Transition metals consist of elements from the d-block found between the group IIa and the group IIb elements of the periodic table. A transition metal is an element that forms one or more stable ions which have incompletely filled d sub-orbitals. While these transition metals contain at most two electrons in their outer shell, they are called d-block elements because their next highest energy shell has incompletely filled d sub-orbitals.

Introduction

The d sub-orbitals in transition metals are filled up, progressively going across the periodic table from left to right. These d sub-orbitals of transition metals are readily available for metallic bonding. They give way to general properties of transition metals such as good electrical and heat conductivity and high melting points. Since both the outer shell and the d sub-orbital shells can be used for bonding, it allows transition metals to bond with a variety of elements in many shapes. It should be noted, however, that not all d-block elements are transition metals. Some of the elements, such as Scandium and Zinc, have either empty or completely filled d sub-orbitals and do not meet the criteria to be considered transition metals.

Electronic Structure

The electronic configuration of transition metal elements are characterized as having full outer sub-orbitals and the second outermost d sub-orbitals incompletely filled, with the exception of Copper which loses one 4s orbital electron to the 3d sub-orbital for increased stability. The electron configuration for copper is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ or given in terms of a noble gas configuration which is $[\text{Ar}]4s^1 3d^{10}$ and not $[\text{Ar}]4s^2 3d^9$, as would be expected from the Aufbau principle. The loss of the electron from the 4s orbital completes the 3d sub-orbital and leaves it in a more stable, lower energy state. This lowest energy electron configuration is determined by the electron-pairing energy and the exchange energy. The two electrons in the 4s orbital will repel each other slightly, and this will cause a minor increase in the energy of the atom. The removal of one of the electrons from the 4s shell will remove this energy increase which is caused by the pairing energy. When electrons can exchange between orbitals, the energy of the atom is lowered. This electron exchange can occur when there are degenerate electron configurations, and the electrons of the same spin can exchange between orbitals. This exchange energy is defined by the spin-Hamiltonian:

$$H_o = -2S_1S_2$$

where J is the set of many electron exchange parameters, and $S_1$ and $S_2$ are the spin operators of the two electrons.

When J is positive, the exchange energy favors electrons with parallel spins. When J is negative, it favors antiparallel spins. This leads to the primary cause of ferro and anti-ferro magnetism. The spin-Hamiltonian is summed over all pair interactions, and it is maximized when the electronic shells are either completely filled or half-filled. Such is the case with copper and its loss of one 4s electron to the 3d sub-orbital to form the noble gas configuration of $[\text{Ar}]4s^1 3d^{10}$.

Manganese, on the other hand, has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ and a noble gas configuration of $[\text{Ar}]4s^2 3d^5$, resulting in one unpaired electron in each 3d sub-orbital. Similar to copper, the exchange energy is maximized since the 3d sub-orbital is exactly half-filled with 5 electrons without the need to steal electrons from the 4s orbital.
electrons in the d sub-orbitals of both copper and manganese are subject to Pauli's exclusion principle which says that no two fermions in an atom can have the same quantum number.

Since electrons are fermions with a spin of 1/2, the wavefunction of the system must be antisymmetric when the electrons are exchanged. The spin-Hamiltonian, that determines the exchange energy interaction, defines the important properties of both manganese and copper.

Copper is found in two common ionic forms, Cuprous Cu(I) with a noble gas electron configuration of [Ar]4s03d10 and Cupric Cu(II) with [Ar]4s03d9. Cu(III) and even Cu(IV) ionic forms of copper have been formed.

The unpaired electron in the 4s orbital is lost in Cu(I) which leaves a complete d sub-orbital. However, Cu(II) is actually more stable, due to a higher ionization energy. The relatively unstable Cu(I) ion disproportionates as:

\[ 2Cu(I) \rightarrow Cu(0) + Cu(II) \]

Manganese has seven ionic forms from Mn(I) to Mn(VII). The two most common forms are Mn(II), with a noble gas electronic configuration of [Ar]4s03d5 and Mn(VII), with a configuration of [Ar]4s03d0 and a formal loss of all seven electrons from the 3d and 4s orbitals.

Crystal Field Splitting

Crystal field splitting diagrams can be used to determine the way strong and weak ligands will affect the magnitude of ligand field, splitting parameters and determining the number of unpaired electrons are in each transition metal. Using H2O as a weak field ligand, complexed with Mn(II) in the form of [Mn(H2O)6]2+, the low oxidation state of manganese will cause a high spin with five unpaired electrons.

