whose energies depend on their orientations. As shown in Figure 8.5.1b the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals point directly at the six negative charges located on the  $x$ ,  $y$ , and  $z$  axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the  $e_g$  orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three  $d$  orbitals ( $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ , collectively called the  $t_{2g}$  orbitals) are all oriented at a  $45^\circ$  angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

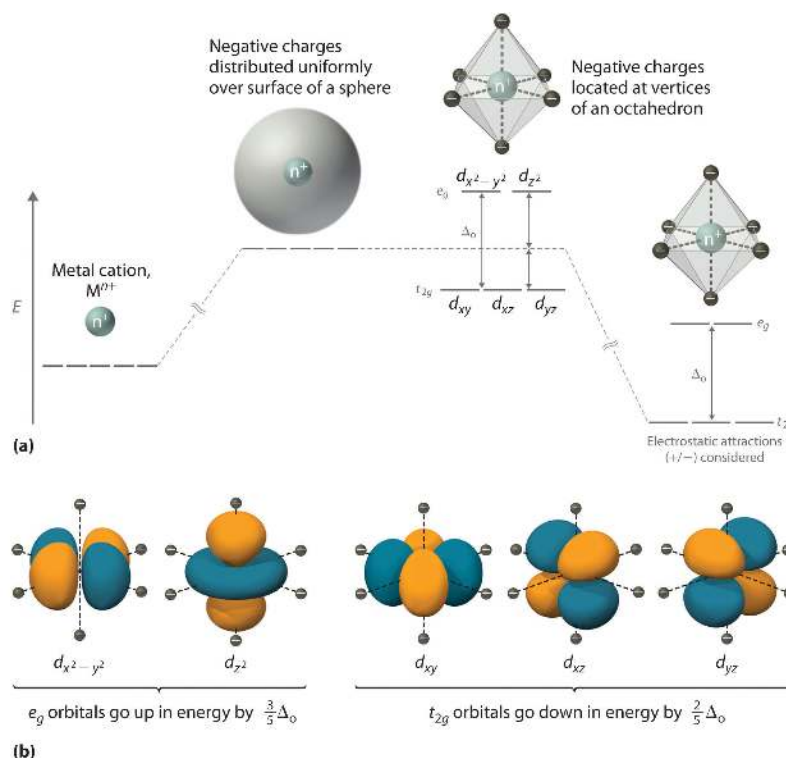


Figure 8.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of  $-6$  uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of  $-1$  at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals increase in energy, while the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a  $-6$  charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two  $e_g$  orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three  $t_{2g}$  orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy ( $\Delta_o$ ), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes:  $\Delta_t$ .) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two  $e_g$  orbitals increase in energy by  $0.6\Delta_o$ , whereas the three  $t_{2g}$  orbitals decrease in energy by  $0.4\Delta_o$ . Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

**Crystal field splitting does not change the total energy of the d orbitals.**

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 8.5.1a).

## Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 8.5.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the  $Ti^{3+}$  ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for  $d^1$ – $d^3$  systems—such as  $[Ti(H_2O)_6]^{3+}$ ,  $[V(H_2O)_6]^{3+}$ , and  $[Cr(H_2O)_6]^{3+}$ , respectively—the electrons successively occupy the three degenerate  $t_{2g}$  orbitals with their spins

parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , for example, by saying that the chromium ion has a  $d^3$  electron configuration or, more succinctly,  $\text{Cr}^{3+}$  is a  $d^3$  ion.

