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Synthesis and Characterization of Coordination Compounds Using Schiff Base Ligands

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Abstract

Compounds developed from Schiff base ligands have gained continuous research attention due to their various structural possibilities, easy synthesis methods, and proven biological activity. This study investigates the basic chemistry of Schiff base formation and discusses how these ligands coordinate to transition metal ions. The notion also reviews the main analytical and spectroscopic methods used to establish compound identity and geometry. The metal complex's properties depend on how the ligands are designed for the formation of specific types. The text is aimed at readers who are first encountering coordination chemistry at an advanced undergraduate or graduate level. It is developed sufficiently to connect laboratory observations with theoretical interpretations.

1. Introduction

A coordination compound has a central atom (usually a metal) to which several molecules or anions are coordinated. The groups that surround this entity are termed ligands and the number of donor atoms that are attached to metal determines coordination number of this complex. Coordination compounds were studied formally by Alfred Werner in the late nineteenth century. Over the years, these compounds have found uses in areas like industrial catalysis, medical imaging, and antimicrobial drug development (Da Silva et al. 2011)

Schiff bases occupy a rather convenient position among the many ligands available to synthetic chemists. These are formed by having a primary amine react with carbonyl compound, usually an aldehyde, under mild, low-cost conditions, which can be easily tuned to incorporate a

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wide variety of functional groups. Schiff bases contain a donor site due to the imine (C=N) linkage, which is the main site. However, most Schiff bases will have other heteroatoms such as O, N, and S that can bind to the metal. Schiff bases have stability enabling them to bind to metals and create stable chelate rings, thus functioning as effective polydentate ligands (Wilkinson et al. 2016)

The coordination chemistry of Schiff bases has practical relevance, mainly because the electronic and steric character of the ligand can be modified readily by selecting appropriate amine and aldehyde starting materials. A researcher desiring a ligand that better donates electrons can select substituents as desired; one wanting a bulkier ligand to influence geometric preference can introduce branched or aromatic groups near donor atoms. It is harder to obtain this level of design control with ligands that require multi-step syntheses.

This research discusses the formation chemistry of Schiff bases, the structural types resulting from their coordination (grouping) with metals, and characterization tools allowing unambiguous identification of the products. We aim to tell a coherent, logical story by synthesizing a structure and analyzing it (Mahmudov et al. 2016)

2. Formation of Schiff Base Ligands

Condensation reaction occurs when a primary amine reacts with an aldehyde to produce an imine with a concurrent release of a water molecule. The process functions in two steps. In the first step, the nitrogen of the amine attacks the electrophilic carbon of the carbonyl to form an unstable hemiaminal intermediate that has both an OH and an NH group on the same carbon. In the second step, upon mild heating or acid catalysis, this intermediate loses water to give the imine product, called an azomethine or a Schiff base.

The reactions are named after Hugo Schiff, who described them back in 1864. Despite their great age, the reactions are still quite useful: the majority of Schiff base ligands used in coordination chemistry today are made by refluxing an amine and a carbonyl compound in either ethanol or methanol for one to three hours, letting the product crystallise on cooling. Yields often exceed 80%, and purification is typically uncomplicated.

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The donor ability of the resulting ligand is most strongly influenced by the choice of carbonyl component. 2-hydroxybenzaldehyde provides an OH group ortho to the aldehyde carbon. After imine formation, this OH is in a position to lose its proton and coordinate to the metal through oxygen, engaging the oxygen and imine nitrogen in a five-membered chelate ring on metal binding. The Schiff base derived from salicylaldehyde has been studied extensively as it has a greater tendency to form a stable 5-membered ring with a variety of transition metals (Jesmin et al. 2010)

In Heteroaromatic aldehydes, 2-Pyridinecarboxaldehyde, the coordinating ability of ring nitrogen is also discerned. As a result the formed Schiff base might in some instances be a tridentate donor. If you put an amine function in a diamine, e.g., ethylenediamine or o-phenylenediamine, one gets a bis-Schiff base with two imine functions capable of binding the metal at one time with four donor atoms (Swamy et al. 2011)

The imine bond has relevance to biochemical activity. Many amino acids and their derivatives react with carbonyl compounds by the same condensation mechanism, and the formation of a Schiff base between pyridoxal phosphate and amino acid substrates lies at the heart of a family of enzyme-catalyzed reactions. This biochemical piece of evidence might assist explain why synthetic Schiff base metal complexes are extensively screened for enzyme inhibition and antimicrobial action.

