

# Azomethine Metal Chelates as an Efficient Catalyst for Oxidation of Organic Compounds

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## Abstract

Azomethine ligands and their metal chelates are flexible compounds synthesized from the condensation of an amino compound with carbonyl compounds and extensively used for industrial purposes and also show a broad range of biological efficiencies including antibacterial, antifungal, antiviral, antimalarial, antiproliferative, anti-inflammatory, anticancer, anti-HIV, anthelmintic and antipyretic properties. Azomethine metal chelates show excellent catalytic activity in diversity reactions. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis. The high thermal and moisture stabilities of many azomethine metal chelates were useful attributes for their application as catalysts in reactions involving at high temperatures. Recent researches in oxidation catalysis have focused on how to employ the metal-catalyzed oxidation of organic substrates. This review concerns with the current developments for the oxidations of organic compounds.

**Keywords:** Catalyst; Oxidation; Azomethine ligands; Metal chelates;  $H_2O_2$

## Introduction

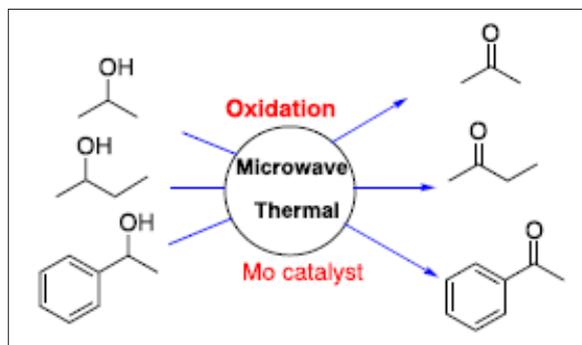
Azomethine compounds played an important role as ligands due to their excellent coordinative capability and have a wide variety of industrial applications in many fields including analytical, biological, coordination inorganic chemistry and organic synthesis, such as pigments, dyes and catalyst intermediates, semiconductors and as chemo-sensors [1-15]. The chemistry of azomethine ligands is an important area of research with increasing interest due to the simple synthesis, versatility and diverse ranges of applications of their metal chelates, e.g. in biology and as catalysts in various reactions [16-20]. Thus, a review highlighting the oxygen affinity of azomethine metal chelates would be needed.

## Oxidation of organic compounds

Life would not exist without oxidation, which is very important from scientific and practical points of view. In organic chemistry, oxidation reactions are some of the most important ones. Thus, selective catalytic oxidations represent a severe challenge for modern organic chemistry, and their importance has been highlighted in terms of Nobel Prizes. The reaction between ONS donor ligands  $H_2L$  (derived from 2-hydroxy benzaldehyde or its derivatives or 2-hydroxy-1-naphthaldehyde and o-amino-thiophenol) and  $[RuHCl(CO)(PPh_3)]$  afforded new Ru(II) metal chelates of  $[Ru(L)(CO)(PPh_3)]$  (L=dianionic ONS donor Azomethine ligand). These metal chelates were found to be effective for the oxidations of alcohols and sulfides at room temperature using N-methyl-morpholine-N-oxide as oxidant. This provided a general method for the oxidations of different kinds of alcohols under mild conditions. Benzylic primary and secondary alcohols were oxidized to products in excellent yield, and aliphatic and cyclic alcohols gave carbonyl compounds in moderate yield [21].

Four di-oxido molybdenum(VI) chelates with ONO tridentate Azomethine ligands derived from 3-acetyl-6-methyl-(2H)-pyran-2,4-(3H)-dione (dehydrocetic acid, Hdha) and aromatic hydrazides (benzoyl hydrazide (bhz), isonicotinoyl hydrazide (inh), nicotinoyl hydrazide (nah) and furyl hydrazide (fah)) have been prepared, and then analyzed by elemental analysis, infrared, UV-visible,  $^1H$ NMR and  $^{13}C$ NMR spectroscopies and thermogravimetric analyses. The di-oxidomolybdenum (VI) chelates have been studied as catalysts for the homogeneous oxidation of secondary alcohols (1-phenylethanol, 2-propanol and 2-butanol; Figure 1), using

30%  $H_2O_2$  as an oxidant. Both microwave and liquid-phase oxidation methods have been tested for catalytic reactions. Also, the various parameters of the reaction, such as amount of catalyst, oxidant, solvent and temperature, have been taken into consideration for the maximum conversion of substrates. Under the optimized reaction conditions, secondary alcohols gave high yields of the respective ketones. Addition of N-based additive reduced the reaction time and increased the conversion of alcohol [22].