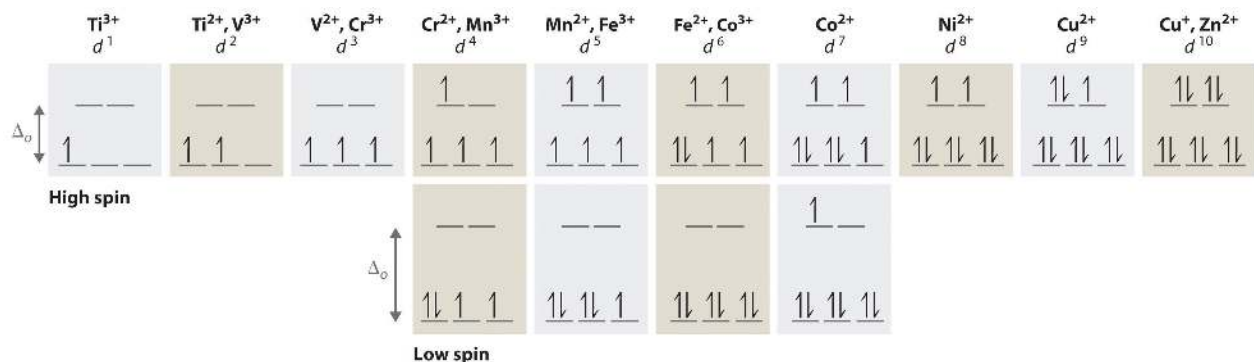


Figure 8.5.2: The Possible Electron Configurations for Octahedral  $d^n$  Transition-Metal Complexes ( $n = 1-10$ ). Two different configurations are possible for octahedral complexes of metals with  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  configurations; the magnitude of  $\Delta_o$  determines which configuration is observed.

When we reach the  $d^4$  configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty  $e_g$  orbitals or one of the singly occupied  $t_{2g}$  orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the **spin-pairing energy (P)**. If  $\Delta_o$  is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty  $e_g$  orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion, is called a high-spin complex. Conversely, if  $\Delta_o$  is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied  $t_{2g}$  orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the  $[\text{Mn}(\text{CN})_6]^{3-}$  ion, is called a low-spin complex. Similarly, metal ions with the  $d^5$ ,  $d^6$ , or  $d^7$  electron configurations can be either high spin or low spin, depending on the magnitude of  $\Delta_o$ .

In contrast, only one arrangement of d electrons is possible for metal ions with  $d^8$ – $d^{10}$  electron configurations. For example, the  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion is  $d^8$  with two unpaired electrons, the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion is  $d^9$  with one unpaired electron, and the  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  ion is  $d^{10}$  with no unpaired electrons.

*If  $\Delta_o$  is less than the spin-pairing energy, a high-spin configuration results. Conversely, if  $\Delta_o$  is greater, a low-spin configuration forms.*

### Factors That Affect the Magnitude of $\Delta_o$

The magnitude of  $\Delta_o$  dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of  $\Delta_o$  (i.e.,  $\Delta_o > P$ ) yield a low-spin complex, whereas small values of  $\Delta_o$  (i.e.,  $\Delta_o < P$ ) produce a high-spin complex. As we noted, the magnitude of  $\Delta_o$  depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of  $\Delta_o$  for some representative transition-metal complexes are given in Table 8.5.1.

Table 8.5.1: Crystal Field Splitting Energies for Some Octahedral ( $\Delta_o$ )\* and Tetrahedral ( $\Delta_t$ ) Transition-Metal Complexes

| Octahedral Complexes                     | $\Delta_o$ ( $\text{cm}^{-1}$ ) | Octahedral Complexes                     | $\Delta_o$ ( $\text{cm}^{-1}$ ) | Tetrahedral Complexes  | $\Delta_t$ ( $\text{cm}^{-1}$ ) |
|------------------------------------------|---------------------------------|------------------------------------------|---------------------------------|------------------------|---------------------------------|
| $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ | 20,300                          | $[\text{Fe}(\text{CN})_6]^{4-}$          | 32,800                          | $\text{VCl}_4$         | 9010                            |
| $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  | 12,600                          | $[\text{Fe}(\text{CN})_6]^{3-}$          | 35,000                          | $[\text{CoCl}_4]^{2-}$ | 3300                            |
| $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  | 18,900                          | $[\text{CoF}_6]^{3-}$                    | 13,000                          | $[\text{CoBr}_4]^{2-}$ | 2900                            |
| $[\text{CrCl}_6]^{3-}$                   | 13,000                          | $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | 9300                            | $[\text{CoI}_4]^{2-}$  | 2700                            |

\*Energies obtained by spectroscopic measurements are often given in units of wave numbers ( $\text{cm}^{-1}$ ); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters:  $1 \text{ cm}^{-1} = 11.96 \text{ J/mol}$ .

