

Zn(II) metal complex of Benzedrine derivatives

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Abstract : Zinc(II) metal complexes of Benzedrine (amphetamine) derivatives represent a novel frontier in coordination chemistry with potential implications for neuropharmacology. Amphetamine, chemically 1-phenyl-2-aminopropane, possesses an amine group capable of coordinating with Zn(II), a d^{10} metal ion known for forming tetrahedral or octahedral complexes with nitrogen donors. This study explores the theoretical synthesis, structural characterization, and stability of such complexes analogous to known Zn(II)-amine complexes. Modifications to the amphetamine backbone, including phenyl ring substitutions with electron-donating (e.g., methyl, methoxy) or electron-withdrawing (e.g., fluoro) groups, are investigated to enhance coordination strength and tune electronic properties. Computational modelling, employing density functional theory, predicts binding affinities and coordination geometries, while spectroscopic techniques such as IR, NMR, and UV-Vis are proposed to confirm amine-Zn(II) interactions and complex purity. Although direct evidence for these complexes is absent in current literature, zinc's biological role in modulating amphetamine's dopamine transporter activity suggests a chemical basis for their feasibility. These complexes could potentially stabilize amphetamine derivatives, or reduce toxicity, offering new therapeutic avenues for conditions like attention-deficit/hyperactivity disorder. Challenges include the weak ligand properties of amphetamine's amine group and potential instability in aqueous environments. This work highlights the need for experimental synthesis and crystallographic studies to validate theoretical predictions. By bridging coordination chemistry with pharmacological insights, Zn(II) complexes of Benzedrine derivatives may pave the way for innovative drug delivery systems or targeted neuropsychiatric treatments, warranting further interdisciplinary research to explore their chemical and biological potential.

(Keywords : Zn(II)-amine complexes, IR, NMR, and UV-Vis).

Introduction

Benzedrine (amphetamine) is an amine. It is specifically classified as a primary aliphatic amine and a sympathomimetic amine, meaning it is a member of a class of drugs that mimics the effects of the body's natural adrenaline and norepinephrine. The chemical name for the active compound in Benzedrine is alpha-methylphenethylamine or 1-phenylpropan-2-amine, with the molecular formula $C_9H_{13}N$. The key functional group that makes it an amine is the amino group. This nitrogen-containing group is attached to a carbon atom that is not part of the benzene (phenyl) ring, making it an aliphatic, rather than aromatic, amine.

- **Classification:**

- **Primary Amine:** The nitrogen atom is bonded to only one carbon atom (and two hydrogen atoms), classifying it as a primary amine.

- **Sympathomimetic Amine:** Benzedrine's structure is similar to the body's natural neurotransmitters like epinephrine (adrenaline) and norepinephrine. This structural similarity allows it to interact with the same receptors and systems in the brain, producing stimulant effects.

- **Discovery:** The sympathomimetic action of amines, including the substance that would become Benzedrine, was first described in a classic study in 1910 by British scientists George Barger and Sir Henry Dale. The compound itself was later synthesized in 1927 by American chemist Gordon Alles, who was searching for a substitute for ephedrine

as a nasal decongestant. Benzedrine was the trade name for the racemic mixture of the dextro and levo isomers of amphetamine sulfate, marketed by the pharmaceutical company Smith, Kline & French in the 1930s.

- **Function:** In the body, Benzedrine increases the levels of monoamines, particularly dopamine and norepinephrine, in the brain by affecting their transporters and release from nerve cells. This action is the basis for its use as a central nervous system stimulant to treat conditions like narcolepsy and attention deficit hyperactivity disorder (ADHD).

In essence, Benzedrine is an amine because of its specific chemical composition that includes a primary amino functional group, and its classification within a broader group of pharmacologically active “sympathomimetic amines”.

