

## Schiff bases and schiff base metal complexes: from syntheses to applications.

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**Abstract:** The synthesis and applications of Schiff bases and their metal complexes have attracted much interest and concern in all aspects of chemistry and related fields such as biology and physics. As versatile ligands, Schiff bases are formed when carbonyl compounds (aldehydes or ketones) are condensed with amines. Schiff bases and their metal complexes have been used in quantitative analysis, photometric analysis, fluorometry, as potentiometric sensors, in solvent extraction, as solid phase extraction sorbent, in high performance liquid chromatography, in antimicrobial studies, as plant growth regulators, as insecticides, as catalyst, in antifertility and enzymatic activity, as dyes, polymer and other miscellaneous applications. There are limited papers on the applications of Schiff bases and their metal complexes. This review summarizes the preparation of Schiff bases as donors and stabilizers of metals in high oxidation state and their applications.

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### 1.0 INTRODUCTION

Schiff bases are important chelating agents which offer great versatility in the design of useful, interesting and commercial ligand system. They are derived from aromatic amine and carbonyl compound by nucleophilic addition and dehydration thereafter to generate imine (fig 1) which binds metal ions through the lone electron pair resident in nitrogen atom (Jurrapour and Zarei, 2004).

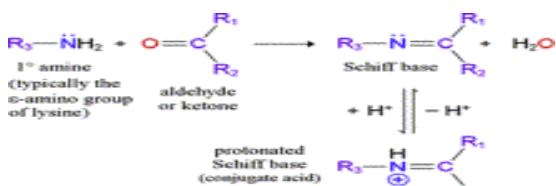


Fig 1. Formation of Schiff base(Jurrapour and Zarei, 2004).

Researches (Harvey and Clifford,1950) have shown that bis-imine Schiff bases are stable metal complexing agents which when used with one or more donor atoms forms macrocycles and are germane in stabilizing high oxidation state of metals. There has been extensive chemistry on the use of Schiff bases and their complexes in inorganic chemistry over the years. Mogan and Drew (1920) noted that Schiff bases are simply and cheaply synthesized which is of high industrial importance. Also, they are multidentate as several binding sites are unoccupied for some metals and the presence of vacant sites are good sites for potential catalytic or enzymatic reaction.

Furthermore, studies (Abu *et al.*,1999; Boghaei *et al.*, 2006; Dong *et al.*, 2006; Morgan and Drew, 1920) have shown that the electronic and steric properties of complexes of Schiff bases are modified on substitution at the aromatic moiety thereby fine tuning the properties of the Schiff base and its complexes. Schiff bases have been noted (Baleiza *et al.*, 2006, Katsuki, 2006; Green and Alexander,1965; Nworie *et al.*, 2013;Zhang *et al.*,1990) to form complexes with most metals such as Mn, Cr, Co, V, Cu, Ti, Pd, Ru, Au, Zn, Fe, Cr, Be, Th, Zr, U, Ni and Mo. The complexes of these metals to the ligand/Schiff bases) depending on the tetradentate  $N_2O_2$  or pentadentate  $N_2O_2x$  coordination around the metal centre exhibits a distorted square planar, square pyramidal, octahedral or distorted octahedral geometry (Hansen *et al.*,1996; Klein *et al.*,2000; Ye *et al.*,2005 ;Zhang *et al.*,1990;).

Isse *et al* (1992) and Klein *et al*(2000) noted that the co-ordination chemistry of nickel metal complexed with salen-type ligands had been a subject of study because of their oxygen binding activity. The unusual magnetic and structural properties, redox chemistry and catalytic ability of epoxidation and oxidation reactions have been observed (Veli and Seniz, 2005) to be promising. Interest in Schiff bases and their complexes have been applied in structural elucidation especially for unsymmetrical Schiff base ligands as they give the geometry of the metal ion binding sites in the metal enzymes and proteins, selectivity of manufactured

materials and natural systems (Bu et al., 1997; Daneshvar et al., 2003).

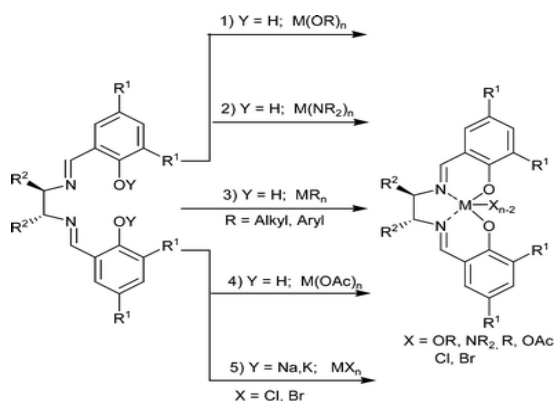


Fig 2. Preparation of metal complexes of Schiff bases (Cozzi, 2004)

Cristin and Castro (1998); Garg and Kumar (2003); Yamada (1999); Katsuki (2006) noted separately that the structural features of salen allows flexibility due to the presence of ethylene unit, thus the synthesis is simple, the ligand versatile, the applications diverse and can undergo oxidation and reduction to accommodate envisaged changes in metal size. Schiff bases though are stable solids easily undergo degradation and the metal complexes undergo demetallation in the presence of strong acids, bases, oxidizing and reducing agents and as such great care is needed in its purification and use. Baleiza and Garcia (2006) noted that Salen metal complexes undergo ligand degradation and demetallation due to competitive complexation at low pH and in the presence of strong oxidizing and reducing agents.

The preparation of Schiff base metal complexes are achieved generally by treating metal salts with the Schiff base ligands under favourable experimental conditions. Recently (Ukoha et al., 2012) prepared and characterized the complexes of Cu(II) and Ag(I) bis(4-hydroxypent-2-ylidene) diaminoethane by liquid-liquid extraction method. The review work (Cozzi, 2004) showed that there are five synthetic routes to the preparation of Schiff base metal complexes. The routes as outlined are

- (1) The use of metal alkoxide, though early transition metal alkoxides ( $M = Ti$ ) are commercially available and easy to handle but other ones are moisture-sensitive and not easy to handle.
- (2) The use of metal amides as precursors by elimination of acidic phenolic proton of the Schiff bases.
- (3) Refluxing of metal acetate with the Schiff bases.
- (4) Treatment of the metal alkyl complexes with Schiff bases.
- (5) Deprotonation of Schiff bases using NaH or KH in the presence of a co-ordinating solvent

followed by reaction with the metal halides. The preparation of Schiff base metal complexes by constituent combination method has been in use but most recently the solvent extraction method.

## 2.0 APPLICATIONS OF SCHIFF BASES AND THEIR METAL COMPLEXES

Schiff bases and their metal complexes are very important organic compounds which have wide applications in the following areas.

### Quantitative Analysis/spectrophotometry

Several Schiff base ligands are used for the qualitative and quantitative detection of metal ions. In all the processes involved in the detection of metal ions in solution by the use of Schiff base ligands (spectrophotometry, fluometry, potentiometry, solvent extraction, solid phase extraction, high performance liquid chromatography) complexation is necessary and is dependent on pH, size of cation, structure of ligand and temperature.

