



MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

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Abstract

An electron is a charged particle (negatively charged) which revolves around the nucleus and spins on its own axis. A magnetic field is generated due to the orbital motion and spin of the electron. The spinning of an electron in an orbit is very much similar to flow of electric current in a closed circuit. Therefore, an unpaired electron is regarded as a micro magnet which has a definite magnetic moment. A substance which contains an unpaired electron when placed in a magnetic field interacts with the applied field. Consequently, an attractive force is exerted and the paramagnetic property is shown. The number of unpaired electrons determines the magnitude of magnetic moment. Higher the number of unpaired electrons more is the magnetic moment and greater will be the paramagnetic behaviour of the substance. In the case of paired electrons, the electrons in each pair will have opposite spin. The magnetic field created by the electrons of same pair is equal and opposite in nature. Hence, the magnetic field which is created by one electron is cancelled by the other. So the net effect of the magnetic moment is zero. These kinds of substances show diamagnetic property and are repelled by the applied magnetic field.

Keywords: *Electron, Transition Metal Complexes, Magnetic field, Paramagnetic, Diamagnetic behavior*

Introduction

There are various substances which show magnetic behaviour. We have substances that are attracted by the magnetic field and are called paramagnetic. This phenomenon is called paramagnetism. Paramagnetic property is only shown when the substance contains one or more unpaired electrons. When a substance acquires a permanent magnetic moment, it is known as ferromagnetic and the phenomenon is called ferromagnetism. On the other hand, we also have substances which are repelled by magnetic field and are called as diamagnetic substances. A substance shows diamagnetism when it contains only paired electrons. Most of the transition elements show paramagnetic behaviour. The unpaired electrons in (n-1) d orbitals are responsible for the magnetic properties. The paramagnetic character of the

transition metals increases on moving from left to right as the number of unpaired electron increases from one to five. The middle elements are found to possess the maximum paramagnetic property. The magnetic properties decrease with the decrease in the number of unpaired electrons. The transition metals which contain paired electrons depict diamagnetic behaviour. 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 behavior including paramagnetism, diamagnetism, and ferromagnetism.

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the *d* orbitals, this magnetism must be due to having unpaired *d* electrons. The spin of a single electron is denoted by the quantum number m_s as $+(1/2)$ or $-(1/2)$. This spin is negated when the electron is paired with another, but creates a weak magnetic field when the electron is unpaired. More unpaired electrons increase the paramagnetic effects. The electron configuration of a transition metal (*d*-block) changes in a coordination compound; this is due to the repulsive forces between electrons in the ligands and electrons in the compound. Depending on the strength of the ligand, the compound may be paramagnetic or diamagnetic.

Characteristic Properties

There are a number of properties shared by the transition elements that are not found in other elements, which results from the partially filled *d* shell. These include

- the formation of compounds whose color is due to *d-d* electronic transitions
- the formation of compounds in many oxidation states, due to the relatively low energy gap between different possible oxidation states
- the formation of many [paramagnetic](#) compounds due to the presence of unpaired *d* electrons. A few compounds of main group elements are also paramagnetic (e.g. [nitric oxide](#), [oxygen](#))

Most transition metals can be bound to a variety of [ligands](#), allowing for a wide variety of transition metal complexes.

Coloured Compounds



From left to right, aqueous solutions of: [Co\(NO₃\)₂](#) (red); [K₂Cr₂O₇](#) (orange); [K₂CrO₄](#) (yellow); [NiCl₂](#) (turquoise); [CuSO₄](#) (blue); [KMnO₄](#) (purple).

Colour in transition-series metal compounds is generally due to electronic transitions of two principal types.

- charge transfer transitions. An electron may jump from a predominantly ligand orbital to a predominantly metal orbital, giving rise to a ligand-to-metal charge-transfer (LMCT) transition. These can most easily occur when the metal is in a high oxidation state. For example, the colour of chromate, dichromate and permanganate ions is due to LMCT transitions. Another example is that mercuric iodide, HgI_2 , is red because of a LMCT transition.

A metal-to-ligand charge transfer (MLCT) transition will be most likely when the metal is in a low oxidation state and the ligand is easily reduced.

