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# Salen and Related Ligands

*Ashish K. Asatkar, Mamta Tripathi and Deepali Asatkar*

## Abstract

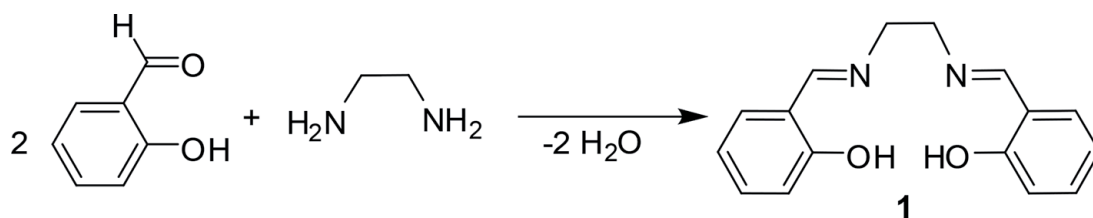
The salen and related ligands are very popular among the inorganic chemists due to multiple reasons such as ease in synthesis, coordinating ability with very long range of metal ions, facilitating the metal ions to adopt various geometries, ability of stabilising the metal ion in variable oxidation states and potential applications of metallosalen in several fields. The most common application of metallosalen is in the field of catalysis because of their recoverability, reusability, high efficiency, high selectivity and their capability of working as homogeneous as well as heterogeneous catalysts for numerous functional group manipulations including asymmetric synthesis. Molecular magnetism, sensory applications, bioinorganic activities and medicinal applications of metallosalen are also very promising areas of their applications. Porous materials involving metal organic frameworks (MOFs) and supramolecular building blocks are increasingly getting attention of researchers for the gas absorption and heterogeneous catalysis.

**Keywords:** salen, salphen, Schiff-base, chelate ligand, metallosalen

## 1. Introduction

The coupling of aldehyde group with primary amine yields imine bond which is called Schiff's base. Salen ligand system, one of the most studied classes of chelate ligands, is also a Schiff's base ligand. The earliest report of salen-metal complexes is probably by Pfeiffer et al. in the year 1933 [1]. The word 'salen' is composed of two abbreviations, sal+en; 'sal' stands for salicylaldehyde and 'en' stands for ethylenediamine. When two equivalents of salicylaldehyde reacts with one equivalent of ethylenediamine potential tetradentate chelating ligand known as 'salen' is produced (**Figure 1**).

Usually, these reactions do not need any catalyst and proceed straightforwardly but sometimes the products may be hydrolysed in reversible manner. To overcome this problem, dehydrating agents or molecular sieves (3 Å) are used so that the water molecules produced during the reaction can be absorbed. Dean Stark apparatus is also used for the removal of water molecules when water-immiscible solvent (e.g., toluene or benzene) is used. Sometimes template synthesis is also performed to get metal-salen complexes directly in which process first metal-salicylaldehyde complex is prepared *in-situ* as template then ethylenediamine is added to get salen ligand. Although, the salen ligands are sensitive towards hydrolysis which is catalysed by acid, their metal complexes are quite stable and thus to avoid the hydrolysis of salen ligands during the applications, their metal-complexes are often used. Metal salen can work even in aqueous medium. Moreover, the salen ligands have potential to stabilise metal ions in various oxidation states, making them good candidates as catalysts.



**Figure 1.**  
*Synthesis of salen ligand.*

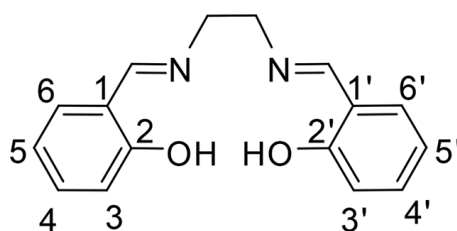
Salen ligand possess  $N_2O_2$  donor sites which offers metal ions to adopt various geometries such as square planar, tetrahedral, square pyramidal and octahedral as well, with additional ligand(s) if required. A large number of metal ions have been introduced to salen to produce variety of complexes [2–4]. A very broad range of transition metals, main group metals and inner transition metals have been coordinated with salen ligand systems. Being the multidentate ligand, their complexes often have very high formation constants. Salen based complexes have potentially been used in several fields like catalysis, biochemistry, electrochemistry, sensors, molecular magnetism and materials science. Salen-metal complexes are still leading in the field of homogeneous catalysis for various organic reactions. In the past few decades, numerous reviews based on salen ligand system have been published, highlighting its importance [5–8].