Structure

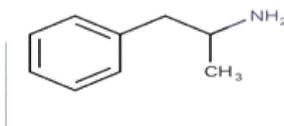


Fig- 1. Benzedrine

Schiff Base: Hugo Schiff, a German chemist, initially reported Schiff base in 1864¹. Schiff bases are organic molecules formed via condensation reaction of carbonyl compounds and primary amines². The typical structure can be expressed as R'-CR=N-R'', where R, R' and R'' might vary. R and R' could be alkyl, aryl and heterocyclic structures with various substituents. Because Schiff bases contain an azomethine (>C=N-) group, they are also known as azomethine or imine. The Schiff bases derived from aldehydes and ketones are known as aldimines and ketoimines respectively. A general Schiff base

condensation reaction involving the amine and the carbonyl functional group could be represented as follows (**Figure 2**). Schiff bases with aryl substituents are significantly more stable and easier to synthesize, but those with alkyl substituents are relatively unstable^{3,4}. Aliphatic aldehyde Schiff bases are highly unstable and easily polymerizable, but aromatic aldehyde Schiff bases with efficient conjugation are more stable. Because aldehydes have less steric hindrance than ketones, thus react faster. Extra carbon in ketones makes them less electrophilic than aldehydes. Schiff bases have received a great deal of attention due to their simplicity of synthesis, availability, and electronic characteristics. There is great interest in developing a wide range of applications in organic⁵, inorganic^{6,7}, coordination⁸⁻¹⁰, bioinorganic^{11,12} and environmental chemistry¹³⁻¹⁶. Schiff base have been utilized in medical, pharmaceutical, metal refining, metallurgy, catalysis, food, sensing, filtration, environmental, photography and diagnostic applications. The discovery of Schiff base was a major step forward for the discipline of coordination chemistry. When combined with a variety of transition metal ions, Schiff base ligands can generate stable metal complexes with a wide range of applications. The Schiff base has remarkable chelating characteristics. The presence of hydroxyl and thio-groups in azomethine groups may result in forming a penta or hexa ring structure with metal ions. Bidentate, tridentate, tetradentate, and polydentate Schiff bases are also possible. Because of the availability of a lone pair on the nitrogen atom, the Schiff base forms complexes with many metals. This lone pair aids in creating monodentate complexes, while adding other groups, such as OH and SH, may result in the formation of bidentate chelates. The azomethine nitrogen atom has lone pair of electrons and is sp² hybridized. As a result, it has substantial biological and chemical significance. Because there are more donor atoms in heterocyclic rings containing Schiff bases, they play a larger role in coordination

chemistry¹⁷⁻¹⁹. Schiff bases show biological activities like nematocidal²⁰, insecticidal²¹, antibacterial²², antifungal²³, antileukemia²⁴, anti-inflammatory²⁵, anti-HIV activity²⁶, antimycobacterial activity²⁷, antioxidant²⁸, anticancer²⁹ and plant growth regulatory activity³⁰.

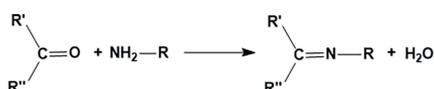


Figure 2 General scheme of formation of Schiff bases

Besides biological applications, Schiff base and their metal complexes have enormous applications in analytical chemistry³¹, dye industry³², and corrosion inhibitors³³. Schiff base has attracted the attention of many experimental and theoretical researchers due to their particular photo-luminescence³⁴ in the visible range and at room temperature and so applied in many realms such as microelectronics³⁵, optoelectronics³⁶ and biological sensors³⁷. Schiff base shows excellent catalytic activity in various reactions such as polymerization reaction and reduction of thionyl chloride, reduction reaction of ketones, oxidation of organic compounds, aldol reaction, epoxidation of alkenes, hydrosilylation of ketones, Henry reaction, synthesis of bis (indolyl) methanes and Diels Alderreaction³⁸⁻⁴⁰. Synthetic chemists have used Schiff bases and related complexes for a wide variety of processes, including the oxidation of alkenes and the catalytic transformation of hydrocarbons into useful oxygenated derivatives such alcohols, aldehydes, and epoxides. A further area of intense curiosity is the catalysis of alkene oxidation by soluble transition metal complexes. Schiff base metal complexes have been used in biological applications, resulting in important recent improvements in a variety of chemistry areas. Because of their unique treatment method, metal-containing antibacterial compounds appear to be promising candidates for brand-new antibiotic medications that restrict the growth of bacterial strains. The characteristics of Schiff base metal complexes vary depending on the

ligands and the transition metal ion. Schiff bases have attracted a lot of interest because of their various chemical and physical properties, as well as their ease of production.

