

Objective 16. Understand coordinate covalent bond and structure of coordination compounds.

Key ideas:

Chem 1A: metal and non-metal form an ionic compound (ionic bond).

Some metals form covalent bond to a non-metal, usually to C or N. This bond is a coordinate covalent bond (2 electrons from non-metal combines with metal). Compare to covalent bond (1 unpaired electron from one atom combines with 1 unpaired electron from another atom).

Chem 1A: octet rule

Coordination compounds have an expanded octet – more than 8 electrons around central atom (usually metal).

Electrons in atoms and molecules are responsible for color.

Practice problems solutions:

1. Octet rule compared to the 18 electron rule.

In carbon-containing compounds, e.g., organic compounds, carbon obeys the octet rule.

Scientists use quantum theory (see Chem 1A) to describe electrons in atoms. Since electrons are very small and move very fast, quantum theory is based on probability and statistics. We use quantum theory to give us information about the finding an electron in a certain region of space and its energy.

Quantum theory uses a wave function to describe electrons in atoms.

The wave function of an electron in an atom describes an atomic orbital.

4 quantum numbers describe an electron in an atom:

principal (n) quantum number tells us about the energy of an electron. Higher n means higher energy.

Angular momentum (ℓ) quantum number tells us about the atomic orbital shape of the region of space. $\ell = 0$ is a s atomic orbital. $\ell = 1$ is a p atomic orbital. $\ell = 2$ is a d atomic orbital.

Magnetic (m_ℓ) quantum number tells us about the orientation of space of an atomic orbital. The possible values of m_ℓ depends on ℓ with this formula: $m_\ell = 0, \pm 1, \pm 2, \dots \pm \ell$. So if $\ell = 0$, then $m_\ell = 0$. This means there is only one orientation in space for a s atomic orbital. So if $\ell = 1$, then $m_\ell = 0, 1, -1$. This means there three orientations in space for a p atomic orbital, the p_x , p_y , and p_z orbitals.

a. How many orientations in space are there for d atomic orbitals?

Spin (m_s) quantum number tells us about electron spin. There are two possible spin states, $+1/2$ and $-1/2$.

Carbon is a Period 2 element so quantum theory states the n quantum number for the valence electrons is 2, $\ell = 0$ and 1. $n = 2$ and $\ell = 0$ is a 2s atomic orbital. If $\ell = 0$, the m_ℓ quantum number = 0. This tells us there is one orientation in space for the 2s atomic orbital.

$n = 2$ and $\ell = 1$ is a 2p atomic orbital. If $\ell = 1$, the m_ℓ quantum number = 1, 0, -1. This tells us there are three orientations in space for the 2p atomic orbitals: the $2p_x$, $2p_y$, and $2p_z$.

There are a maximum of 2 electrons in a s atomic orbital and 6 electrons in the three p atomic orbitals for a total of 8 electrons.

For elements in Period 3 or higher, $n = 3$, $\ell = 0, 1, 2$ for the valence electrons.

$n = 3$ and $\ell = 0$ is a 3s atomic orbital. If $\ell = 0$, the m_ℓ quantum number = 0. This tells us there is one orientation in space for the 3s atomic orbital.

$n = 3$ and $\ell = 1$ is a 3p atomic orbital. If $\ell = 1$, the m_ℓ quantum number = 1, 0, -1. This tells us there are three orientations in space for the 3p atomic orbitals: $3p_x$, $3p_y$, and $3p_z$.

$n = 3$ and $\ell = 2$ is a 3d atomic orbital. If $\ell = 2$, the m_ℓ quantum number = 2, 1, 0, -1, -2. This tells us there are five orientations in space for the 3d atomic orbitals: the $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, and $3d_{z^2}$.

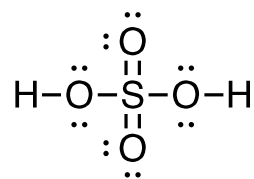
There are a maximum of 2 electrons in a s atomic orbital, 6 electrons in the three p atomic orbitals, and 10 electrons in the five d atomic orbitals for a total of 18 electrons.