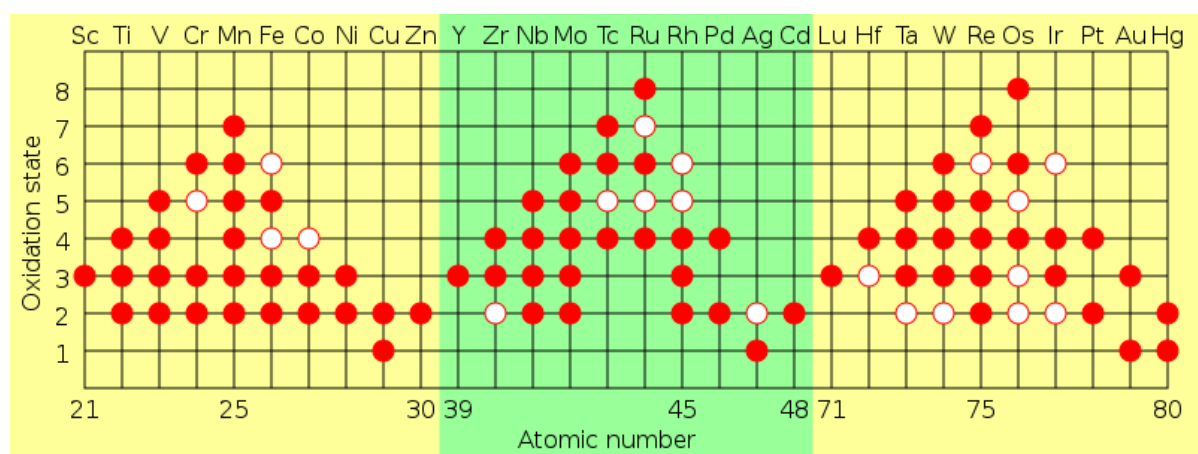
In general charge transfer transitions result in more intense colours than d-d transitions.

- *d-d* transitions. An electron jumps from one d-orbital to another. In complexes of the transition metals the *d* orbitals do not all have the same energy. The pattern of splitting of the *d* orbitals can be calculated using crystal field theory. The extent of the splitting depends on the particular metal, its oxidation state and the nature of the ligands. The actual energy levels are shown on Tanabe–Sugano diagrams.

In centrosymmetric complexes, such as octahedral complexes, *d-d* transitions are forbidden by the Laporte rule and only occur because of vibronic coupling in which a molecular vibration occurs together with a *d-d* transition. Tetrahedral complexes have somewhat more intense colour because mixing *d* and *p* orbitals is possible when there is no centre of symmetry, so transitions are not pure *d-d* transitions. The molar absorptivity (ϵ) of bands caused by *d-d* transitions are relatively low, roughly in the range $5\text{--}500\text{ M}^{-1}\text{cm}^{-1}$ (where $\text{M} = \text{mol dm}^{-3}$). Some *d-d* transitions are spin forbidden. An example occurs in octahedral, high-spin complexes of manganese(II), which has a d^5 configuration in which all five electron has parallel spins; the colour of such complexes is much weaker than in complexes with spin-allowed transitions. Many compounds of manganese(II) appear almost colourless. The spectrum of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ shows a maximum molar absorptivity of about $0.04\text{ M}^{-1}\text{cm}^{-1}$ in the visible spectrum.

Oxidation states

A characteristic of transition metals is that they exhibit two or more oxidation states, usually differing by one. For example, compounds of vanadium are known in all oxidation states between -1 , such as $[\text{V}(\text{CO})_6]$, and $+5$, such as VO_3^{3-} .



Oxidation states of the transition metals. The solid dots show common oxidation states, and the hollow dots show possible but unlikely states.