Synthetic methods of Schiff bases: Schiff base ligands, a class of molecules having imine groups, have grown in popularity due to their physiological and pharmacological properties. They are fascinating class of chelating agents capable of coordinating metal ions in a complex, which is used to imitate biological processes. Many studies have been conducted on synthesizing Schiff bases⁴¹⁻⁴³. Schiff bases have been prepared using conventional and green synthetic methods (**Figure 3**). Heat is required in many condensation processes, and traditional reaction conditions often involve heating the reactants in a metal, oil, or sand bath for hours or even days. The conventional procedure involves refluxing or stirring different aldehydes or ketones with various types of primary amines. Green chemistry refers to the tools and procedures that provide considerable environmental and financial benefits over conventional synthetic approaches. It depicts that the current in green chemistry has triggered a new demand for organic synthesis in which distinct reaction environments must be located, reducing the usage of harmful organic solvents or toxic chemicals. Green approaches must improve selectivity, reduce reaction time, and simplify product isolation over conventional methods. Microwave-assisted synthesis of Schiff bases has been carried out without solvent or low-solvent conditions and reduces reaction time significantly, improves conversion, and sometimes increases selectivity. Since the development of solventless microwave synthesis of Schiff bases, it has become the most well-known and simple technique for these reactions and is used in various applications. Many researchers reported using the microwave-assisted synthesis of various types of Schiff bases and their derivatives. The grindstone technique reaction creates local heat by grinding substrate crystals and reagent with

a mortar and pestle. Grinding starts reactions by transmitting a relatively small quantity of energy through friction. In some circumstances, a mixture and reagents form a glassy substance. Such reactions are simple to handle, eliminate pollutants, relatively cheaper to operate, and may be considered more economical and environmentally friendly in chemistry¹⁸. Because molecules in a crystal are organized tightly and regularly, solid-state reactions are more efficient and selective than solution reactions¹⁹.

Classification of Zn(II) Schiff Base Complexes

Zn(II) is a d^{10} metal ion, favouring flexible coordination geometries. Schiff base ligands stabilize Zn(II) in different structural

motifs: By Coordination Geometry: Tetrahedral complexes – common with bidentate ligands. Square planar complexes – less common, stabilized by rigid ligands. Octahedral complexes – formed with polydentate or macrocyclic Schiff bases. By Ligand Type: Salicylaldehyde-based Schiff bases – Zn(II) complexes mimic enzymatic active sites. Amino acid-based Schiff bases – biomimetic, useful in studying transamination reactions. Macrocyclic Schiff bases – provide stability and selectivity in catalysis. Heterocyclic Schiff bases – enhance biological activity (antimicrobial, anticancer).

Homoleptic and heteroleptic Schiff base metal complexes

The primary distinction between homoleptic⁴¹ and heteroleptic⁴² complexes is that homoleptic complexes have identical ligands linked to a metal centre. In contrast, heteroleptic complexes have at least one distinct ligand coupled to the complex's metal centre (**Figure 4**).

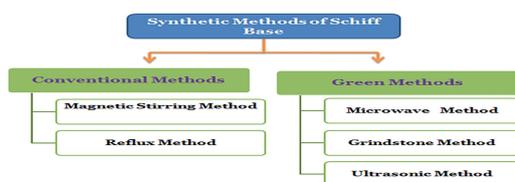


Figure 3. Synthetic methods of Schiff bases.