3. Coordination Chemistry of Schiff Base Ligands

The Schiff base is dissolved in a solution of a transition metal salt and donor atoms of the ligand replace the original anions or solvent molecules around the metal to form the complex. The driving force is the formation of coordinate bonds (dative bonds). In this case, the ligands give an e.p. to the vacant orbital of the metal.

3.1 Chelate Effect

Polydentate ligands make complexes that are more thermodynamically stable than the complexes made by monodentate ligands of comparable donor strength because of the release of multiple solvent molecules on chelation which increases the disorder of the system. Also, breaking

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up one chelate ring will require breaking more than one bond simultaneously. The chelate effect is the stabilization. Metal complexes that contain bidentate, tridentate, or tetradentate Schiff base ligands are, in general, quite stable in solution they dissociate less readily than analogous complexes with simple monodentate ligands (e.g. ammonia or pyridine).

The dimensions of the chelate ring too are essential. Generally, five-membered rings are the most stable in first-row transition metal complexes, when donor atoms are separated by two atoms in the ligand backbone. Six-membered rings are also stable and common. Larger rings are rare because larger linkers show flexibility that permits higher disorder thus reducing chelation's entropic advantage (Mahmudov et al. 2016)

3.2 Structural Geometries

The shape of the transition metal complexes depends on the nature of the metal, its oxidation state, the number of ligands and its electronic structure. The four-coordinate complex may be tetrahedral or square planar in shape. The most frequent are the six-coordinate complexes, which usually have an octahedral configuration, but distortion effects are seen in cases where constraints are placed on geometry by the ligands. For complexes containing five coordinated atoms, there are two possible coordination possibilities, trigonal bipyramidal and square pyramidal.

Schiff base ligands typically prescribe geometry by fixing the donor atom distance and arrangement. A type of Schiff base that is composed of a diamine with two equivalents of salicylaldehyde forms a tridentate ligand. If this ligand contains two phenolic OH groups which are called a salen-type ligand. This particular ligand holds its four donor atoms in a plane. Metals that favour square planar geometry, Cu(II), Ni(II), and Pd(II), strongly bind to salen ligands and yield flat complexes in which the four donors occupy the four equatorial sites. Metals which are capable of forming five or six ligands often recruit solvent molecules or extra anions in axial positions (Chandra and Tyagi 2011)

In tridentate meridional ligands, two donor atoms are arranged trans to one another while the third occupies an equatorial site. All three practitioners are cis for facial coordination. The arrangement available depends on ligand geometry.

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3.3 Common Metal Ions Used

Commonly used Schiff base ligands for the most commonly studied metals are copper, nickel, cobalt, zinc, manganese, iron and vanadium. Each of them is specifically chosen for its chemistry and uses.

Copper(II) has a d9 configuration, which gives rise to compounds with characteristic EPR signals and magnetic moments of about 1.73 BM for mononuclear species. Given that most tetradentate Schiff bases are planar, most of them would tend to prefer square planar or square pyramidal geometry. It has been extensively tested as an antifungal and antibacterial agent.

Nickel(II) can produce square planar geometry in the presence of strong-field ligands. Whereas tetrahedral and octahedral geometry in the presence of weaker ligands. Nickel complexes are useful stereochemical probes because the change in geometry can be detected from the color and magnetic properties of the complex (Khan and Khan 2015)

The study of Schiff base complexes of zinc(II) and cobalt(II) is partly motivated by the fact that the former has coordination chemistry rich in essential trace elements, whereas the latter has been evaluated as models of vitamin B12 as well as anticancer agents.