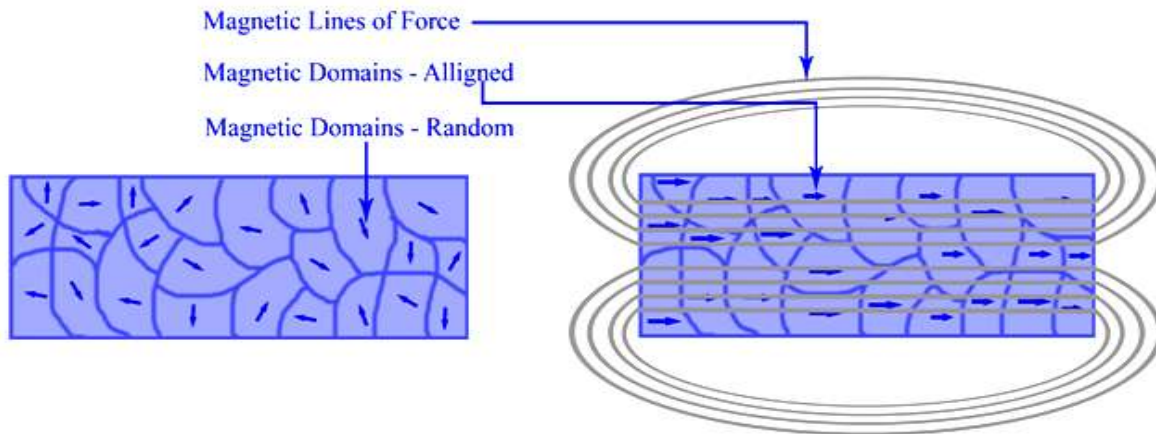
Main group elements in groups 13 to 18 also exhibit multiple oxidation states. The "common" oxidation states of these elements typically differ by two instead of one. For example, compounds of gallium in oxidation states +1 and +3 exist in which there is a single gallium atom. No compound of Ga(II) is known: any such compound would have an unpaired electron and would behave as a free radical and be destroyed rapidly. The only compounds in which gallium has a formal oxidation state of +2 are dimeric compounds, such as $[\text{Ga}_2\text{Cl}_6]^{2-}$, which contain a Ga-Ga bond formed from the unpaired electron on each Ga atom. Thus the main difference in oxidation states, between transition elements and other elements is that oxidation states are known in which there is a single atom of the element and one or more unpaired electrons. The maximum oxidation state in the first row transition metals is equal to the number of valence electrons from titanium (+4) up to manganese (+7), but decreases in the later elements. In the second row, the maximum occurs with ruthenium (+8), and in the third row, the maximum occurs with iridium (+9). In compounds such as $[\text{MnO}_4]^-$ and OsO_4 , the elements achieve a stable configuration by covalent bonding. The lowest oxidation states are exhibited in metal carbonyl complexes such as $\text{Cr}(\text{CO})_6$ (oxidation state zero) and $[\text{Fe}(\text{CO})_4]^{2-}$ (oxidation state -2) in which the 18-electron rule is obeyed. These complexes are also covalent. Ionic compounds are mostly formed with oxidation states +2 and +3. In aqueous solution, the ions are hydrated by (usually) six water molecules arranged octahedrally.

Magnetism

Transition metal compounds are paramagnetic when they have one or more unpaired *d* electrons. In octahedral complexes with between four and seven *d* electrons both high spin and low spin states are possible. Tetrahedral transition metal complexes such as $[\text{FeCl}_4]^{2-}$ are high spin because the crystal field splitting is small so that the energy to be gained by virtue of the electrons being in lower energy orbitals is always less than the energy needed to pair up the spins. Some compounds are diamagnetic. These include octahedral, low-spin, d^6 and square-planar d^8 complexes. In these cases, crystal field splitting is such that all the electrons are paired up. Ferromagnetism occurs when individual atoms are paramagnetic and the spin vectors are aligned parallel to each other in a crystalline material. Metallic iron and the alloy alnico are examples of ferromagnetic materials involving transition metals. Antiferromagnetism is another example of a magnetic property arising from a particular alignment of individual spins in the solid state.

Ferromagnetism (Permanent Magnet)

Ferromagnetism is the basic mechanism by which certain materials (such as iron) form **permanent magnets**. This means the compound shows permanent magnetic properties rather than exhibiting them only in the presence of an external magnetic field (Figure). In a ferromagnetic element, electrons of atoms are grouped into domains in which each domain has the same charge. In the presence of a magnetic field, these domains line up so that charges are parallel throughout the entire compound. Whether a compound can be ferromagnetic or not depends on its number of unpaired electrons and on its atomic size.