Comparison Table

| Category | Schiff Base Type | Zn(II) Complex Geometry | Applications |
|----------------------------|-----------------------------|----------------------------|--|
| Aliphatic | Simple imines | Tetrahedral | Basic coordination studies |
| Aromatic (salicylaldehyde) | Bidentate (N,O donors) | Tetrahedral/ Octahedral | Biomimetic, catalysis |
| Amino acid-based | Polydentate (N,O donors) | Octahedral | Enzyme mimics, bioinorganic chemistry |
| Macrocyclic | Multidentate cyclic ligands | Octahedral | Stability, selectivity |
| Heterocyclic | N/S/O donor heterocycles | Tetrahedral/ Octahedral | Biological activity |

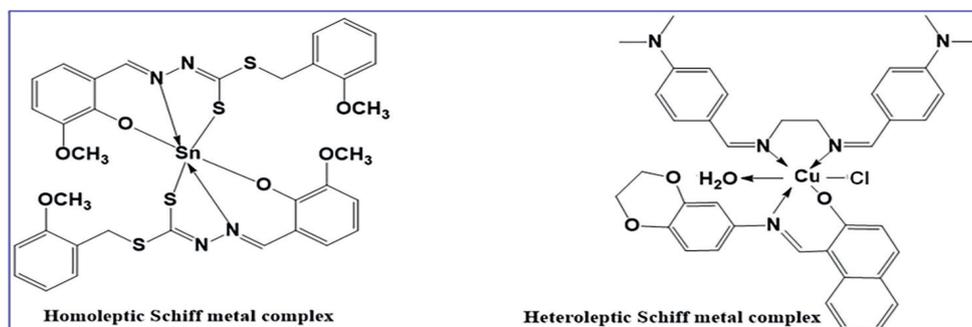


Figure 4. Homoleptic and heteroleptic Schiff base metal complexes.

Mononuclear and polynuclear Schiff base metal complexes

A single metal atom or ion is contained within the most basic type of Schiff base metal complex, and it is surrounded by monodentate, bidentate, tridentate, and polydentate ligands. Polynuclear Schiff base metal complexes are attributed to the presence of two or more atoms of metal, or ions, co-ordinated within a single coordination sphere. The two atoms may be linked together by direct metal-metal bonds, bridging ligands, or all of these things. As versatile ligands, Schiff bases form various polynuclear metal complexes such as homonuclear and heteronuclear. These flexible ligands have the ability to act as monodentate, bidentate, or polydentate, and they can be engineered to produce mononuclear, di nuclear, or polynuclear metal-organic frameworks. It is possible to change the nuclearity of Schiff base complexes; for example, it is possible to synthesize either mono- or di nuclear complexes using nearly identical ligands and synthetic processes for both types of complexes.

Achiral and chiral Schiff base metal complexes

A chiral Schiff base metal complex is not superimposable with its own mirror image because the two structures are not identical in all respects. The mirror image of an achiral Schiff base metal complex is identical to the complex itself and can be superimposed on it. The phenomena of optical activity have traditionally been defined in terms of asymmetry and dissymmetry; however, the term chirality has recently superseded these earlier classifications. Chiral entities exist as two species with the same chemical constitution. The only way they are distinguishable from one another is that they have the opposite configuration of an object and the mirror image of that thing. Chemical compounds can be said to be stereoisomers if their chemical constitutions are same but their spatial arrangements of their atoms are different. Chiral refers to the property of molecules that prevents

them from being brought into coincidence with their mirror copies by the use of stiff motions.

Application of Schiff bases and its Zn(II) metal complexes

Schiff bases and their Zn(II) complexes are widely applied in medicine (antimicrobial, anticancer, enzyme mimics), catalysis (organic transformations, polymerization), materials science (fluorescent sensors, optoelectronics), and environmental chemistry (metal ion detection, pollutant removal) Zn(II) complexes are especially important because Zn is biologically essential and its d^{10} configuration allows flexible geometries:

Biological/Medical Applications

Antimicrobial activity: Effective against bacteria and fungi.

Anticancer potential: Some Zn(II) Schiff base complexes inhibit tumor growth.

Biomimetic chemistry: Amino acid-based Schiff bases with Zn(II) mimic enzyme cofactors like pyridoxal phosphate, helping study transamination reactions.