| Octahedral Complexes                               | $\Delta_o$ (cm <sup>-1</sup> ) | Octahedral Complexes                               | $\Delta_o$ (cm <sup>-1</sup> ) | Tetrahedral Complexes | $\Delta_t$ (cm <sup>-1</sup> ) |
|----------------------------------------------------|--------------------------------|----------------------------------------------------|--------------------------------|-----------------------|--------------------------------|
| [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> | 13,900                         | [Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | 27,000                         |                       |                                |
| [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | 17,400                         | [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> | 22,900                         |                       |                                |
| [Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> | 21,500                         | [Co(CN) <sub>6</sub> ] <sup>3-</sup>               | 34,800                         |                       |                                |
| [Cr(CN) <sub>6</sub> ] <sup>3-</sup>               | 26,600                         | [Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> | 8500                           |                       |                                |
| Cr(CO) <sub>6</sub>                                | 34,150                         | [Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup> | 10,800                         |                       |                                |
| [MnCl <sub>6</sub> ] <sup>4-</sup>                 | 7500                           | [RhCl <sub>6</sub> ] <sup>3-</sup>                 | 20,400                         |                       |                                |
| [Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> | 8500                           | [Rh(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | 27,000                         |                       |                                |
| [MnCl <sub>6</sub> ] <sup>3-</sup>                 | 20,000                         | [Rh(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> | 34,000                         |                       |                                |
| [Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | 21,000                         | [Rh(CN) <sub>6</sub> ] <sup>3-</sup>               | 45,500                         |                       |                                |
| [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> | 10,400                         | [IrCl <sub>6</sub> ] <sup>3-</sup>                 | 25,000                         |                       |                                |
| [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | 14,300                         | [Ir(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> | 41,000                         |                       |                                |

\*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm<sup>-1</sup>); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm<sup>-1</sup> = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

### Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of  $\Delta_o$  increases as the charge on the metal ion increases. Typically,  $\Delta_o$  for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for [V(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>,  $\Delta_o$  = 11,800 cm<sup>-1</sup>; for [V(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>,  $\Delta_o$  = 17,850 cm<sup>-1</sup>.

### Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of  $\Delta_o$  increases with increasing principal quantum number:  $\Delta_o$  (3d) <  $\Delta_o$  (4d) <  $\Delta_o$  (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[\text{Co}(\text{NH}_3)_6]^{3+}: \Delta_o = 22,900 \text{ cm}^{-1}$$

$$[\text{Rh}(\text{NH}_3)_6]^{3+}: \Delta_o = 34,100 \text{ cm}^{-1}$$

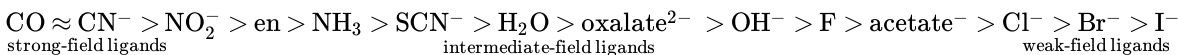
$$[\text{Ir}(\text{NH}_3)_6]^{3+}: \Delta_o = 40,000 \text{ cm}^{-1}$$

The increase in  $\Delta_o$  with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

### The Nature of the Ligands

Experimentally, it is found that the  $\Delta_o$  observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of  $\Delta_o$  decreases as the size of the donor atom increases. For example,  $\Delta_o$  values for halide complexes generally decrease in the order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$  because smaller, more localized charges, such as we see for  $\text{F}^-$ , interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as  $\text{NH}_3$ , results in significantly larger  $\Delta_o$  values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as  $\text{F}^-$ . The

experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing  $\Delta_o$ :



The values of  $\Delta_o$  listed in Table 8.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

*The largest  $\Delta_o$  splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

## Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of  $\Delta_o$ .

Figure 8.5.3: A d–d Transition. In a d–d transition, an electron in one of the  $t_{2g}$  orbitals of an octahedral complex such as the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion absorbs a photon of light with energy equal to  $\Delta_o$ , which causes the electron to move to an empty or singly occupied  $e_g$  orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of  $\Delta_o$ , which depends on the structure of the complex. For example, the complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  has strong-field ligands and a relatively large  $\Delta_o$ . Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain  $\text{Cr}^{3+}$  in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different ( $\text{Al}_2\text{O}_3$  in rubies and  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes  $\Delta_o$  relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large  $[\text{Si}_6\text{O}_{18}]^{12-}$  silicate rings; this results in decreased d orbital–ligand interactions and a smaller  $\Delta_o$ . Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of  $\text{Cr}^{3+}$  impurities in octahedral sites in an otherwise colorless metal oxide lattice.

## Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the  $t_{2g}$  orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a  $d^1$  complex such as  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is located in one of the  $t_{2g}$  orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by  $0.4\Delta_o$ . The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in  $t_{2g}$  orbitals by the energy of those orbitals ( $-0.4\Delta_o$ ), multiplying the number of electrons in  $e_g$  orbitals by the energy of those orbitals ( $+0.6\Delta_o$ ), and summing the two. Table 8.5.2 gives CFSE values for octahedral complexes with different d electron

configurations. The CFSE is highest for low-spin  $d^6$  complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the  $d^3$  configuration.

Table 8.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of  $\Delta_o$ )

|          | High Spin   |         | CFSE ( $\Delta_o$ ) |             | Low Spin |  | CFSE ( $\Delta_o$ ) |
|----------|-------------|---------|---------------------|-------------|----------|--|---------------------|
| $d^0$    |             |         | 0                   |             |          |  |                     |
| $d^1$    | 1           |         | 0.4                 |             |          |  |                     |
| $d^2$    | 1 1         |         | 0.8                 |             |          |  |                     |
| $d^3$    | 1 1 1       |         | 1.2                 |             |          |  |                     |
| $d^4$    | 1 1 1       | 1       | 0.6                 | 1 ↓ 1 1     |          |  | 1.6                 |
| $d^5$    | 1 1 1       | 1 1     | 0.0                 | 1 ↓ 1 ↓ 1   |          |  | 2.0                 |
| $d^6$    | 1 ↓ 1 1     | 1 1     | 0.4                 | 1 ↓ 1 ↓ 1 ↓ |          |  | 2.4                 |
| $d^7$    | 1 ↓ 1 ↓ 1   | 1 1     | 0.8                 | 1 ↓ 1 ↓ 1 ↓ | 1        |  | 1.8                 |
| $d^8$    | 1 ↓ 1 ↓ 1 ↓ | 1 1     | 1.2                 |             |          |  |                     |
| $d^9$    | 1 ↓ 1 ↓ 1 ↓ | 1 ↓ 1   | 0.6                 |             |          |  |                     |
| $d^{10}$ | 1 ↓ 1 ↓ 1 ↓ | 1 ↓ 1 ↓ | 0.0                 |             |          |  |                     |

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

*Octahedral  $d^3$  and  $d^8$  complexes and low-spin  $d^6$ ,  $d^5$ ,  $d^7$ , and  $d^4$  complexes exhibit large CFSEs.*

#### ✓ Example 8.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

- $[\text{CoF}_6]^{3-}$
- $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$

**Given:** complexes

**Asked for:** structure, high spin versus low spin, and the number of unpaired electrons

#### Strategy:

- From the number of ligands, determine the coordination number of the compound.
- Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
- Predict the relative magnitude of  $\Delta_o$  and decide whether the compound is high spin or low spin.
- Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

#### Solution

- A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a  $d^6$  electron configuration.

C Because of the weak-field ligands, we expect a relatively small  $\Delta_o$ , making the compound high spin.

D In a high-spin octahedral  $d^6$  complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the  $t_{2g}$  orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a  $d^8$  electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large  $\Delta_o$ , making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order  $d_{z^2}d_{yz}$ , and  $d_{xz}$  (these are degenerate);  $d_{xy}$ ; and  $d_{x^2-y^2}$ .

D The eight electrons occupy the first four of these orbitals, leaving the  $d_{x^2-y^2}$  orbital empty. Thus there are no unpaired electrons.

### ? Exercise 8.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a.  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

b.  $[\text{PtCl}_4]^{2-}$

#### Answers

a. octahedral; high spin; five

b. square planar; low spin; no unpaired electrons

## Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy ( $\Delta_o$ ), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the  $\Delta_o$  is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the  $\Delta_o$  is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large  $\Delta_o$ , whereas weak-field ligands interact more weakly and give a smaller  $\Delta_o$ . The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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## 8.6: Optical Properties and the Spectrochemical Series

### Learning Objectives

- To get a simple overview of the origin of color and magnetism in complex ions.

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 8.6.1).