A number of spectrophotometric determinations of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $V^{4+}$ ,  $Ce^{4+}$  and oxo-manganese (II) ion have been carried out using bis(salicylidene)ethylenediamine. Green and Alexander (1965) reported that beryllium is extractable into non-aqueous solvents by bis(salicylidene)ethylenediamine as a chelating Schiff base. The Be-Salen complex is bidentate, yellow in colour, of low solubility and stable to hydrolysis in the pH range of 6-10. Panda et al (1998) reported the extraction of Uranium (VI) with binary mixtures of a quadridentate Schiff base bis(Salicylidene)ethylenediamine and various neutral donors at equilibrium pH range of 2.5 to 5.5.

Panda et al (1987) also noted quadridentate Schiff base bis(Salicylidene)ethylenediamine as an extractant for thorium, uranium, zirconium(IV) in benzene as a diluents and at pH of 6.5. The solubility of bis(Salicylidene)ethylenediamine was studied (Seugheun et al., 2003) with in situ UV- vis spectrophotometer and discovered that there is a Lewis base interaction between Salen and  $CO_2$ . Alizadeh et al (1999) synthesized and studied the complexation reaction of 2, 2<sup>1</sup> - (1,2-ethanediyl bis (nitrilomethylidyne) bis (1-naphthalenol) with  $Cu^{2+}$  ions spectrophotometrically in different dimethylsulphoxide acetonitrile mixtures. Nworie et al [(2013) studied the complexation ability of metal cations  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  spectrophotometrically using bis (2,2<sup>1</sup> - methylilydenephenol) diaminoethane.

Nwabue and Okafor(1991) reported the extraction and spectrophotometric determination of Ni(II), Fe(II), Fe(III) and V(IV) ions with bis(4-hydroxypent-2-ylidene) diaminoethane where the maximum absorption was at 445nm, 435nm, 560nm and 660nm respectively. Tantarú *et al* (2002) determined manganese(II) spectrophotometrically from pharmaceutical forms using 1-ethylsalicylidene bis ethylenediamine. The brown complex had maximum absorption at 460nm at pH 6 with molar absorptivity of  $9.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

### As Electroluminescent Materials

Organic electroluminescent materials are fabricated using organic dyes, chelate metal complexes and polymers. Schiff base metal complexes of Zn(II) with N,N<sup>1</sup> – bis (hydroxyl -1 – naphthylidene) – 3, 6 – dioxa – 1, 8, diaminoctane is noted (Yi *et al.*,2004; Yu *et al.*,2007) to be promising as an electroluminescence device since it emits blue light with an emission peak at 455nm and maximum brightness of 650cdm<sup>-2</sup>. The optoelectronic properties, crystal structure and thermal stability of bis (salicylidene (4 – dimethylamino) aniline) Zinc(II) was reported (Xie *et al.*,2008). The application of Schiff base metal complexes as organic light emitting diodes (OLEDs) is never unconnected with the good light emission and charge transfer transporting performance of these complexes.

### As Electrochemical Sensors

Several Schiff base complexes have been applied in the preparation of potentiometric sensors for the determination of both anions and cations. Ganjali *et al* (2002) and Mohammed *et al*(2006) prepared vanadyl-salen, oxo-molybdenum methyl Salen and cerium-Salen indicator electrodes at pH 3-11 which acts as indicator electrodes (sensors) in potentiometric titration and in monitoring of molybdenum phosphate in granular fertilizers. N, N<sup>1</sup> – bis (salicylidene) -1,2-cyclohexdiamine has been used as a neutral carrier matrix in polyvinyl chloride) and also successfully applied in the determination of aluminum(III) in biological, environmental and industrial samples and as indicator electrode in potentiometric titration of aluminum ion with EDTA (Gupta *et al.*,2009).

Studies (Farias and Bastos, 2009) investigated the electrochemical behaviour of copper(II) salen in aqueous 0.02molL<sup>-1</sup> phosphate buffer of pH 7 at the mercury electrode using polarographic and voltammetric techniques. The work noted that the free ligand Salen, hydrolyzes in aqueous media but on complexation with copper(II) ion is stabilized. The reduction of copper(II) salen in phosphate buffer (pH 7.0) was shown to follow three distinct processes; electrochemically quasi-

reversible Cu(II) salen/ Cu(I) salen, the reduction of Cu(I) salen to Cu(0) and the reduction of free dianionic ligand or the disproportionation of Cu(I) salen which is an irreversible chemical process. An effective assay for the determination of trace amount of copper(II) in the presence of Salen with detection limit of  $1.0 \times 10^{-8} \text{ mol L}^{-1}$  was proposed.

### As non-linear Optical devices

Non linear optical devices are materials capable of manipulating photonic signals efficiently due to the interactions of applied electromagnetic fields with various materials to arrive at a new electromagnetic field different in phase, physical properties and frequency and are applied in optical computing, dynamic image processing and optical communication (Benning, 1995; Verbiest *et al.*,1997). Studies (Lacroix, 2001) have shown that bis (Salicylaldiminato) metal Schiff base complexes exhibit good second order non-linear optical properties.

The application of metal –salen complex as red phosphorescent light emitting diode (Ph OLEDs) was done by group of scientists (Bae *et al.*, 2011). The Monomeric and dimeric salen-aluminium complexes were investigated as host layer materials in red phosphorescent organic light emitting diodes. The complexes have high thermal stability with decomposition temperature of 330 and 370°C. Results indicated that the complex formed based on vacuum deposition host shows intense brightness, luminosity and quantum efficiencies than the device fabricated based on solution process whose performance is poor. Disc scanning calorimetry (DSC) analysis on the complexes indicated that they form amorphous glasses upon cooling of melt samples with glass transition temperature (GTT) of 112 and 172°C respectively.

### In medicinal chemistry

Schiff bases contain the azomethine derivatives which according to literature( Anant and Devjani,2011, Ramasamy *et al.*,2010;Shalin *et al.*,2009) posses antibacterial, anticancer, antifungal and antidiuretic properties and this biological activity increase or decrease upon chelation of the Schiff base with metal cations. Schiff base complexes are medicinally important and used to design models of biological compounds. Roy *et al* (2007) noted that the covalent or non covalent interaction between transition metal complexes and DNA is a means of developing sensitive chemical probe for DNA and also building drug models. Consequently, if the interaction is covalent, the labile part of the complexes is co-ordinatively replaced by a nitrogen base of DNA whereas in non-covalent binding, there is electrostatic, intercalative and groove binding of cationic transition metal complexes

along the periphery of the DNA Helix as illustrated in fig 3.

Ramasamy *et al* (2010) studied the antimicrobial activities of complexes of tridentate Schiff base ligands containing pyrazolone moiety and observed that metal complexes of Vo(II), Cu(II), Fe(III) and Co(II) with the ligand showed enhanced antibacterial activity against *staphylococcus aureus*, *Escherichia Coli*, and antifungal activity against *C. albicans*, *Rhizopus Sp*, *Aspergillus niger*. Metal complexes of 2 – thiophenecarboxaldehyde and 2-aminobenzoic acid have been noted (Roy *et al.*,2007) to possess antitumor activities. Also Schiff bases derived from gossypol and silver complexes of Schiff bases have been noted to show high antiviral activity (Anant and Devjani,2011). It has been noted that fluorination on aldehyde part of Schiff bases enhances insect acaricidal activity and Schiff bases derived from sulphur thiadizole and salicylaldehyde and their complexes exhibit high toxicity against insects (Anant and Devjani,2011).