4. Synthesis Methods

4.1 Template Synthesis

When templates are used for synthesis, the metal ion will function as an organizer to hold the amine and carbonyl reactants in positions that are favorable for condensation. The metal's coordination preferences control the ligand's geometry which forms efficiently around the metal. This method is employed when free ligand instability and distortion take place in the absence of a metal or in the case of a geometric isomer (Agwara et al. 2010)

In a standard template reaction, a metal salt is mixed with the amine and aldehyde in a suitable solvent. It is at the metal center where the imine bond forms as the metal coordinates with the amine and then brings it to the aldehyde. The resultant metal complex is the product without isolation of the free ligand as an intermediate.

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4.2 Direct Metal-Ligand Combination

Usually, the synthesis of Schiff base ligands leads to a stable and isolable compound. In this case, the Schiff base ligand is prepared first and then reacted with a metal salt in an appropriate solvent. This enables full characterization of the ligand before coordination, thus establishing a clear baseline for the spectroscopic changes upon complex formation.

Chemical reactions are usually performed in refluxing ethanol, methanol or DMF. The complex's expected stoichiometry is employed to choose a molar ratio of metal to ligand. For instance, the 1:2 ratio of metal to bidentate ligand will give a bis-chelate complex. Similarly, the 1:1 ratio with a tetradentate ligand will produce a mono-chelate product (Mishra et al. 2013)

5. Characterization Methods

Characterization of coordination compounds requires complementary techniques; no one technique gives complete structural information.

5.1 Elemental Analysis

The percentage by weight of carbon, hydrogen, nitrogen and other elements is determined by elemental analysis. The empirical composition is confirmed when the measured percentages match those calculated for a proposed molecular formula. Discrepancy indicates the presence of a solvent of crystallization, incompleteness in purity or wrong structural assignment. Elemental analysis is usually the first confirmation that is reported, which identifies the chemical identity before interpretation of spectroscopic measurements.

5.2 Infrared Spectroscopy

Infrared spectroscopy measures and identifies the vibrational frequencies of bonds in the molecule. Two particular absorptions are informative for Schiff base coordination compounds.

The stretch frequency of the C=N bond of the imine in the free ligand generally ranging from 1620–1660 cm-1. When the nitrogen donates a lone pair into one of the metal's orbitals, the metal withdraws electronic density from the C=N bond. This creates a weaker bond thus lowering the force constant associated with this bond causing the absorption to occur at lower wavenumbers.

The absorption usually takes place in the 10 to 30 cm-1 region. Researchers believe that this transfer is one of the strongest evidence that coordination occurs via the imine nitrogen (El-Sherif et al. 2012)

The phenolic C-O groups yield the second diagnostic absorption. In salicylaldehyde-derived Schiff bases, the free phenol's C-O stretch occurs near 1280 cm-1. When the phenolic oxygen undergoes deprotonation and subsequently coordinates with the metal in the form of the phenolate, a noticeable increase in the wavenumber of this band occurs. The resulting positioning of the band now occurs within the wavenumber region of 1300 to 1320 cm-1. The low-frequency region (below 600 cm-1) has metal-nitrogen and metal-oxygen stretching absorptions which when assigned correctly confirm the nature of the metal-ligand bonds directly (Ismail et al. 2012)

5.3 UV-Visible Spectroscopy

Optical characteristics of a metal complex can be determined using ultraviolet-visible spectroscopy, which is a useful and easy method to understand the studies of the complex. The spectrum can help determine significant information about the metal complex.

A d-d transition occurs as an electron fills an energetically less favourable d-orbital as compared to inner and outer orbitals. The energy and intensity of bands will depend on the metal, its oxidation state and the geometry of the complex. A broad d-d absorption at 550–650 nm is characteristic of a Cu(II) complex that has a square planar geometry. This band's molar absorptivity is low (often <100 L mol-1 cm-1) due to the Laporte-forbidden transition.