## 2. Salen ligands and derivatives

Several manipulations have been done on parent salen system to develop the varieties of salen system for various applications. The derivatives of salen are designed to develop desirable properties like solubility, stability, chirality, catalysis, extended conjugation, etc. Aromatic ring and diamine linkage (e.g., ethylene link) are two main portions in salen ligand system, which are used to put various substituents. 3-,5-Positions of salicylideneimine are frequently used for substitution. Substitution at 3- and 5-positions of salicylideneimine also improves the catalytic activities and prevents dimerization as well. The numbering of positions in salen system is shown in **Figure 2**. Substitution at aromatic ring of salicylaldehyde is very popular to enhance solubility of salen ligand and its metal complexes while the substitution at diamine linkage is commonly used to get the chiral ligand. Another position available for the substitution is carbon atom of imine bond.

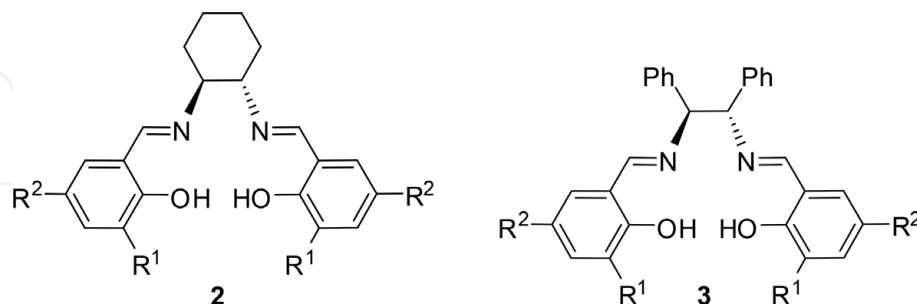
### 2.1 Chiral salen

The asymmetry is introduced to salen system mostly by the use of chiral diamine. Chiral salen are of particular importance in asymmetric synthesis as enantioselective catalyst. Many procedures are known for chiral synthesis of

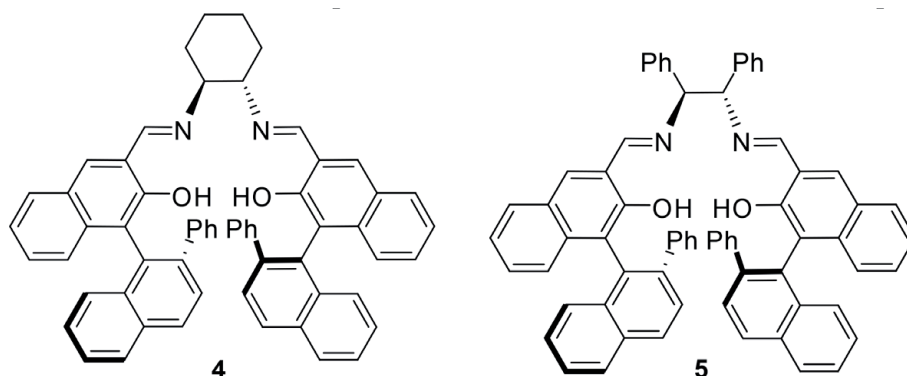


**Figure 2.**  
*Numbered positions in salen ligand.*

ligands using diamine having one or more stereocentres [9, 10], or a stereoaxis [11], through the incorporation of axial [12] or planar [13–15] chirality within the salicylaldehyde. *Trans*-1,2-diaminocyclohexane and 1,2-diphenylethylene-1,2-diamine are often used as 1,2-diamine to produce the chiral salen. These two chiral salen (**2** and **3**) are very popular and their several derivatives have been reported [16]. Very often, tertiary butyl group and long alkyl chain are put to modify solubility, steric factor and electronic factor.