In a compound, a central atom that has 8 electrons around follows the octet rule.

In a compound, a central atom that has **more than** 8 electrons around it has an expanded octet.

Example: H_2SO_4 is the most produced chemical in this country. One use is battery acid.

We have to account for 32 electrons in the structure (2 from 2 H, 6 from S, 24 from 4 O)



Each O has 8 electrons around it and fits the octet rule.

b. S is in Period ____ and Group _____. The S has ____ valence electrons and has an expanded octet.

c. Phosphoric acid, H_3PO_4 , is added to soda to give it a tart taste.

Draw the structure of phosphoric acid.

Which atom(s) have an expanded octet?

2. Coordination compounds often have a transition element as a central atom.

a. Where are the transition elements in the Periodic Table?

b. Are transition elements metals or non-metals?

Example: how many valence electrons does Fe have?

See Group number for Fe. Fe is a Group 8B element so it has 8 valence electrons.

Note there are three columns that are called Group 8B – the Fe group, Co group, and Ni group.

The Fe group has 8 valence electrons.

The Co group has 9 valence electrons.

The Ni group has 10 valence electrons.

c. Co is used as an electrode material in Li ion batteries and is a blue pigment. How many valence electrons does Co have?

d. Cr is used to chrome plate materials. How many valence electrons does Cr have?

e. Cu is used in pennies and electrical wiring. How many valence electrons does Cu have?

3. Many transition metals form covalent bonds, rather than ionic bonds, to atoms or groups of atoms.

In Chem 1A, we learned an ionic bond forms between a metal and non-metal.

In Chem 1A, we learned a covalent bond forms between two non-metal.

In Chem 1A, we learned the difference between a polar covalent bond and non-polar covalent bond is due to electronegativity.

Electronegativity is the ability of an atom in a bond to attract electrons toward itself. The two atoms bonded to each other are having a “tug of war” for the electrons in the bond.

The **difference in electronegativity** determines whether the **bond is ionic or covalent**.

Example: NaCl. The bond between Na and Cl is an ionic bond.

Na has an electronegativity of 0.9.

Cl has an electronegativity of 3.0.

The difference in electronegativity = $3.0 - 0.9 = 2.1$.

Big difference in electronegativity so Cl wins “tug of war” for the electrons so an electron is transferred from Na to Cl to form Na^+ and Cl^- ions.

Example: Fe forms a bond to C.

Fe has an electronegativity of 1.8.

C has an electronegativity of 2.5.

The difference in electronegativity = 0.7.

Small difference in electronegativity so electrons are shared (not equally) between Fe and C.

General “rule”: When the difference in electronegativity is 1.7 or greater, the bond is an ionic bond.

a. In hemoglobin, a bond forms between Fe and N. Is this bond an ionic bond or covalent bond? Give reasons.

b. Are the Main Group metals more electronegative or less electronegative than the Transition metals?

c. A bond between a Main Group metal and non-metal is a ____ bond whereas a bond between a transition metal and non-metal is a ____ bond.

4. The atom or group of atoms that is covalently bonded to a metal is called a Ligand.

In Chem 1A, we learned a covalent bond forms when an unpaired electron from one atom combines with an unpaired electron from another atom. The single covalent bond is an electron pair (bonding pair).

A **Coordinate Covalent bond** forms when an electron pair (lone pair) from one atom combines with an empty atomic orbital in another atom.

Ligands have lone pairs that can form a Coordinate Covalent bond to a metal.

Compounds that have Coordinate Covalent bonds are called **Coordination Compounds**.

Note: H_2SO_4 is NOT a coordination compound.

Example: see Chem 1B Objective 16, Lecture Slide 3 and Chem 1B Lab 5, Reaction C.

Drierite is drying agent (a drying agent is a substance that removes water from a substance) that consists of CaSO_4 and a tiny amount of cobalt chloride (CoCl_2). CoCl_2 is used as a color indicator. CoCl_2 is a blue substance. As it absorbs water, it turns pink to $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$. For example, CoCl_2 is used as a humidity indicator in weather instruments.

