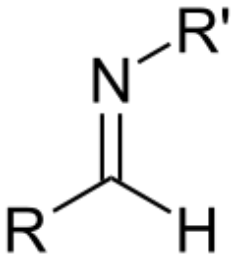
Schiff base

A **Schiff base** (named after Hugo Schiff) is a compound with the general structure $R_1R_2C{=}NR'$ (R' ≠ H).[1][2][3][4][5] They can be considered a sub-class of imines, being either secondary ketimines or secondary aldimines depending on their structure. The term is often synonymous with **azomethine** which refers specifically to secondary aldimines (i.e. R-CH=NR' where R' ≠ H).[6]

A number of special naming systems exist for these compounds. For instance a Schiff base derived from an aniline, where R^3 is a phenyl or a substituted phenyl, can be called an *anil*,[7] while bis-compounds are often referred to as salen-type compounds.

The term Schiff base is normally applied to these compounds when they are being used as ligands to form coordination complexes with metal ions. Such complexes occur naturally, for instance in corrin, but the majority of Schiff bases are artificial and are used to form many important catalysts, such as Jacobsen's catalyst.

General structure of an imine. Schiff bases are imines in which R^3 is an alkyl or aryl group (not a hydrogen). R^1 and R^2 may be hydrogens

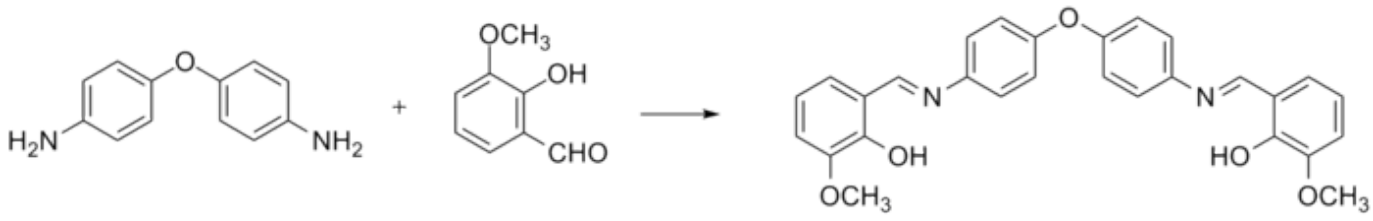


General structure of an azomethine compound

Contents

Synthesis

Schiff bases can be synthesized from an aliphatic or aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine. In a typical reaction, 4,4'-diaminodiphenyl ether reacts with *o*-vanillin:[8]



A mixture of 4,4'-oxydianiline **1** (1.00 g, 5.00 mmol) and *o*-vanillin **2** (1.52 g, 10.0 mmol) in methanol (40.0 ml) is stirred at room temperature for one hour to give an orange precipitate and after filtration and washing with methanol to give the pure Schiff base **3** (2.27 g, 97%)

Biochemistry

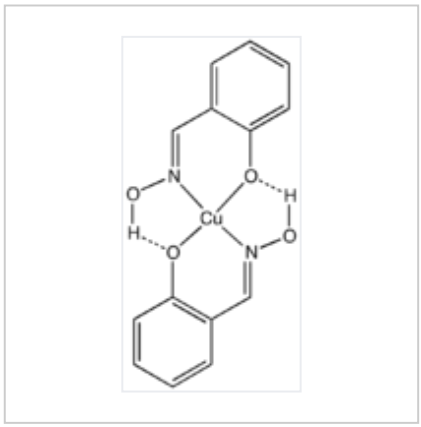
Schiff bases have been investigated in relation to a wide range of contexts, including antimicrobial, antiviral and anticancer activity. They have also been considered for the inhibition of amyloid-β aggregation. [9]

Schiff bases are common enzymatic intermediates where an amine, such as the terminal group of a lysine residue, reversibly reacts with an aldehyde or ketone of a cofactor or substrate. The common enzyme cofactor PLP forms a Schiff base with a lysine residue and is transaldiminated to the substrate(s).[10] Similarly, the cofactor retinal forms a Schiff base in rhodopsins, including human rhodopsin (via Lysine 296), which is key in the photoreception mechanism.

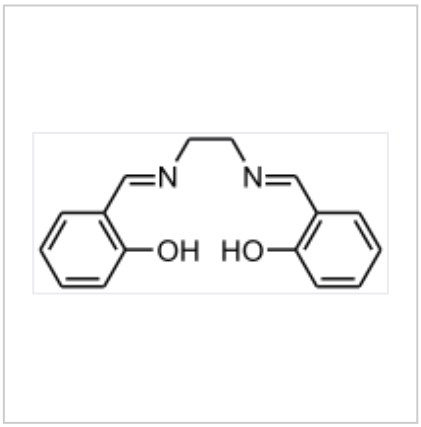
Coordination chemistry

Schiff bases are common ligands in coordination chemistry. The imine nitrogen is basic and exhibits pi-acceptor properties. The ligands are typically derived from alkyl diamines and aromatic aldehydes.[11]