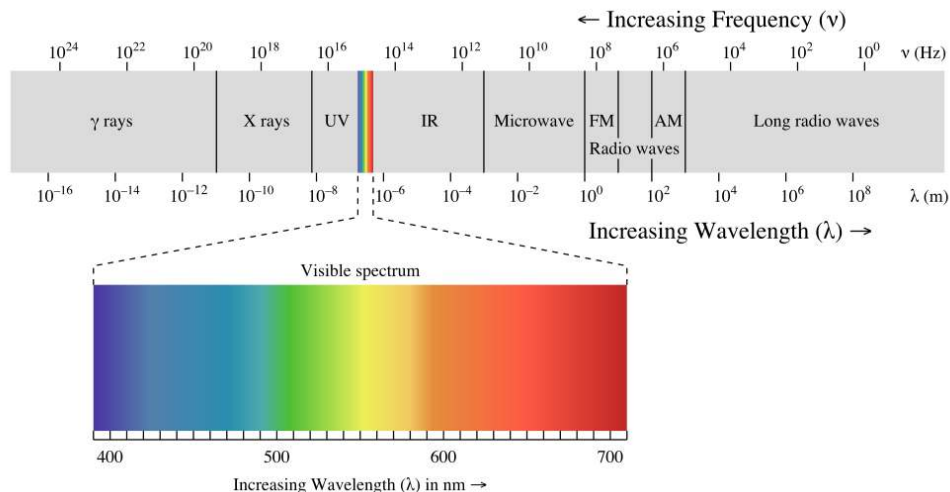


Figure 8.6.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

1. Electromagnetic radiation can travel through empty space, while most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through to be heard.
2. The speed of light ( $c$ ) is always a constant ( $2.99792458 \times 10^8 \text{ m s}^{-1}$ ).
3. Wavelengths ( $\lambda$ ) are measured between the distances of either crests or troughs.

The energy of a photon is expressed by Planck's law in terms of the frequency ( $\nu$ ) of the photon

$$E = h\nu \quad (8.6.1)$$

since  $\lambda\nu = c$  for all light Planck's law can be also expressed in terms of the wavelength of the photon

$$E = h\nu = \frac{hc}{\lambda} \quad (8.6.2)$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 8.6.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from  $10^{-16}$  meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer =  $10^{-9}$  meters).

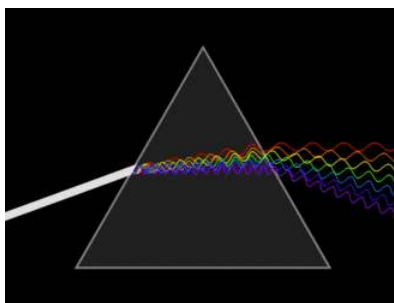
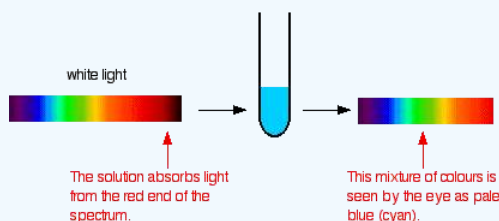


Figure 8.6.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

### ✓ Example 8.6.1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.



Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

### Origin of Colors

The process of absorption involves the excitation of the valence electrons in the molecule typically from the low lying level called the Highest Occupied Molecular Orbital (HOMO) into a higher lying state called the the Lowest Unoccupied Molecular Orbital (**LUMO**). When this HOMO and LUMO transition (Figure 8.6.3) involves the absorption of visible light, the sample is colored.

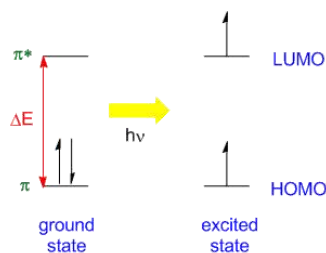


Figure 8.6.4: The general electron excitation process from a HOMO to a LUMO.

The HOMO-LUMO energy difference

$$\Delta E = E_{HOMO} - E_{LUMO} \quad (8.6.3)$$

depends on the nature of the molecule and can be connected to the wavelength of the light absorbed

$$\Delta E = hu = \frac{hc}{\lambda} \quad (8.6.4)$$

Equation 8.6.4 is the most important equation in the field of light-matter interactions (spectroscopy).

As Example 8.6.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 8.6.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

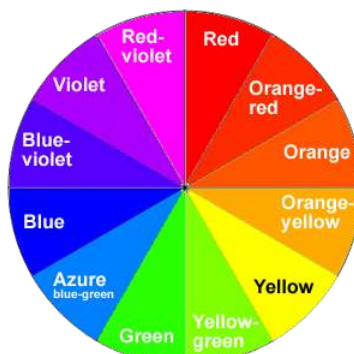


Figure 8.6.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 8.6.1).