Catalysis Zn(II) Schiff base complexes catalyse organic reactions such as oxidation, polymerization, and condensation. Useful in green chemistry as non-toxic alternatives to heavy metals. Optoelectronics & Materials Science Many Zn(II) Schiff base complexes exhibit fluorescence, making them valuable in OLEDs, sensors, and photonic devices. Applied in luminescent probes for biological imaging. Environmental Applications Used in metal ion detection and pollutant removal due to selective binding properties.

Application in Catalysis

Catalytic activity is enhanced in both homogeneous and heterogeneous reactions by

Comparison Table

| Field | Schiff Bases | Zn(II) Complexes |
|-------------------------|--|---|
| Medicine | Antibacterial, anticancer, enzyme inhibitors | Enhanced antimicrobial & anticancer activity; enzyme mimics |
| Catalysis | Organo catalysts in organic reactions | Catalysts in oxidation, polymerization, condensation |
| Materials Science | Dyes, pigments, stabilizers | Fluorescent sensors, OLEDs, luminescent probes |
| Environmental Chemistry | Metal ion sensors, pollutant binding | Selective ion detection, pollutant removal |

Schiff base metal complexes. The ligands, coordination sites, and metal ions employed in a given compound determine its activity. Many different reactions, such as polymerization, ring-opening polymerization, oxidation, epoxidation, allylic alkylation, reduction of ketones, hydrazination of acetophenones, the Michael addition reaction, the decomposition of hydrogen peroxide, the annulation reaction, the Heck reaction, the carbonylation reaction, and the Diels-Alder reaction, have been used to critically evaluate the catalytic activity of metal complexes. There is significant potential for Schiff base ligands to be used as metal complexes in catalysis due to their simple synthesis method and heat stability. The catalytic activity of Schiff base complexes differed greatly depending on the structure and kind of ligands used^{44,45}.

Application in Agrochemical industry

Metal complexes with diverse Schiff base ligands have attracted the attention of chemists in recent years due to their agricultural applications, such as pesticidal, nematocidal, and insecticidal. Unsymmetrical Schiff bases glyoxal salicylaldehyde succinic acid di hydrazide and its Ni(II), Co(II), Zn(II), and Cu(II) complexes have been synthesized and studied; at greater concentrations, they display considerable insecticidal action⁴⁶. H₂L [2, 22 -[(1E, 2E)-ethane-1,2- diylidenedi (E) azanylylidene]dibenzenethiol] and its new Zn(II), Ni(II) metal complexes have

been employed as insect repellent agents⁴⁷. Coumarin-based Schiff base and its earth metal complexes⁴⁸ have been used to treat pests (*Tribolium castaneu*) and worms (*Meloidogyne incognita*).

Analytical applications

Schiff bases have been used as analytical probes or reagents by researchers. These are used to analyze primary amines, carbonyl compounds, and functional groups. In complexes, azomethine bonds are formed through complex formation reactions or changes in their spectroscopic properties caused by pH and solvent variations (pH of solvent polarity indicators). Schiff bases are a great carrier for the selective and efficient extraction of certain metal ions. They are well-known for their effective chelating capabilities. Schiff bases extract metal ions, essential in regulating heavy metal pollution. N, N -bis(3-methylsalicylidene)-ortho-phenylene diamine, Schiff base used in spectrophotometric detection of nickel. The approach has been used successfully to quantify trace quantities of nickel in natural food samples. Schiff bases are renowned for their ability to form complexes and serve as good chelating ligands. They have been widely employed as analytical reagents due to their ligation property. Schiff bases made of salicylaldehyde are employed in gravimetric and spectro photometric analyses. In addition, the same reagent was recently

employed for the spectrophotometric detection of Ni (II) at a trace level. Cu^{2+} ions have been detected using the fluorescent 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(2-hydroxy-5-bromobenzylidene) aminothiazole Schiff base. This chemical sensor operates in the visible region, has a wide dynamic operating range, and may be used over a wide pH range⁴⁹.