In Chem 1B Lab 5, Reaction C, solid $\text{Co}(\text{NO}_3)_2$ is dissolved in water to form pink $\text{Co}^{2+}(\text{aq})$.

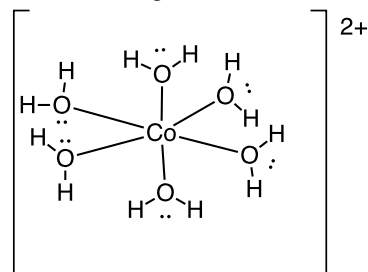
$\text{Co}^{2+}(\text{aq})$ is a pink compound that is actually $\text{Co}(\text{H}_2\text{O})_6^{2+}$.

The **ligands** are Cl^- and H_2O .

Cl^- has four lone pairs; one lone pair forms a coordinate covalent bond to cobalt.

H_2O has two lone pairs; one lone pair forms a coordinate covalent bond to cobalt.

The +2 charge on this ion comes from Co^{2+} ion = +2. H_2O is neutral.



How many electrons does Co have around it?

Co^{2+} ion = 7 valence electrons (Co atom has 9 valence electrons – 2 electrons (removed to give +2 charge)).

Lone pair from H_2O = 2 electrons.

6 H_2O = 12 electrons.

So Co has $7 + 12 = 19$ electrons ==> expanded octet.

What is the shape of $\text{Co}(\text{H}_2\text{O})_6^{2+}$?

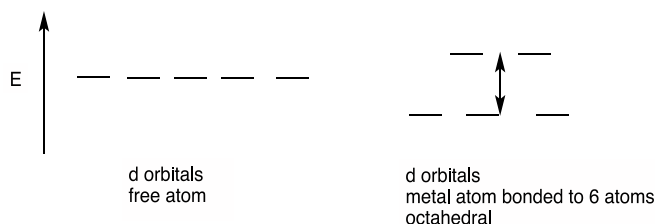
Apply VSEPR theory (Chem 1A). 6 electron pairs around a central atom ==> octahedral shape.

Why is $\text{Co}(\text{H}_2\text{O})_6^{2+}$ pink?

See Chem 1B Objective 16, Lecture Slides 16-17.

It has to do with the d atomic orbitals in the metal; in this case, Co.

The 5 d atomic orbitals in a Co atom are at the same energy (this is called a *degenerate* state).



When 6 atoms (ligands) bond to Co to form a compound, the energy of 2 of the d orbitals increases and the energy of 3 other d orbitals decreases. This has to do with the shape of each d orbital and how much the d orbital repels the ligand. More repulsion means higher energy d orbital; less repulsion means lower energy d orbital.

The energy difference between the d orbitals is called the “splitting”. (The d orbitals in the free atom are split into higher energy and lower energy d orbitals when the atom bonds to atoms.)

Back to Chem 1A – We learned how light is produced.

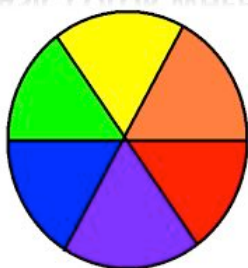
When a substance absorbs the “right” amount of energy that corresponds to the energy difference between energy states, an electron undergoes a transition from a lower energy state to higher energy state. This is called an absorption process (endothermic). The amount of energy absorbed corresponds to a wavelength of light ($E = h\nu = hc/\lambda$, where h = Planck’s constant, ν = frequency, c = speed of light, and λ = wavelength).

The higher energy state is called an excited state. A substance does not stay in an excited state for long – an electron undergoes a transition from a higher energy state to lower energy state. This is called an emission process (exothermic). This process releases energy in the form of light or heat. If energy is released in the form of light, the energy difference between energy states determines the wavelength of light emitted ($E = hc/\lambda$).

Use the **absorption process to explain the color of substances**.