: Ferromagnetism (a) nonmagnetized material and (2) Magnetized material with corresponding magnetic fields shown.

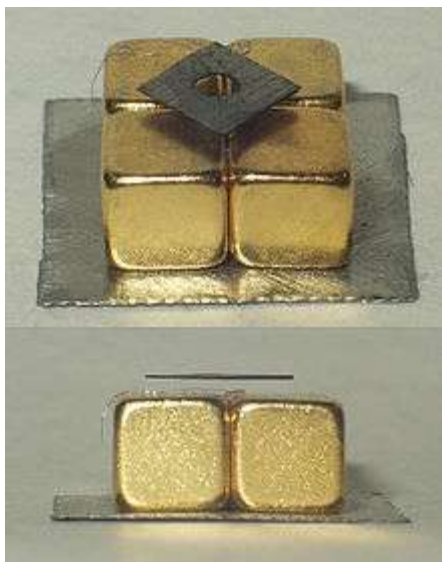
Ferromagnetism, the permanent magnetism associated with nickel, cobalt, and iron, is a common occurrence in everyday life. Examples of the knowledge and application of ferromagnetism include Aristotle's discussion in 625 BC, the use of the compass in 1187, and the modern-day refrigerator. Einstein demonstrated that electricity and magnetism are inextricably linked in his theory of special relativity.

Paramagnetism (Attracted to Magnetic Field)

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.

Diamagnetism (Repelled by Magnetic Field)

is paramagnetic and is attracted to is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen, N_2 , has no unpaired electrons and is diamagnetic; it is therefore unaffected by the magnet. Diamagnetic substances are characterized by paired electrons, e.g., no unpaired electrons. According to the Pauli Exclusion Principle which states that no two electrons may occupy 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 as demonstrated with the pyrolytic carbon sheet in Figure



: 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).

How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic properties of a substance can be determined by examining its electron configuration: If it has unpaired electrons, then the substance is paramagnetic and if all electrons are paired, the substance is then diamagnetic. This process can be broken into three steps:

1. Write down the electron configuration
2. Draw the valence orbitals
3. Identify if unpaired electrons exist
4. Determine whether the substance is paramagnetic or diamagnetic

Example 1

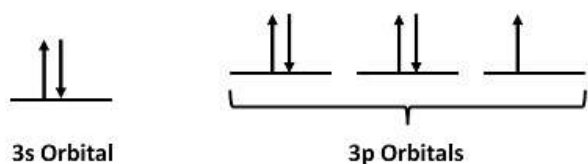
: Chlorine Atoms

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

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 (albeit, weakly).

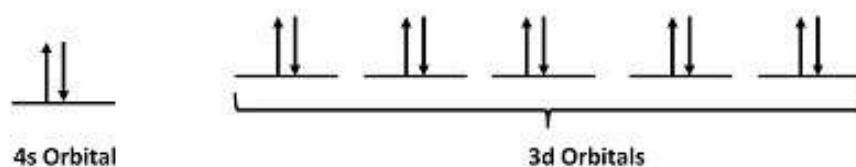
Example 2

: 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.

Conclusion

The transition metals and their compounds are known for their homogeneous and heterogeneous catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in the contact process), finely divided iron (in the Haber process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysts at a solid surface (nanomaterial-based catalysts) involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilize 3d and 4s electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowered). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. An interesting type of catalysis occurs when the products of a reaction catalyse the reaction producing more catalyst (autocatalysis). One example is the reaction of oxalic acid with acidified potassium permanganate (or manganate (VII)). Once a little Mn^{2+} has been produced, it can react with MnO_4^- forming Mn^{3+} . This then reacts with $C_2O_4^{2-}$ ions forming Mn^{2+} again. transition metals possess a high density and high melting points and boiling points. These properties are due to metallic bonding by delocalized d electrons, leading to cohesion which increases with the

number of shared electrons. However the group 12 metals have much lower melting and boiling points since their full d sub-shells prevent d–d bonding, which again tends to differentiate them from the accepted transition metals. Mercury has a melting point of $-38.83\text{ }^{\circ}\text{C}$ ($-37.89\text{ }^{\circ}\text{F}$) and is a liquid at room temperature.