Energy storage

There is a resurgence of interest in the search for effective, clean, and sustainable energy sources (like wind and solar) as well as cutting-edge energy conversion and storage technologies as a result of the rapid growth of the world economy, the depletion of fossil fuels, and rising environmental pollution. Energy storage technologies are more important in our lives since the sun does not shine at night and the wind does not blow all the time. Currently, there is a lot of interest in electrical energy storage technologies including batteries and electrochemical capacitors (supercapacitors). Recent research has shown that organic oligomeric Schiff bases and electroactive polymeric (linear or hyperbranched) Schiff bases perform satisfactorily as negative electrodes (anodes) in sodium-ion batteries⁵⁰. Lithium-ion batteries have also made use of nitrogen-rich carbon nanosheets produced by the Schiff base reaction in a molten salt solution as anode materials⁵¹. The linear polymeric Schiff bases developed by Armand et al.⁵² as a consequence of the condensation of aromatic dialdehydes with aliphatic and aromatic diamines performed well as anodes for sodium-ion batteries. Polymeric Schiff bases are also produced by combining terephthalic-aldehyde, phenylenediamine, and polyether amine blocks, resulting in polymers with high adhesive qualities that can be used as redox-active binders for sodium-ion anodes. Similarly, Zhang et al.⁵³ developed another Im COF (Imine bonds containing *covalent organic frameworks*) that performed again as an anode material for lithium-ion batteries derived from 2,4,6-triaminopyrimidine and terephthalaldehyde.

Chemo-sensing applications

Schiff base-based fluorescent probes have recently been invented for detecting and monitoring numerous hazardous analytes in biological systems. Schiff base compounds with nitrogen-oxygen-rich coordination as a receptor site provide a stable platform for fluorescence sensing with significant, visible color shifts. Detecting metal ions with diverse mechanisms in an accurate sample using Schiff base-based sensors is appealing currently. In the recent decade, Schiff base probes based on fluorescence live-cell imaging have been used to detect metal ions such as Co^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , Ag^{+} , Al^{3+} , and ClO^{-} ions⁵⁴⁻⁵⁶.

Bio-sensing applications

Within cells, Schiff base compounds have been used as biosensors for H_2O_2 , glucose, and Onco marker CA-125⁵⁷. Evaluation of the sensitivity and specificity of the *gold Schiff base complex-doped sol gel nano optical sensor* for the detection of CA-125 in ovarian cancer patient samples was performed and compared to results obtained from samples taken from healthy women serving as a control group⁵⁸. Sheta M. Sheta et al. created an ultrasensitive method of detecting human creatinine using cerium(III)-is at in Schiff base complex as an optical sensor⁵⁹.

Biomedical applications

Schiff bases and their metal complexes have numerous applications in various biomedical pharmaceuticals such as antimicrobial, anti-malarial, anticancer, antiviral, anti-inflammatory, antioxidant, anticonvulsant, anti-anthelmintic, bioprinting, tissue regenerating, enzyme inhibition and drug delivery. In biological systems, the azomethine nitrogen of Schiff bases serves as a binding site for metal ions to attach to diverse biomolecules such as proteins and amino acids for anti-germ activity. Our bodies' Schiff bases catalyzed many metabolic events in the form of enzymes that are active against certain bacteria. Several studies have been conducted to improve the bio-functions of Schiff bases and

their metal complexes. Schiff bases can fight cancer, fungus, germs, ulcers, and viruses, depending on which transition metal ions they contain⁶⁰⁻⁶².

Conclusion

Schiff bases and their Zn(II) complexes represent a significant class of compounds in coordination chemistry due to their structural versatility, ease of synthesis, and broad functional applications. The ability of Schiff bases to act as

multidentate ligands enables Zn(II) to adopt diverse geometries, resulting in complexes with notable biological, catalytic, and material properties. Their roles as enzyme mimics, antimicrobial and anticancer agents, as well as catalysts and luminescent materials, highlight their interdisciplinary importance. Overall, Schiff base–Zn(II) complexes continue to serve as valuable models and functional materials, bridging fundamental research with practical applications in medicine, industry, and environmental science.

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