Table 8.6.1: The Visible Spectrum

| Color   | Wavelength (nm) | $\Delta E$ HOMO - LUMO gap (eV) |
|---------|-----------------|---------------------------------|
| UV      | 100 - 400       | 12.4 - 3.10                     |
| Violet  | 400 - 425       | 3.10 - 2.92                     |
| Blue    | 425 - 492       | 2.92 - 2.52                     |
| Green   | 492 - 575       | 2.52 - 2.15                     |
| Yellow  | 575 - 585       | 2.15 - 2.12                     |
| Orange  | 585 - 647       | 2.12 - 1.92                     |
| Red     | 647 - 700       | 1.92 - 1.77                     |
| Near IR | 700 - 10,000    | 1.77 - 0.12                     |

If the compound absorbs in one region of the spectra, it appears with the opposite (complementary) color, since all of the absorbed color has been removed. For example:

- the material absorbs violet light  $\Rightarrow$  color is yellow
- the material absorbs blue light  $\Rightarrow$  color is orange
- the material absorbs yellow-green light  $\Rightarrow$  color is red-violet

## The Origin of Color in Complex Ions

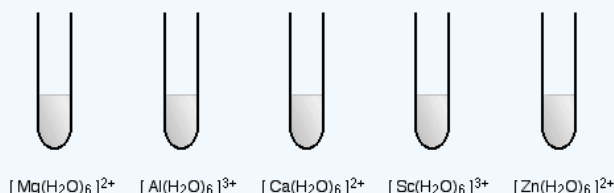
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called **d block elements** rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] 3d<sup>10</sup>4s<sup>2</sup> does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] 3d<sup>1</sup>4s<sup>2</sup>) does not

really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The  $\text{Sc}^{3+}$  ion does not count as a transition metal ion because its 3d level is empty.

### ✓ Example 8.6.3: Hexaaqua Metal Ions

The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula  $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ . The charge on these ions is typically 2+ or 3+.

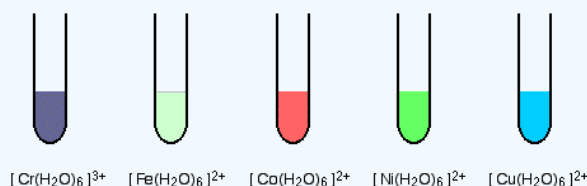
- Non-transition metal ions



These ions are all colorless.

Ions are  $[\text{Mg}(\text{H}_2\text{O})_6]$  two plus,  $[\text{Al}(\text{H}_2\text{O})_6]$  three plus,  $[\text{Ca}(\text{H}_2\text{O})_6]$  two plus,  $[\text{Sc}(\text{H}_2\text{O})_6]$  three plus, and  $[\text{Zn}(\text{H}_2\text{O})_6]$  two plus

- Transition metal ions



Ions are  $[\text{Cr}(\text{H}_2\text{O})_6]$  three plus,  $[\text{Fe}(\text{H}_2\text{O})_6]$  two plus,  $[\text{Co}(\text{H}_2\text{O})_6]$  two plus,  $[\text{Ni}(\text{H}_2\text{O})_6]$  two plus, and  $[\text{Cu}(\text{H}_2\text{O})_6]$  two plus.

The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion? This is discussed in the next sections.

## Magnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only the first two are introduced below.

### Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. **Hund's Rule** states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen,  $\text{O}_2$  is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



*A chemical demonstration of the paramagnetism of oxygen, as shown by the attraction of liquid oxygen to a magnet. Carleton University, Ottawa, Canada.*

As shown in the video, molecular oxygen ( $O_2$ ) is paramagnetic and is attracted to the magnet. In contrast, Molecular nitrogen,  $N_2$ , however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include  $Sc^{3+}$ ,  $Ti^{4+}$ ,  $Zn^{2+}$ , and  $Cu^+$ . These metals are not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

### Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the [Pauli Exclusion Principle](#) which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly **repelled** by a magnetic field. In fact, diamagnetic substances are weakly **repelled** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 8.6.6.