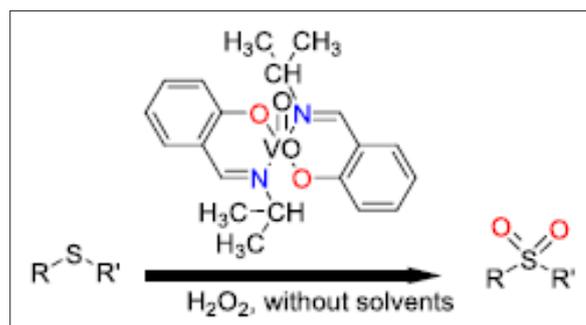


**Figure 1:** Oxidation of alcohols and sulfides into corresponding aldehydes and sulfoxides..

Oxidation of sulfides to sulfoxides and oxidative coupling of thiols into their corresponding disulfides were carried out using hydrogen peroxide as oxidizing agent in the presence of Ni (II), Co (II), Cr(III), Zn(II) or Cd(II) chelates immobilized on  $Fe_3O_4$  magnetic nanoparticles (M-Salen-MNPs) as stable, heterogeneous, efficient and magnetically recoverable nano catalysts under mild reaction conditions. Also, a variety of aromatic and aliphatic sulfides and thiols with various functional groups were successfully oxidized with short reaction times in good to excellent yields. Recovery of the catalyst is easily achieved by magnetic decantation and it can be reused for several consecutive runs without significant loss of its catalytic efficiency [23,24].

A new bidentate ON azomethine ligand (HL) was prepared by simple condensation reaction of isopropylamine and salicylaldehyde in methanol or chloroform as solvent at ambient temperature. Then, by reaction of HL and VO (acac)<sub>2</sub> in a ratio of 2:1 in the presence of triethylamine at room temperature, a new oxovanadium (IV) Azomethine complex, VOL2, was prepared. The catalytic performance of the VOL2 complex was tested in the selective oxidation of thioanisole with the green oxidant  $H_2O_2$  (35% aqueous) under solvent-free conditions and with organic solvent (EtOH,  $CHCl_3$ ,  $CH_2Cl_2$ , DMF,  $CH_3CN$ , EtOAc) as model reaction. Owing to the excellent catalytic performance of the VOL2 complex (Figure 2) under solvent-free conditions, this complex was used for the oxidation of various sulfides to the corresponding sulfones under solvent-free conditions. The use of  $H_2O_2$  as oxidant and the absence of solvent made these reactions interesting from environmental and economic points of view. The amounts of  $H_2O_2$  played an important role in leading to the selective oxidation of thioanisole into the corresponding sulfone. Also, different sulfides, such as phenyl-alkyl sulfides, di-alkyl sulfides and unsaturated sulfides, were converted into the corresponding sulfones in the presence of VOL2 as catalyst. Sulfide with C=C double bond was selectively oxidized into its

corresponding sulfone without affecting reactive functional groups [20]. Cu and Ni nanosized azomethine chelates, namely ahpvCu, ahpnbcu, and ahpvNi, incorporating azomethine ligands derived from the condensation of 2-amino-3-hydroxypyridine, with either 3-methoxysalicylaldehyde (ahpv) or 4-nitrobenzaldehyde (ahpnb), were synthesized using sono chemical approach. The structure and properties of the new ligands and their chelates with Ni (II) and Cu (II) were determined via infrared, nuclear magnetic resonance, electronic spectra, elemental analysis, thermal gravimetric analysis, molar conductivity, and magnetic moment. The combined results revealed the formation of 1:1 (metal: ligand) chelates for ahpvCu and ahpvNi and 1:2 for ahpnbcu. Additionally, CuO and NiO nanoparticles were prepared by calcination of the respective nanosized Cu/Ni chelates at 500 °C and characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Significantly, the as prepared nanosized Azomethine Cu/Ni chelates and their oxides showed remarkable catalytic activity towards the selective oxidation of benzyl alcohol (BzOH) in aqueous  $H_2O_2$ /di-methyl sulfoxide (DMSO) solution. Thus, catalytic oxidation of BzOH to benzaldehyde (BzH) using both ahpvCu complex and CuO nanoparticles in  $H_2O_2$ /DMSO media at 70 °C for 2h yielded 94% and 98% BzH, respectively, with 100% selectivity [20].



**Figure 2:** Oxidation of sulfides to corresponding sulfones under solvent free conditions..

## Conclusion

Azomethine ligands are known as an important class of organic compounds because of their capacities to bind metal ions from environmental media as well as being efficient catalysts for oxidation of alkanes and alcohols, epoxidation of alkenes and sulfoxidation of organic compounds in the presence of suitable oxidants, e.g. alkyl hydroperoxides,  $H_2O_2$  or  $O_2$ , under mild conditions. The results reviewed here showed that Schiff bases and their complexes exhibit efficient catalytic activity towards the selective epoxidation of simple alkenes, and primary and secondary alcohols. Immobilization on solid supports was one of the desirable strategies for facilitating catalyst separation and recycling. The topics reviewed in this study are industrially promising in the fields of catalysis with multi- and interdisciplinary approaches. Although the developments of interest have been made in oxidation catalysis using azomethine complexes as discussed herein, it is necessary to address further the development of green processes. Consequently, the use of  $H_2O_2$  as a mild oxidant in the presence of the synthesized catalysts would provide an efficient, easy and safe approach, leading to oxidations of alcohols to corresponding compounds.

Thus, green (using H<sub>2</sub>O<sub>2</sub>), simple, clean and economical procedures for oxidation of various organic compounds is recommended.

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