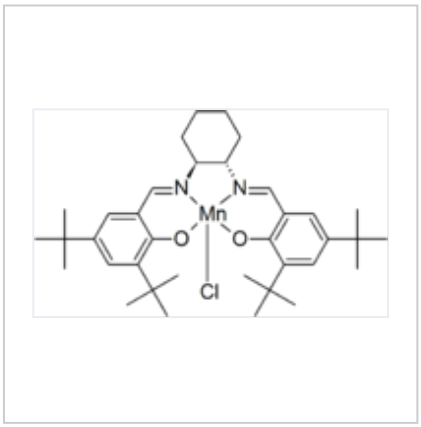
Schiff base ligands



Copper(II) complex of the Schiff base ligand salicylaldoxime.

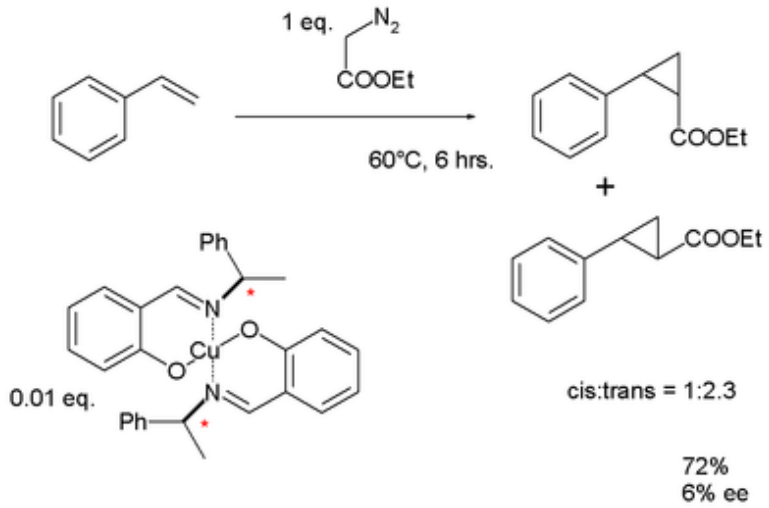


Salen is a common tetradentate ligand that becomes deprotonated upon complexation.



Jacobsen's catalyst is derived from a chiral salen ligand.

Chiral Schiff bases were one of the first ligands used for asymmetric catalysis. In 1968 Ryōji Noyori developed a copper-Schiff base complex for the metal-carbenoid cyclopropanation of styrene.[12] For this work he was later awarded a share of the 2001 Nobel Prize in Chemistry. Schiff bases have also been incorporated into MOFs.[13]

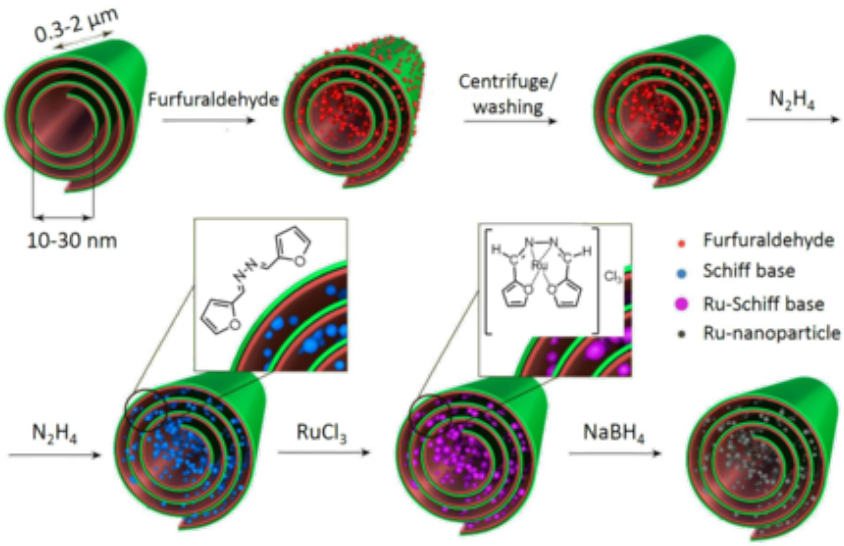


Conjugated Schiff bases

Conjugated Schiff bases absorb strongly in the UV-visible region of the electromagnetic spectrum. This absorption is the basis of the anisidine value, which is a measure of oxidative spoilage for fats and oils.

Nanotechnology

Schiff bases can be used to mass-produce nanoclusters of transition metals inside halloysite. This abundant mineral naturally has a structure of rolled nanosheets (nanotubes), which can support both the synthesis and the metal nanocluster products. These nanoclusters can be made of Ag, Ru, Rh, Pt or Co metals and can catalyze various chemical reactions.[14]



Formation of metal clusters in halloysite nanotubes via a Schiff base reaction on example of ruthenium.[14]

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