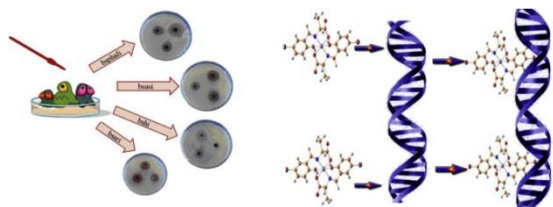


Fig.3.diagram for antibacterial activity and DNA interaction of Schiff base complexes (Roy *et al.* ,2007).

Hodnett *et al* (1987) have noted that Schiff base derived from 2 – thiophene carboxaldehyde and 2 – aminobenzoic acid possesses possible antitumor effect and is recommended for clinical and experimental tumor chemotherapy. Young and Cooper (1983) noted that organocobalt complexes with tridentate Schiff base act as initiator of emulsion polymerization and copolymerization of diene and vinyl monomers and amine terminated liquid natural rubber glyoxal yields poly Schiff base that acts as an anti-ageing agent.

Studies (Osman and Basch,1984;Sharpe *et al.*, 2007) proposed the mechanism for the dismutation of  $O_2^-$  and catalase mimetic action of Mn-salen. The dismutation of  $O_2^-$  involves the reduction of Mn(III) to Mn(II) by  $O_2^-$  which forms  $O_2$ . The Mn(II) is oxidized to Mn(III) in the presence of  $O_2$  giving  $H_2O_2$ .

Similarly,(Doctrow *et al.*,2012) reported the beneficial application of Mn – salen complexes as a synthetic superoxide dismutase (SOD) and catalase mimetics in models of oxidative stress. The Mn-Salen complexes though not designed to affect the mitochondria, exhibited “mito protective” activity, prevented respiratory chain abnormality caused by ionizing radiation in rat astrocyte cultures and attenuated ischemia reperfusion injury and mitochondrial dysfunction. Similarly, Mn –

Salen complexes play pharmacokinetics and cytotoxic role in addition to the low molecular weight, antioxidant, superoxide dismutase and catalase and catalytic scavenging mechanism and action against multiple destructive species placing it above other antioxidants (Doctrow *et al.*, 2005).

Salen manganese complexes have been shown to be beneficial in vivo models for neurodegenerative disorders, radiation injury, endotoxemia, age related impairment and radiation injury to kidney, lung and skin (Doctrow *et al.*, 2012; Malfroy and Doctrow, 2006 ). As a catalytic mimetic, Mn-salen is oxidized to an oxomanganese salen complex by  $H_2O_2$  liberating water. Consequently, the Mn-salen complex is reduced by  $H_2O_2$  to generate the water and oxygen.

Metal –salen compounds with magnetic properties which can be employed as magnetic materials and magnetic drugs was invented (Ishikawa and Eguchi, 2014). The study revealed that the percentage of metal salen complex compound with a crystal grain size of  $1\mu m$  or more  $3\mu m$  or less is preferable and the crystal grain size of  $100nm$  or more to  $500nm$  or less is preferable to ensure passage and retention through the cell capillaries and retain the autoferromagnetism respectively. The study was generalized to Salen – metal complexes such as Fe, Cr, Mn, Co, Ni, Mo, Ru, Rh, Rd, W, Re, Os, Ir, Pt, Nd, Sm, Eu Os, Gd and their derivatives substitution. This work was in support of the previous work by the same authors (Ishikawa and Eguchi, 2013) on metal salen complex derivative and process for production thereof where a target component containing an enzyme, an antigen, a peptide, a protein, an antibody or an oligonucleotide and a medical molecule is allowed to bind to the metal – Salen complex through the amide or disulphide bond.

### In catalytic reactions

Schiff base metal complexes exhibit catalytic activities and chiral Schiff base complexes play a central role in epoxidation, oxidation, hydroxylation and aldol condensation reactions. Kim *et al* (2008) noted that manganese Salen complex known as Jacobsen catalyst has been applied as a catalyst in the formation of epoxy resin having a stereoregularity. The complexes of Co(II), Fe(III) and Ru(III) with Schiff bases derived from hydroxyl benzaldehyde are important in the oxidation of cyclohexane into cyclohexanol and cyclohexanone in the presence of hydrogen peroxide. Balaeiza and Garcia (2006) and Tumer *et al* (2008) and noted that Salen – metal complexes are well known as catalysts both in heterogeneous and homogenous phases.

Maneiro *et al* (2003) noted that manganese(II) and Manganese(III) complexes of substituted  $N,N^1$  – bis (salicylidine) 1,2- diimino-2-methylene is an efficient model for peroxidase

activity. Electron transfer in a copper system (oxidation – reduction process) was observed using copper(II) complexes of indoxyl thiosemicarbazone (Murugkar *et al.*,1999). Cobalt(II) Schiff base complexes are known to bind and store oxygen and in organic synthesis as a result of their catalytic properties. Co(salen) and its analogues have been noted to be promising for catalyzing oxidation of alcohols, phenols and alkenes with oxygen as oxidant (Simandi, 2003).

The asymmetric epoxidation of conjugated olefins in the presence of various terminal oxidants by Ruthenium(II) complex of a chiral tetradentate  $N_2O_2$ ,  $N_2P_2$  and  $H_2O_2$  donor Schiff base ligands have been reported (Takeda *et al.*,1999). Fig 4 and 5 illustrated the catalytic applications of Schiff base complexes.

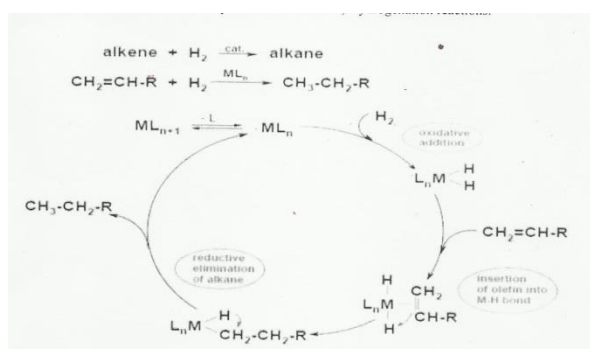


Fig 4. Catalytic applications of transition compounds for organic reactions (Takeda *et al.*,1999).

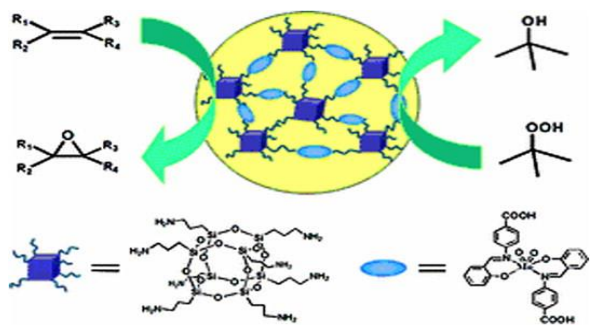


Fig 5. Mechanism of the catalytic reaction using Mo-salen complex (Cavallo and Jacobsen ,2003)

Group of workers(Cavallo and Jacobsen ,2003; Schaus *et al.*,2002; Srinivasan *et al.*,1986;Zhang *et al.*,1990) studied the variety of catalytic applications of metal salen complexes in asymmetric reactions involving enantioselective epoxidation of cis-olefins using Mn(salen) complexes, asymmetric induction and its efficiency due to structural features and catalytic activity modulation through substituent variation of cationic manganese (III) salen complexes in olefinic epoxidation reactions, hydrolytic kinetic resolution of epoxides and asymmetric ring opening catalyzed by Cr(salen) and Co(salen)

complexes, moderate enantioselective alkylation of ketones using zinc (salen) complexes.