A red shirt is red because a substance in the shirt absorbs the “complementary” color of red, which is green. See the color wheel.

BASIC COLOR WHEEL



<http://trehautecouture.blogspot.com/2012/06/how-to-mix-colors-in-your-wardrobe.html>

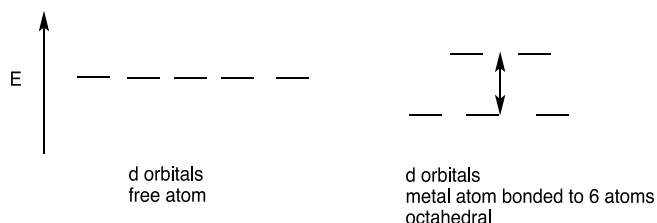
$\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pink. This means $\text{Co}(\text{H}_2\text{O})_6^{2+}$ absorbs the complementary color of pink (red), which is green.

In Chem 1B Lab 5, Reaction C, add NaCl (a source of Cl^- ions) and the pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ turns to blue CoCl_4^{2-} (aq). CoCl_4^{2-} (aq) is a blue compound that is actually $\text{CoCl}_4(\text{H}_2\text{O})_2^{2-}$.

Replacing four H_2O ligands with four Cl^- ligands changed the color of the compound.

Why did the color change?

See the d orbital diagram. If the color changes, that means the energy difference between the d orbitals must have changed.



$\text{CoCl}_4(\text{H}_2\text{O})_2^{2-}$ is blue. The complementary color of blue is orange.

$\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pink. The complementary color of pink (red) is green.

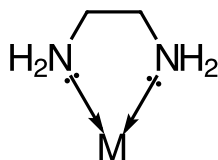
Orange is a lower energy than green.

Conclusion: the Cl^- ligand decreases the energy difference (splitting) between the d orbitals. This means Cl^- splits the d orbitals less than H_2O in a coordination compound.

Experiments show a **spectrochemical series** that shows how much a ligand splits the d orbitals in a coordination compound:

spectrochemical series: $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{OH}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{ethylene diamine} < \text{CN}^- < \text{CO}$

Ethylene diamine is a bidentate ligand. This means ethylene diamine can form two coordinate covalent bonds to a metal. In other words, two atoms in ethylene diamine have lone pairs that can form coordinate covalent bonds.



Ligands that form two or more coordinate covalent bonds are called **polydentate ligands** or **chelates** (from Greek meaning "claw" like claw of a lobster) or **sequestering agents**.

Examples: ethylenediamine tetraacetic acid (EDTA) is used to sequester metal ions in solution, e.g., bind Ca^{2+} and Mg^{2+} ions to soften water, in chelation therapy in medicine to treat Hg and Pb poisoning, and in shampoos and personal care products to improve the stability of these products in air.

Hemoglobin is the oxygen carrier in our blood. Myoglobin is the oxygen binding protein found in muscle. Iron is the metal in hemoglobin and myoglobin. Porphyrin is a tetradentate ligand that binds to iron (this compound is called heme). When O_2 binds to the Fe^{2+} in hemoglobin, the hemoglobin is red – the color of your blood.

a. CoCl_4^{2-} (aq) is a blue compound that is actually $\text{CoCl}_4(\text{H}_2\text{O})_2^{2-}$.

(i) The ligands are _____.

(ii) Why does this ion have a -2 charge?

(iii) How many electrons does Co have around it?

b. You do not like the blue color of $\text{CoCl}_4(\text{H}_2\text{O})_2^{2-}$ and want to change it. You replace one Cl^- ligand with a NH_3 ligand to make $\text{CoCl}_3(\text{NH}_3)(\text{H}_2\text{O})^-$. The energy difference between the d orbitals in this compound _____ and the color changes from _____ to _____. You've designed your own color!

c. You have your blue $\text{CoCl}_4(\text{H}_2\text{O})_2^{2-}$ and want to make a green compound. You would replace the ____ ligand with a ____ ligand because _____.