FIGURE HERE

The crystal field splitting of a ligand in the case with water, has an important effect on the d-orbital energy levels. Since the ligand electrons have repulsions with the d sub-orbital electrons, the d-orbital energy levels are raised. However, they are not raised equally. In the case of this octahedral complex ion, ligands approach along the x-, y- and z-axis. When the six ?-donor water molecules are coordinated with the manganese ion, the orbitals (d_{z^2} and d_{x^2-y^2}) are head-to-head with the ligand and have a greater repulsion and thus, a higher energy. The energy levels of the (d_{xy}, d_{xz}, d_{yz}) orbitals are also increased, due to this repulsion but to a lesser extent.

Using NH3 as a strong field splitting ligand coordinated to copper, such as [Cu(NH3)4]2+, which has an ionic form of copper Cu(II). The Cu(II) has nine d sub-orbital electrons, and since there are only five orbitals, there can only be one configuration of the electrons which results in one unpaired electron. The complex is paramagnetic, but the structure cannot be determined from magnetic properties.
**Spin of Mn**

With a Mn(II) ion with a weak field ligand, the energy splitting is low and the cost of placing an electron into a higher energy d orbital is lower than the repulsion energy of pairing two electrons together. Thus, the Mn(II) ion in a weak field ligand setting, produces a high spin as all five electrons are unpaired and the ion is paramagnetic. One electron is placed into each d orbital according to **Hund’s rule**, and the “high spin” octahedral complex has all five orbitals singly occupied. The magnetic susceptibility is determined to be 5.92, using the formula:

\[ \chi = [n(n+2)]^{1/2} \]

where \( n \) is the number of unpaired electrons.

In the case of Cu(II) in a strong ligand field such as NH\(_3\), the energy required to pair the electrons is not relevant since there are nine d sub-orbital electrons that need to be placed in five d orbital shells. This results in a single unpaired electron which means that the complex is paramagnetic, but the high spin vs low spin associated energy splittings are not relevant.

If the Cu(II) ion were in a weak ligand field setting, the high spin vs low spin energy levels would not be relevant again, due to the number of electrons. This would result in a tetrahedral stereochemistry which typically displays a high spin arrangement.

The ground state electronic term symbols represent a shorthand notation which is predicted, using Hund’s rule for the angular momentum quantum numbers of an atom with multiple electrons. This is related to the energy level of the electronic configurations of the atoms.

The term symbol has the form:

\[ ^{2S+1}L_J \]

where \( S \) is the spin quantum number; \( L \) is the orbital momentum quantum number in spectroscopic notation given in L= 0,1,2,3,4,5 are S,P,D,F,G,H, respectively; and finally, \( J \) is the angular momentum quantum number. This symbol assumes that all spins are combined to produce \( S \); all orbital angular momenta are combined to produce \( L \); and all the spin and orbital angular momenta are combined to produce \( J \). The multiplicity of a term is the value of \( 2S+1 \), provided that \( L \geq S \), and is the number of levels of the term. The values for \( S \), \( L \), and \( J \) are constructed by the application of Clebsch-Gordan series. To construct a term symbol arising from an electronic configuration, first determine the possible values of \( L \), and identify the spectroscopic letters for the terms. The possible values of \( S \) are determined similarly, using a Clebsch-Gordan series, and the multiplicities are calculated. Finally, the values for \( J \) are constructed again, using a Clebsch-Gordan series by combining \( S \) and \( L \).
Clebsch-Gordan Series

\[ j = j_1+j_2, j_1+j_{2-1}, \ldots, |j_1-j_2| \]

Using the ground state electronic configuration, the electrons are distributed according to Pauli’s exclusion principle to the available orbitals. The first orbitals filled are those with the highest \( m_l \) values; \( S \) is calculated by added all the \( m_s \) values; \( L \) is calculated by added together the \( m_l \) values for each electron; and \( J \) is then determined, using a set of rules. If the subshell is half-filled, then the \( L=0 \) and \( J \) will be equal to \( S \). If the subshell is more than half-filled, then \( J=L+S \); if the subshell is less than half-filled, then \( J=|L-S| \). The ground electronic term symbol for copper is thus determined to be \( ^2S_{1/2} \). The term symbol for \( \text{Cu(II)} \), with an electronic configuration \([\text{Ar}]4s^03d^9\) is calculated to be \( ^2D_{5/2} \). The ground electronic term symbol for manganese is thus determined to be \( ^6S_{5/2} \). The term symbol for \( \text{Mn(II)} \) is also \( ^6S_{5/2} \), since the orbital with the highest \( m_l \) value still has 5 electrons in it and thus, \( L=0 \).

Outside Links


References


2. On the Connection between the Completion of Electron Groups in an Atom with the Complex Structure of Spectra. Wolfgang Pauli, Z. Physik 31, 1925, Pages 373-385


5. Cu(III), Cu(IV), Cu (oxidation state). E. König and G. König, Landolt-Börnstein - Group II Molecules and Radicals, 1984, Pages 1615-1852


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