Similarly, (Cozzi, 2003; Dioso and Jacobs,2005; Jiang and Chen,2008;Kleij,2008; Wezemberg and Kleij ,2008) studied the catalytic application of metal- salen complexes in the creation of sophisticated multimetal, functional and homogeneous salen framework catalysts, incorporation of salen moieties into macrocyclic compound in the study of supramolecular interactions and development of active catalysts using salen metal complexes possessing lewis base or lewis acid activating group.

Some authors (Rulev *et al.*,2015) studied the catalytically induced oxidation of terminal epoxides leading to the formation of cyclic carbonates under mild reaction conditions of 25 – 35°C and 1 – 10 bar carbon dioxide pressure using robust bifunctional aluminium salen catalysts. The catalysts composed of aluminium – salen chloride complexes with trialkyl ammonium groups directly co-ordinated to the aromatic rings of Salen ligand was recovered from the reaction mixture and reused. The incorporation of the quaternary ammonium salts directly co-ordinated to the Salen ligand (introduction of ammonium moieties into the aromatic rings of Salen ligands) greatly enhanced the stability of the structure by reducing the number of  $SP^3$ - hybridized carbon atoms attached to the nitrogen atoms of ammonium salts enhancing the steric hindrance around the ammonium salts and robustness of the catalytic coupling of epoxides and a carbon dioxide under solvent free conditions.

Studies(Choi *et al.*,2003) reported a high spin metal – cyanide clusters incorporating  $[Mn(salen)]^+$  complexes as a source of significant magnetic anisotropy. The complex  $\{Cr[CN Mn(salen)(H_2O)_6]\}$  formed by the reaction of  $[Mn(salen)(H_2O)]^+$  with  $[Cr(CN)_6]^{3-}$  in aqueous solution revealed the presence of weak antiferromagnetic coupling in fitting the variable temperature magnetic susceptibility data and magnetic anisotropy in the ground state from variable field magnetization data collected at low temperatures. The study revealed that the compound consisted of heptanuclear cluster  $\{Cr[CN Mn(Salen) H_2O]_6\}^{3+}$  with the central  $(Cr(CN)_6)^{3-}$  specie co-ordinated through the resident nitrogen atom to the Jahn –Teller type distorted  $Mn^{III}$  salen bound octahedral complex.

### In kinetic reactions

The role of iron(III) salen chloride as oxidizing agent with Thiodiglycolic acid and the effect on axial ligands was studied (Perumal *et al.*,2014). The study shows a substantial red shift in the  $\lambda_{max}$  value of  $Fe^{III}$  –salen in aqueous medium while spectrophotometric kinetic studies indicated that  $(Fe^{III}(salen))^+$  is the active oxidant. Mechanism of electron transfer from sulphur atom resident on

thiodiglycolic acid to the central iron atom of  $(\text{Fe}^{\text{III}}(\text{salen}))^+$  was proposed whereas the reaction proceeds through Michaelis-Menten kinetics with respect to the substrate. The reduction of the reaction rate on the addition of nitrogenous bases such as pyridine and imidazole was explained on the ligation of these ligands (bases) to the coordination sphere of  $(\text{Fe}^{\text{III}}(\text{salen}))^+$  before reacting with the substrate.

Similarly, the kinetics and mechanism of the reduction of  $\text{N}, \text{N}^1$ -salicylideneiminatoiron (III) complex ion by L-ascorbic acid in aqueous perchloric acid medium was carried out (Alioke et al., 2012). The reduction of iron (III) Salen complex ion,  $(\text{Fe}^{\text{III}}\text{salen}(\text{H}_2\text{O}))^+$  by L-ascorbic acid follows a first order dependence of rate on concentration of ascorbic acid but the rate of reaction increased as the acidity increased.

Vafazadeh and Bagheri (2015) studied the kinetics and mechanism of the ligand exchange reaction between tetradentate Schiff base  $\text{N}, \text{N}^1$ -ethylen-bis(salicyladmine) and  $\text{Ni}(\text{N}, \text{N}^1$ -propylen-bis(salicyladmine)) spectrophotometrically with or without triethylamine and water in dimethylformamide (DMF) solvent at  $25 \pm 0.1^\circ\text{C}$  and  $0.01\text{m NaNO}_3$ . The study noted that the interaction between  $\text{H}_2\text{salen}$  and triethylamine ( $\text{NET}_3$ ) could lead to the formation of  $\text{Hsalen}^-$  and  $\text{Salen}^{2-}$  ions by the deprotonation of phenolic moiety of  $\text{H}_2\text{salen}$ . The ligand exchange reaction as proposed was found to be biphasic (two step process) as illustrated by the experimental rate constants. Similar studies (Vafazadeh and Bidaki, 2014) have shown that the  $\text{Hsalen}^-$  ion is more active specie in the ligand exchange reaction between  $\text{H}_2\text{salen}$  and  $\text{Ni}(\text{N}, \text{N}^1$ -Propylen-bis(salicyladmine)) with triethylamine than the  $\text{Salen}^{2-}$  ion.

### As nanocomposites / nanoparticles

A facile method for the preparation of a new family of  $\text{M}/\text{N}/\text{C}$  ( $\text{M}=\text{Co}, \text{Fe}, \text{Ni}$ ) porous nanocomposite by pyrolyzing  $\text{M}(\text{Salen})$  complexes with low over potential, high durability large current density and remarkable electrochemical stability in alkaline conducting solution and high stability for the oxygen reduction reaction due to small metal particle size, and high surface area nanoporous structure uniformly- distributed and active sites in the carbon matrix was developed (Du et al., 2014)(fig 6). The study revealed that transition metal salen compounds are cheap precursors for the synthesis and design of metal incorporated and nitrogen - doped carbon conversion and storage devices. The complex nanocomposite from characteristic applications and analysis using XRD (X - ray diffraction), SEM (scanning electron microscope, thermo-gravimetric analysis (TGA), X- ray photoelectron spectroscopy (XPS) and cyclic voltammeter measurement

revealed its advantage over carbon supported platinum nanoparticles which aggregates or detaches from the substance when subjected to prolonged electrochemical process. The synthesized  $\text{Co}/\text{N}/\text{C}$  and  $\text{Fe}/\text{N}/\text{C}$  exhibited remarkable electrocatalytic activity with onset potential of  $0.96\text{v}$  for  $\text{Fe}/\text{N}/\text{C}$  and half wave potential of  $0.80\text{v}$  for  $\text{Co}/\text{N}/\text{C}$ .