The LMCT bands are more intense and also found in the shorter-wavelength region. An LMCT band is formed by the transfer of an electron from a filled ligand to a metal. The intensity and energy of LMCT bands are influenced by the metal's electron affinity and the donor strength of the ligand as well. Consequently, comparison of these absorptions in a series of complexes with architecture-related ligands yields useful information pertaining to the electronic effects.

5.4 Magnetic Susceptibility Measurements

The number of unpaired electrons present in a coordination compound determine their magnetic behaviour. While a diamagnetic substance has all its electrons paired, a paramagnetic

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substance will have at least one unpaired electron. Through the use of susceptibility measurements, the effective magnetic moment was computed and compared to the spin-only ones corresponding to the various electron configurations.

A Cu(II) complex has an effective magnetic moment near 1.73BM with one unpaired electron. A Mn(II)complex with five unpaired electrons should give a moment near 5.92 BM. When the values do not fit spin-only values, the moment has an orbital contribution or, if they are much lower, antiferromagnetic coupling between adjacent metal centres via bridging ligands. Magnetic measurements help determine oxidation state and possibly reveal exchange interactions between polynuclear complexes.

5.5 Mass Spectrometry

Mass Spectrometry determines the analysis of elemental or molecular ions from the compound. As a means of generating ions from a solution, electrospray ionization is the most common method used for coordination compounds. It does so under gentle conditions which result in fragmentation being minimized. If the spectrum contains a signal that corresponds to a molecular ion or a closely related species and the measured mass allows confirmation of molecular weight within a few ppm when high-resolution instruments are employed (Siddappa and Mayana 2014)

Examining the fragmentation behaviour in the lower mass region can provide useful information. The loss of ligand fragments or counterions in sequence often follows pathways consistent with the proposed structure.

6. Biological Relevance

Many published works on Schiff base coordination compounds evaluate them against either bacterial or fungal strains. The Tweedy chelation theory explains that when a metal is complexed with a donor ligand, the polarity of the metal ion is reduced due to charge delocalization over donor atoms. Thus the resulting complex will cross the membrane more rapidly than either the free metal or the uncomplexed ligand. The outcome is often a complex that has greater biological activity than the individual components (Jayaseelan et al. 2016)

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This rationale is supported by many case studies. It should be considered a working hypothesis rather than a proven mechanism or law. Having lipophilicity, membrane permeability and antimicrobial activity are not simple. It also pertains to the intracellular target, stability of the complex under physiological conditions and whether the complex is intact or the metal and ligand are released separately inside the cell ()

Research has been conducted on vanadium and copper Schiff base complexes as insulin mimetics and superoxide dismutase mimics, respectively, due to their structural similarities to the respective active sites of the natural enzymes. Research in synthetic inorganic chemistry is related to medicinal chemistry in ways that lead to findings which are publishable and, at times, clinically useful (Hernández et al. 2016)

7. Conclusion

The versatile ligands possible in synthetic coordination chemistry are Schiff bases. Because they are easy to prepare, have tunable electronic and steric properties, and form stable chelate rings with a range of transition metal ions, they are a logical choice for anyone seeking to prepare coordination compounds with specific geometry and properties. The characterization of the resulting complexes will be based on elemental analysis for composition, infrared spectroscopy for coordination via bond, UV-visible spectroscopy and magnetic measurements for electronic and geometric assignment, mass spectrometry for molecular weight confirmation, and X-ray diffraction for the final three-dimensional structure.

A reliable assignment of structure is available due to the combined evidence of these methods rather than one single technique. One of the analytical skills required is an understanding of how a method probes one facet of a compound's structure and how the data from one technique places constraints upon the interpretation of another. Many of these compounds display a biological activity that provides a worthwhile motivation for a study that otherwise asked only for a structural investigation. It thus places Schiff base coordination chemistry in a useful intervening zone between fundamental inorganic chemistry and applied materials or medicinal chemistry.

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