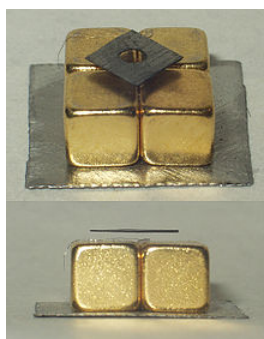


Figure 8.6.6: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

#### 📌 How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration

2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more unpaired electrons) or diamagnetic (all electrons paired)

#### ✓ Example 8.6.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

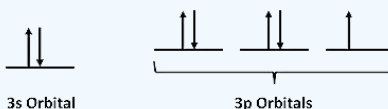
##### Solution

##### Step 1: Find the electron configuration

For Cl atoms, the electron configuration is  $3s^23p^5$

##### Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



##### Step 3: Look for unpaired electrons

There is one unpaired electron.

##### Step 4: Determine whether the substance is paramagnetic or diamagnetic

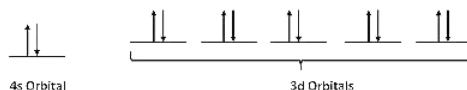
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

#### Example 2: Zinc Atoms

##### Step 1: Find the electron configuration

For Zn atoms, the electron configuration is  $4s^23d^{10}$

##### Step 2: Draw the valence orbitals



##### Step 3: Look for unpaired electrons

There are no unpaired electrons.

##### Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

#### References

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2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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## 8.7: Bonding in Coordination Complexes

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth (**dent**) is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.



Figure 8.7.1: The hypothetical "lobster ligand" binds to the  $Ni^{2+}$  via two donor sites.

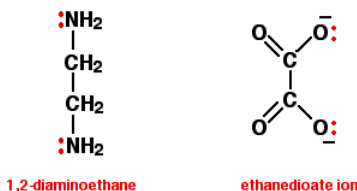
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek *chelos*, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

### Complex metal ions containing more complicated ligands

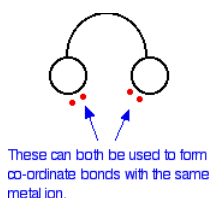
In the examples previously discussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

#### Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).

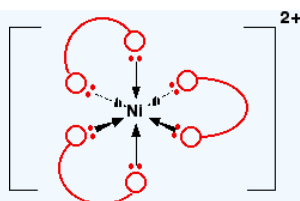


In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snugly around a metal ion.



#### ✓ Example 8.7.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to  $[Ni(en)_3]^{2+}$ . The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the  $\text{NH}_2$  groups - and the "bit that goes over your head" is the  $-\text{CH}_2\text{CH}_2-$  group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

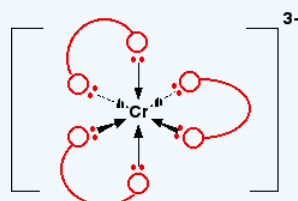
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

#### ✓ Example 5: $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3) + (3 \times -2) = -3.$$

The structure of the ion looks like this:

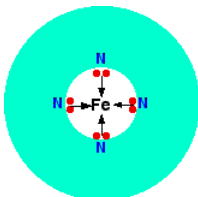


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

### A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

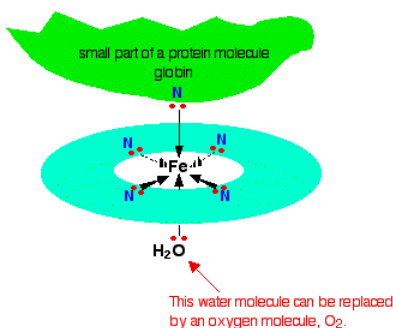


Figure 8.7.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

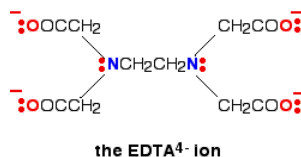
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O<sub>2</sub>) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

### Carbon Monoxide Poisoning

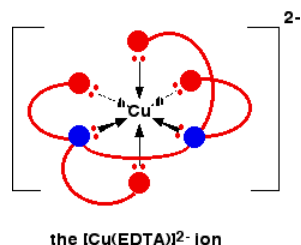
You probably know that carbon monoxide is poisonous because it reacts with haemoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that haemoglobin molecule useless for any further oxygen transfer.

## A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the EDTA<sup>4-</sup> ion.

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