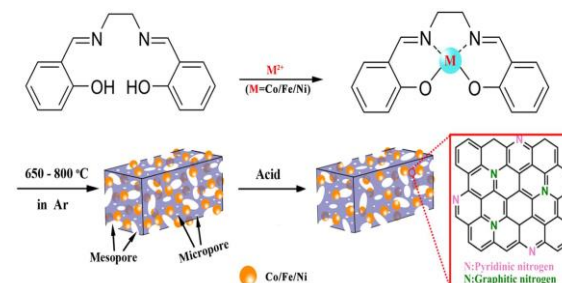


Fig 6. Illustration of the preparation of  $\text{M}/\text{N}/\text{C}$  ( $\text{M} = \text{Co}, \text{Fe}, \text{Ni}$ ) porous nanocomposite catalyst (Du et al., 2014)

Similarly, (Zhu et al., 2014) reported the synthesis of ultra small  $\text{Sn}$  (tin) nanoparticles embedded in  $\text{N}$ -doped porous carbon network. The carbonizing of  $\text{Sn}(\text{Salen})$  gave nanoparticles in  $\text{N}$ -doped porous carbon network with excellent electrochemical properties for  $\text{Li}$ -ion batteries. The pyrolyzed  $\text{Sn}(\text{salen})$  at  $650^\circ\text{C}$  under argon atmosphere was embedded in nitrogen doped porous carbon network with initial discharge capacity of  $1014\text{mAhg}^{-1}$  and capacity retention of  $722\text{mAhg}^{-1}$  after 200 cycles at current density of  $0.2\text{Ag}^{-1}$ . The study noted that a reversible capacity of about  $480\text{mAhg}^{-1}$  was obtained at much higher density of  $5\text{Ag}^{-1}$ . The high performance of the nanoparticle was attributed to the uniform distribution and effective combination of ultra small tin nanoparticles and porous carbon network structure which eliminated the problems of pulverization, particle aggregation facing tin anode and loss of electrical contact.

Some authors (Dardfarnia et al., 2015) synthesized nanopore size silver ion imprinted polymer in the presence of  $\text{Ag}(\text{I})$ - $\text{N}, \text{N}^1$ -bis(salicylidene)ethylenediamine complex using 4-vinylpyridine as the functional polymer, ethyleneglycol dimethacrylate as the crosslinker and 2,2-azobis(isobutyronitrile) (AIBN) as the initiator. The silver imprinted polymer characterized using scanning electron microscope, fourier transform infrared spectroscopy and Brunauer-Emmett-Teller/Barrett Joyner-Halenda analysis was used for the extraction and preconcentration of silver ions followed by its determination with flame atomic absorption spectrometry (FAAS) and spectrophotometry after leading with  $0.5\text{molL}^{-1}$  thiourea.

The result indicated that under the optimized conditions a sample volume of  $80\text{mL}$  gave an enhancement factor of 312, detection limit

of  $0.06\mu\text{gL}^{-1}$  and relative standard deviation at  $n=10$  and  $10\mu\text{gL}^{-1}$  level of 2.9% for FAAS whereas for localized surface Plasmon resonance peak (LSPRP) method they were  $0.5\mu\text{gL}^{-1}$  and 10.3% respectively. The method was applied for the determination of silver (Ag) in water radiology film, hair and nails samples.

#### As corrosion inhibitor

The corrosion inhibitor property of N, N<sup>1</sup>-bis (salicyli-dene -1,2-Diaminoethane) for mild steel in aqueous phosphoric acid medium using weight loss method and potential dynamic polarization methods at 303K-333K was studied (Murugaiyan et al., 2014/ 2015). The study revealed that increased concentration of Salen and temperature variation increased the inhibitor efficiency of Salen. FTIR and scanning electron microscope (SEM) analysis was employed in the surface characteristics of inhibited and uninhibited samples of mild steel. The negative values of  $\Delta G_{\text{(ads)}}$  and thermodynamic parameters indicated spontaneous exothermic adsorption of the inhibitor on the metal surface and or characteristics strong adsorption with the metal.

#### As oxygen binding agent

Co(salen) is the first reported synthetically reversible Co(II) oxygen carrier capable of binding dioxygen in the solid state, believed to form O<sub>2</sub> adduct consisting of dimeric [Co(salen)]<sub>2</sub> O<sub>2</sub> units and said to be inactive (Kumar and Garg, 2002). Co(salen) binds oxygen similarly to iron in the form of ferrous heme in proteins such as myoglobin and hemoglobin.

The oxygen carrying capacity of Salen complexes with Ni(II), Zn(II), Cu(II) and Fe(II) transition metal ion in dimethylsulphoxide (DMSO) was studied (Rosas-Garcia et al., 2012). The result indicated that the complexes are potential oxygen carriers with the degree of carrying capacity in the order Co(II) > Fe(II) > Cu(II). The study noted that the inability of Ni(II) and Zn(II) Salen complexes to transport dioxygen is due to lack of co-ordination with DMSO. They are unable to absorb oxygen in the form of O<sub>2</sub><sup>-</sup> or O<sub>2</sub><sup>2-</sup> and as such inactive. Also, (Emara et al., 2011) investigated the oxygen carrying affinity of cobalt(II) and manganese(II) complexes of H<sub>2</sub>Salen. The metal complexes were characterized using FTIR, UV-vis, molar conductivity measurement elemental analysis, NMR, TGA and mass spectroscopy. The square planar complexes were implicated as good oxygen carrying species.

Several authors (Deiasi et al., 1971; Hutson and Yang, 2000) has reported on the oxygen binding capacity of Co(salen) and the effect of co-ordinated ligand to the Co(salen) complexes and its application in O<sub>2</sub> separation and storage. The authors noted that the formation of

five co-ordinate square pyramidal complexes enhances dioxygen binding.

Studies (Kumar and Garg, 2002) have shown that Co (salen) decomposes at 498K with final decomposition at 779K corresponding to CoO and Co<sub>3</sub>O<sub>4</sub> as products. The Co(salen) complex characterized using UV- visible, IR and magnetic susceptibility measurements exhibited high activation energy from various thermodynamic parameter evaluation. Co(salen) was reported (kumar and Garg, 2002) to be red brown crystals that darken on exposure to air due to reversible uptake of oxygen by the complex to form the inactive form.

The co-ordination number of Co(salen) in anaerobic solution may be four, five or six depending on the co-ordinating solvent. In strongly co-ordinating solutions such as pyridine, species like [Co(salen)(PY)] and [Co(Salen)(PY)<sub>2</sub>] are formed whereas in weakly co-ordinating solvent like chloroform only Co(salen) exists. Similarly, complexes of the form 1:1 (Co:O<sub>2</sub>) or 2:1 (2Co:1) are formed on oxygenation of Co(salen) to oxygen. The process of dioxygen binding involves the reductive formation of dioxygen adduct (fig 6) where the Co<sup>2+</sup> donates electron to the dioxygen forming superoxide (O<sub>2</sub><sup>-</sup>) ligated to the Co<sup>3+</sup>. The dioxygen is said to add to five coordinate Co(salen) specie by replacement of one of the coordinated solvent molecule or as the sixth ligand forming a 2:1 complex or 1:1 co-ordinate complex (Deiasi et al., 1971).