Bibliography

1. Bain, Gordon A.; Berry, John F. (2008). "Diamagnetic Corrections and Pascal's Constants". *J. Chem. Educ.* **85** (4): 532
2. Brant Cage and, Nar S. Dalal. UnhydratedCr(V) Peroxychromates M_3CrO_8 (M = Na, K, Rb): Low-Dimensional Antiferromagnets Exhibiting Large Specific Heats at mK to 5 K Temperatures. CheDanutaPiwowarska, PawełGnutek, CzesławRudowicz. Origin of the Ground Kramers Doublets for $\text{Co}^{2+}(\text{3d}^7)$ Ions with the Effective Spin $3/2$ Versus the Fictitious 'Spin' $1/2$. *Applied Magnetic Resonance***2019**,**50** (6) , 797-808. <https://doi.org/10.1007/s00723-018-1080-4> *Journal of Materials Chemistry***2001**,**13** (3) , 880-890. <https://doi.org/10.1021/cm000643d>
3. Carlin, R.L. (1986). *Magnetochemistry*. Springer. ISBN 978-3-540-15816-5.
4. Caravan, Peter; Ellison, Jeffrey J.; McMurry, Thomas J. ; Lauffer, Randall B., Jeffrey J.; McMurry, Thomas J.; Lauffer, Randall B. (1999). "Gadolinium(III) Chelates as MRI Contrast Agents: Structure, Dynamics, and Applications". *Chem. Rev.* **99** (9): 2293–2352. doi:10.1021/cr980440x. PMID 11749483.
5. Berliner, L.J. (1976). *Spin labeling : theory and applications I*. Academic Press. ISBN 0-12-092350-5. Berliner, L.J. (1979). *Spin labeling II : theory and applications*. Academic Press. ISBN 0-12-092352-1.
6. Weil, John A.; Bolton, James R.; Wertz, John E. (1994). *Electron paramagnetic resonance : elementary theory and practical applications*. Wiley. ISBN 0-471-57234-9.
7. Earnshaw, Alan (1968). *Introduction to Magnetochemistry*. Academic Press.
8. vons, D.F. (1959). "The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance". *J. Chem. Soc.*: 2003–2005.
9. Figgis, B.N.; Lewis, J. (1960). "The Magnetochemistry of Complex Compounds". In Lewis, J. and Wilkins. R.G. (ed.). *Modern Coordination Chemistry*. New York: Wiley.
10. Greenwood, Norman N.; Earnshaw, Alan (1997). *Chemistry of the Elements* (2nd ed.). Butterworth-Heinemann. ISBN 978-0-08-037941-8.
11. Junjie Liu, Paul A. Goddard, John Singleton, Jamie Brambleby, Francesca Foronda, Johannes S. Möller, Yoshimitsu Kohama, Saman Ghannadzadeh, Arzhang Ardavan, Stephen J. Blundell, Tom Lancaster, Fan Xiao, Robert C. Williams, Francis L. Pratt, Peter J. Baker, Keola Wierschem, Saul H. Lapidus, Kevin H. Stone, Peter W. Stephens, Jesper Bendix, Toby J. Woods, Kimberly E. Carreiro, Hope E. Tran, Cecelia J. Villa, and Jamie L. Manson. Antiferromagnetism in a Family of $S = 1$ Square Lattice Coordination Polymers $\text{NiX}_2(\text{pyz})_2$ (X = Cl, Br, I, NCS; pyz = Pyrazine). *Inorganic Chemistry***2016**,**55** (7) , 3515-3529. <https://doi.org/10.1021/acs.inorgchem.5b02991>
12. Orchard, A.F. (2003). *Magnetochemistry*. Oxford Chemistry Primers. Oxford University Press. ISBN 0-19-879278-6.

13. Lawrence Que (March 2000). [*Physical methods in bioinorganic chemistry: spectroscopy and magnetism*](#). University Science Books. pp. 345–348. [ISBN 978-1-891389-02-3](#).
14. Selwood, P.W. (1943). [*Magnetochemistry*](#). Interscience Publishers Inc.
15. Vulfson, Sergey (1998). *Molecular Magnetochemistry*. [Taylor & Francis](#). [ISBN 90-5699-535-9](#).