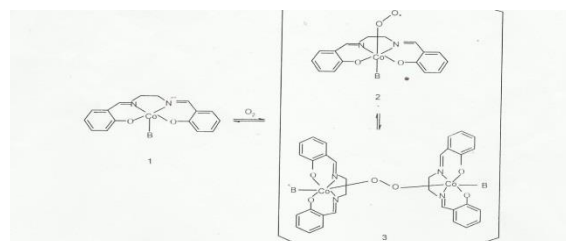


Fig 7. Binding of oxygen to cobalt (salen) complex (Deiasi et al., 1971).

#### As polymeric conductor

A conducting polymer Poly Ni(salen) films was synthesized and characterized (Li et al., 2015) by electrochemical polymerization and deposition of Ni(salen) using constant potential method at 1.3V (vs Ag/AgCl) onto a titanium based substrate in an organic electrolyte system containing mL ethanol and network modifier tetrabutyl ammonium perchlorate (TBAP). The poly Ni(Salen) films deposited was characterized electrochemically using cyclic voltammetry and galvanostatic charge discharge and result obtained indicated that surface coverage of poly Ni(Salen) in the anode substrate increased as the polymerization time increased though with decreased electrochemical activity. The highest discharge specific capacitance of  $73.5 \text{ Fg}^{-1}$  at low current density of  $0.5 \text{ Ag}^{-1}$  was obtained in the

polymerization time of 1000s. The Ni(Salen) orange monomers moved towards the electrode by electron migration and on collision with the electrode got oxidized and deposited on the anodic surface as a dark green polymer film characterized using fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscope (FESEM).

## CONCLUSION

Schiff bases are very important compounds because of their ability to form complexes with transition metal ions, other metal ions and their myriad properties. Schiff bases and their metal complexes have been of much interest over the years, mainly because of its various applications in biological processes, as non linear optical devices, as catalytic agents, as therapeutic agents, in the determination of metal ions, removal of metal ions from aqueous solutions, in dyes and other applications in industrial and biological spheres.

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## REFERENCES

- Abu S, Thewalt U, Riegar B. Chiral palladium(II) complexes bearing tetradentate nitrogen ligand: Synthesis crystal structure and reactivity towards the polymerization of norbornene. *Journal of Organometallic Chem* 1999; 587: 58-66
- Alioke C U, Ukoha P O, Ukwueze N N, Ujam O T, Asegbeloyin J N. Kinetics and mechanism of the reduction of  $N,N^1$ -salicylideneiminatoiron(III) complex ion by L-ascorbic acid in aqueous acid medium. *Chemistry and Materials Research* 2012;2(7):48-57.
- Alizadeh N E, Nacimi S, Sharghi H , Shamsipur M. Synthesis of a new naphthol-derivative salen and spectrophotometric study of the thermodynamics of complexation with copper(II) ion in binary dimethyl sulphoxide-acetonitrile mixtures. *English Journal of Chemistry* 1999;73 (6) :915-925.
- Anant P , Devjani A. Application of schiff bases and their metal complexes – A review. *International Journal of Chem. Tech. Research* 2011; 3(4) :1891-1896.
- Bae H J, Hwang K Y, Lee M H , Do Y . Salen-aluminium complexes as host materials for red phosphorescent organic light emitting diodes. *Bull. Korean. Chem. Soc* 2011; 32(9): 3290-3294.
- Baleiza, C , Garcia, H .Chiral salen complexes. An overview to recoverable and reusable heterogeneous catalyst. *Journal American Chemical Society* 2006; 106 :3987- 4043.
- Benning R G .Spectroscopy for surface science. *Journal of Material Chemistry* 1995;5: 365-378.
- Boghaei D M, Bezatpour A , Behzad M .Synthesis, characterization and catalytic activity of novel monomeric and polymeric vanadyl schiff base complex. *Journal molecular catalyst A<sub>245</sub>* 2006;12-66.
- Bu X R, Jackson C R, Derveer D V, You X Z, Meng QJ , Wang R X. New copper(II) complexes incorporating unsymmetrical tetradentate ligand with  $N_2O_2$  chromophores. *Synth.Molstruct, subst. effect and thermal stability Polyhedron* 1997;16:2991.
- Cavallo L, Jacobsen H. Electronic effects in (Salen) Mn-based epoxidation catalysts. *J. org. Chem* 2003;68: 6202-6207.
- Choi H J, Sokol J J, Long J R. high spin metal cyanide clusters: Species incorporating  $[Mn(salen)]^+$  complexes as a source of anisotropy. *Journal of Physics and Chemistry of Solids*. 2004;65: 839-844.
- Cozzi P G. Enantioselective alkynylation of ketones catalyzed by Zn(salen) complexes. *Angew Chem. Int.Ed* 2003; 42:2895-2898.
- Cozzi PG. Metal-salen schiff base complexes in catalysis. Practical aspects. *Chem. Soc. Rev* 2004;33: 410-421.
- Cristin A F ,Castro B. Reductive electrochemical study of Ni(II) complexes with  $N_2O_2$  schiff base complexes and spectrochemical characterization of the reduced species reactivity towards CO. *J. Chem. Soc. Dalton Trans* 1988;1491.
- Daneshvar N, Entezami A A, Khandar A A , Saghtafarush L A. New nickel(II) complexes incorporating dissymmetric tetradentate schiff base ligands derived from amino anti pyridene with  $N_2O_2$  chromophores. Synthesis, spectrochemical characterization and Crystal Structures of  $[Ni(PyAzosal) ClO_4.H_2O]$  .*Polyhedron* 2003; 22: 1437.
- Dardfarnia S, Haji Shabani A M, Kazemi E, Khormizi S A H, Tammadon F.Synthesis of nanopore size Ag(I)-imprinted polymer for the extraction and preconcentration of silver ions followed by its determination with atomic absorption spectrometry and spectrophotometry using localized surface plasmon resonance peak of silver nanoparticles. *J. Braz. Chem. Soc.* 2015;26(6): 1180-1190.
- Deiasi R, Holt S L, Post B. Crystal structure of oxygen-inactive form of Bis(salicylaldehyde) ethylenediimine cobalt(II). *Inorg. Chem* 1971;10(7): 1498-1504.
- Dioos B M L ,Jacobs P A. Microwave assisted Cr (salen) –catalyzed asymmetric ring



- opening of epoxides. *J. Catal* 2005; 235: 428-430.
- Doctrow S R, Liesa M, Melov S, Shirihai O S, Tofilon P. Salen Mn complexes are Superoxide dismutase/catalase mimetics that protect the mitochondria. *Current Inorganic Chemistry* 2012; 2: 325-334.
- Doctrow S R, Baudry M, Huffinan K, Malfroy B, Melov S. Salen Mn complexes: Multifunctional catalytic antioxidants protective in models for neurodegenerative disease and ageing. In medicinal inorganic Chemistry. Ed. Sessler J L, Doctrow S R, Mc Murry T J and Lippard S J. American Chemical Society 2005; 319-347.
- Dong W K, Duan J G, Wu H L, Shi J Y, Yu T Z. Crystal structure of (2,2,4-butylene)dioxibis nitrilomethylidenedinaphthol). *Kristallogr* 2006; 221: 555-556.
- Du J, Cheng F, Wang S, Zhang T, Chen J. M (salen)-derived nitrogen doped M/C (M=Fe, Co, Ni) porous nanocomposites for electrocatalytic oxygen reduction. *Scientific Reports (4386) Conference Proceedings AP Energy* 2014; 4: 1-7.
- Emara A A A, Ali A M, El-Asmy A F, Ragab E M. investigation of the oxygen affinity of manganese(II), cobalt (II) and nickel(II) complexes with Some Tetradentate Schiff Bases. *Journal of Saudi Chemical Society*. 2011;18 (6): 762-773.
- Faria P A M, Bos M B R. Electrochemical behaviour of copper(II) salen in aqueous phosphate buffer at the mercury electrode. *Int. J. Electrochem Sci* 2009; 4:458-470.
- Ganjali M R, Naji I, Poursaberi T, Taghizadeh P, Pirelahi Y, Yousef Y, Yeganeh-faal B, Shamsipur M. Highly selective iodide membrane electrode based on a cerium salen. *Journal of Japan Society of Anal Chem* 2002;18(3): 445-446.
- Garg B S, Kumar N D. Spectral studies of complexes of Ni(II) with tetradentate schiff bases having  $N_2O_2$  donor groups. *Spectrochimica Acta A* 2003;60:271.
- Green R W, Alexander P T. Beryllium complexes of schiff bases. *Aust. J.Chem* 1965;18:1297-1298.
- Gupta V K, Goyal R N, Jain A k, Sharma R A. Aluminium(III) selective PVC membrane sensor based on a Schiff base complex N,N-bis(salicylidene)-1,2-cyclohexanediamine. *Electrochimica Acta* 2009;54: 3218-3224.
- Hansen K B, Leighton J L, Jacobsen E N. Catalytic epoxidation of schiff base complexes. *AM. Chem. Soc* 1996; 118: 10924.
- Harvey D, Clifford C. Bis (N,N<sup>1</sup>-Disalicyl ethylene diamine- methoxyphenylmethylidene). M 5321J Open Access Publication Mol. Bank 2004; 352.
- Hodnett E M, Wu A W, French F A. Maleic anhydride copolymers and their derivatives. *Eur. J. Med. Chem. Ther* 1987;13: 577.
- Hutson N D, Yang R T. Synthesis and characterization of the sorption properties of oxygen binding cobalt complexes immobilized in nanoporous materials. *Industrial and Engineering Chemistry Research* 2000;39(7): 2252-2259.
- Ishikawa Y, Eguchi H. Metal-salen complex compound and method for producing the same. USA Patent 2014; 0011032A1:1-4.
- Ishikawa Y, Eguchi H. Metal salen complex derivative and process for production thereof. United States Patent 2013; 1002939399A1: 1-7.
- Isse A A, Cenzo A, Vianello E. Electrochemical reduction of schiff base ligands H<sub>2</sub>salen and H<sub>2</sub>salophen. *Electrochim. Acta* 1992; 47:113.
- Jiang C J, Chen Z R. Chiral cobalt salen complexes containing lewis acid: A highly reactive and enantioselective catalyst for the hydrolytic kinetic resolution of terminal epoxides. *Kinet. Catal* 2008;49: 474-478.
- Jurrapour A, Zarei M. Synthesis of 2-hydroxy 3-mu-Aquodicobalt(II). *Inorganic synthesis* 1950; 3:196-201.
- Katsuki K. Functionalization of metallosen complexes. diverse catalytic performance and high asymmetry induced ability. *Chem.. lett* 2006;124, 1-12.
- Kim Y, In G, Choi J. Solid phase extraction of trace Cu(II), Mn(II), Pb(II) and Zn(II) in water samples with pulverized silica-salen (NET<sub>2</sub>)<sub>2</sub>. *Bulletin Korean Chem. Soc* 2008; 27(10) :1557-1561.
- Kleij A W. New templating strategies with salen scaffolds (Salen= N, N'-Bis(salicylidene)ethylenediamine dianion). *Chem. Eur.J* 2008;14: 10520-10529.
- Klein LT, Allemen K S, Peters D G, Karty J A, Reilly J P. Two dimensional cysteine cluster networks on Au(III) disclosed by voltammetry and in situ scanning tunneling microscopy. *J. Electro Anal. Chem* 2000; 481:24.
- Kumar D N, Garg B S. Some new cobalt(II) complexes: synthesis, characterization and thermal studies. *Journal of Thermal Analysis and Calorimetry* 2002; 6(2): 607-616.
- Lacroix P G. Second order optical nonlinearities in coordination chemistry: The case of bis(salicylaldiminato) metal schiff base complexes. *European Journal of Inorganic Chemistry* 2001;339- 348.
- Li M, Jiao H, Zhang H, Jiao S. Electrochemical polymerization of schiff base transition metal polymer poly [Ni (salen)] and its electrochemical performance in organic electrolyte. *International Journal of Electrochemical Science* 2015;10: 8797-8806.

- Malfroy C B , Doctrow S R. Cyclic salen – manganese compounds. reactive oxygen species scavengers useful as antioxidant in the treatment and prevention of diseases. US patent number 2006;7: 122,537.
- Maneiro M, Bermejo M R, Fernadez M I, Forneas E G, Gonzaley-Noya A M , Tyryshkin A M . A new schiff base complex ,catalysts for the disproportionation of hydrogen peroxide as peroxidase mimics. *New J. Chem* 2003;27: 727.
- Mohammed R, Ganjal M R, Parviv N, Nader H , Masoud S .Vanadyl- salen encapsulated on a hydrogen phosphate membrane sensors for the determination of monohydrogen phosphate ion in various species. *Journal of the Brazilian Chem. Soc* 2006; **17**(5): 301-303.
- Morgan G J , Drew H D K .Research on residual affinity and coordination part II. acetylacetones of selenium and tellurium. *J. Chem soc. Trans* 1920; 17 :1456.
- Murugaiyan M, Madhu P, Vennila P, Venkatesh. Investigation of schiff base N, N<sup>1</sup> –bis (Salicylidene)- 1,2- Diaminoethene(salen) as corrosion inhibitor for mild steel in H<sub>3</sub>PO<sub>4</sub> solution. *International journal of Chem Tech Research* 2014/2015;7(5): 2489-2498.
- Murugkar A, Bendre R, Kumber A , Padhye S. X-ray structure of the cytotoxic planar Ni(II) complex of N-dimethyl-2-acetylpyridine-thiosemicarbazone. *Indian. J. Chem* 1999; 38A: 977-981.
- Nwabue F I , Okafo E N . Studies on the extraction and spectrophotometric determination of Ni(II), Fe(II), Fe(III) and V (IV) with bis (4-hydroxypent-2-ylidene) diaminoethane. *Talanta*1991;39(3), 273-280.
- Nworie F S, Nwabue F I , Omaka N O. A study of complexation ability of Bis (2, 2<sup>1</sup> – methylidene phenol) diaminoethane to some metal cations. *Journal of physical Sciences and Environmental Safety* 2013; 3: 46-53.
- Osman R , Basch H. On the mechanism of action of superoxide dismutase: A theoretical study. *J. Am. Chem. Soc* 1984;106: 510-5714.
- Panda C R, Chakravorty V , Dash K C. A Quadritentate. Schiff base as an extractant for thorium(IV), uranium(VI) and zirconium(IV). *Journal of Radioanalytical and Nuclear Chemistry* 1987;108: 65-75.
- Panda S K , Chakravorty V. Extraction of uranium(VI) with binary mixtures of a quadritentate schiff base and various neutral Donors.*Journal of Radioanalytical and Nuclear Chemistry* 1998;227: 163-165.
- Perumal S, Thangadurai V, Thiruthimuthu K, Chandra R S. Role of iron (III)- salen chloride as oxidizing agent with thiodiglycolic acid: The effect of axial ligands. *J. Mex. Chem. Soc.* 2004;58(2): 211-217.
- Ramasamy J, Gnanasambandam V , Pillutla S .Synthesis and antimicrobial studies of tridentate schiff Base ligands with pyrazolone moiety and their metal complexes. *Organic Chemistry International* 2010;2010:165-170
- Rosas-Garia V M, Martinez P E, Rodriguez N P, Martinez B N. Potential oxygen –carrying complexes by design. *Quimica Hoy Chemistry Sciences* 2012;2(4):30-33.
- Roy M, Saha S, Patra A K, Nethaji M , Chakravarty A R. Bioinorganic and medicinal chemistry. *Inorganic Chemistry*2007;46: 4368-4370.
- Rulev Y A, Gugkaeva Z, Maleev V I, North M, Belokon Y N. Robust bifunctional aluminium-salen catalysts for the preparation of cyclic carbonates from carbondioxide and epoxides.*Beilstein Journal of Organic Chemistry.* 2015; 11: 1614-1623.
- Schaus S E, Brandes B D, Larrow J F ,Togunaga M, Hansen K B , Gould A E, Furrow M E, Jacobsen E N. Highly selective hydrolytic kinetic resolution of terminal epoxides catalyzed by chiral (Salen) Co<sup>III</sup> Ccomplexes. Practical synthesis of enantioenriched terminal epoxides and 1, 2-Diols. *J. Am. Chem. Soc* 2002;124: 1307-1315.
- Seunghyun K, Byungwan J, Hakwon, Kwangheon P,Hongdoo K. Solubilities of salen derivatives and their cobalt complex in ligand and supercritical CO<sub>2</sub>. *Bull. Korean Chem. Soc* 2003; 25(4): 471-474.
- Shalin K, Durga N D, Saxena P N. Applications of metal complexes of schiff bases-A review, *J.Sci.Ind.Res* 2009; 68: 181-187.
- Sharpe M A, Ollosos R, Stewart V C, Clark J B. Oxidation of nitric oxide by oxomanganese salen complexes: A new mechanism for cellular protection by superoxide dismutase/catalase mimetics. *Biochem. J* 2007; 366: 97-107.
- Simandi L . Advances in catalytic activation of dioxygen by metal complexes.Kluwer Academic publishers Dordrecht. 2003; chapter 6.
- Srinivasan K, Michaud P, Kochi J. Epoxidation of olefins with cationic (Salen) manganese (III) complexes: The modulation of catalytic activity by substituents. *J. Am Chem. Soc* 1986;108: 2309-2320.
- Takeda T, Irie R, Shinoda Y , Katsuki T .Ru-salen catalyzed asymmetric epoxidation. Photo-activation of catalytic activities. *Synlett* 1999;1157-1159.
- Tantaru G, Dorneanu V ,Stan M . Schiff bases:II:Spectrophotometric determination of manganese from pharmaceutical forms. *J. Pharm. Biomed. Anal* 2002; 27: 827.

- Tumer M, Akgun E, Toroglu S, Kayraldiz A , Donbak L . Synthesis and characterization of Schiff base metal complexes.their antimicrobial ,genotoxicity and electrochemical properties. *J. Coord. Chem* 2008; 61: 1373.
- Ukoha P O, Obasi L N , Nwabue F I . Solvent extraction studies on copper(II) and silver (I) complexes of bis (4-hydroxypen-2-ylidene) diaminoethane separation of Ag(I) from Cu(II). *International Journal Chem* 2012;22: 15-24.
- Vafazadeh R, Bidaki S. kinetics and mechanism of ligand exchange reaction of copper(II) complexes with tetradentate schiff base ligands. *Acta Chim Slov* 2014;61: 153-160.
- Vafazadeh R, Bagheri M. Kinetics and mechanism of the ligand exchange reaction between tetradentate schiff base, N, N<sup>1</sup>-ethylene-bis(salicyladimine) and Ni(N, N<sup>1</sup>- propylene-bis (salicylalidimine). *S Afr. J. Chem* 2015; 68: 21-26.
- Veli T K , Seniz O Y. Synthesis, spectroscopy and electrochemical behaviours of nickel(II) complexes with tetradentate Schiff Bases Derived from 3, 5 – salicylaldehyde. *Esref Tas, Spectrochemical Acta part A* 2005; 62:716.
- Verbiest T, Houbrechts S , Kauranen M, Clays K , Persoons A. Second order optical nonlinear optical materials ;recent advances in chromophore. *Journal of Material Chemistry* 1997;7: 2175-2189.
- Wezemberg S J, Kleij A W. material application for salen frameworks. *Angew. Chem. Int. Ed* 2008;47: 2354-2364.
- Xie J, Qiao J, Wang L, Xie J , Qiu Y . Organic caesium salt as an efficient electron injection material for organic light emitting diodes. *Applied phy .letters* 2008. 3;8: 4451-4458.
- Yamada S .Advancement in stereochemical aspects of schiff base metal complexes. *Coordin. Chem.. Rev* 1999;192:537.
- Ye Y K, Fang M O, Zhanz, Y I, Zhu L. N – (2 – hydroxyethylaminoethylsalicylideneimine) Chromium (III) Chloride. synthesis and structure. *Acta cryst* 2005;61: 1258.
- Yi Y, Wei X Q, Xie M G, Lu Z Y. Synthesis and color tunable flourecence properties of Schiff base Zinc(II) complexes used as electroluminescent materials. *Chinese Chemical Letters* 2004;14:263-266.
- Young R J , Cooper G W . Advances in protein chemistry. *Journal Reprod. Fertil* 1983;37: 334.
- Yu T, Su W, Li W, Hong Z, Hua R , Li B . A schiff base zinc complex and its electroluminescent properties. *Thin Solid Films* 2007;515: 4080-4084.
- Zhang W, Loebach J L, Wilson S R , Jacobsen E N. Enantioselective epoxidation of unfunctionalized olefins catalyzed by (Salen) manganese complexes. *J.Am. Chem. Soc* 1990;112: 2801-2803.
- Zhang W, Loeback S C, Wilson S R , Jacobsen E N. Synthesis and catalytic activity of N, N<sup>1</sup>-bis(salicylidene) ethylenediamine manganese(II) chloride. *Journal of American Chemical Society* 1990;112: 2801.
- Zhu Z, Wang S, Du J, Jin Q, Zhang T, Cheng F , Chen J. Ultrasmall Sn nanoparticle embedded in nitrogen –doped porous carbon as high performance anode for lithium-ion batteries. *Nano Lett.* 2014;14(1): 153-157.