Chiral binaphthyl salen complexes (**4** and **5**) have been designed in such a way that the complexes possess two stereogenic centres and thus considered as second generation metal salen complexes. One of the stereogenic centres belongs to binaphthyl unit while other belongs to diamine unit [17–19]. The complexes were used for non-racemic oxidation of prochiral sulphides.



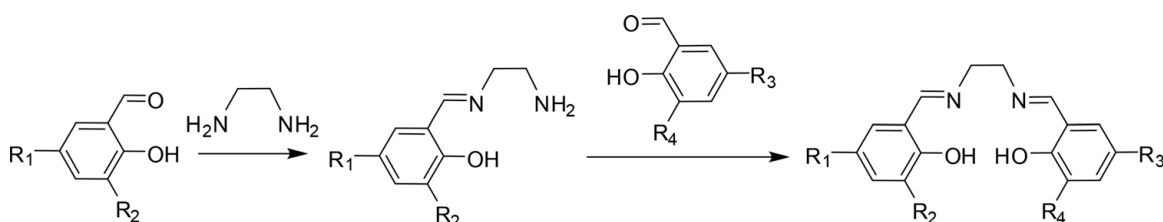
### 2.1.1 Non-symmetrical salen

Salen ligand systems have successfully been employed as homogeneous catalysts for variety of organic functional group manipulations. Very often they are symmetrical and having  $C_2$ -axis of symmetry. Non-symmetrical ligands bring out further magnify opportunities for tuning of electronic, steric and catalytic properties and therefore various nonsymmetrical analogues of salen have also been developed [20]. There are various advantages of unsymmetrical salen over symmetrical salen such as nonsymmetrical salen with single functional group can be immobilised onto heterogeneous and homogeneous traps to recover it after use [21, 22]. Moreover, electron releasing and/or withdrawing groups can be put on aryl rings of salicylideneimine part of salen. Presence of electron releasing and withdrawing groups together acts as push-pull system for electron density. Also, the unsymmetrical salen-metal complexes have shown better enantioselectivity in certain cases [23, 24].

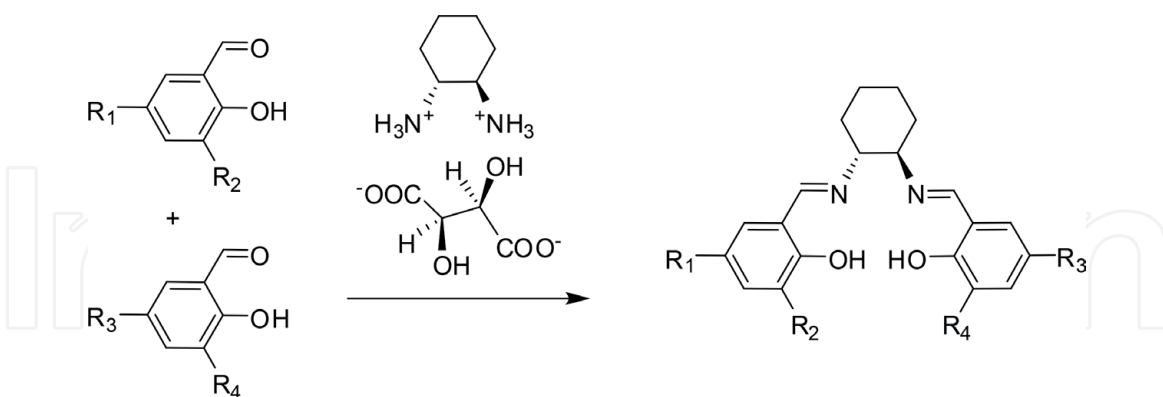
The easiest way to prepare an unsymmetrical salen can be direct two step Schiff base coupling i.e., the reaction between salicylaldehyde and ethylenediamine in 1:1 molar ratio to get mono-keto-imine product followed by the reaction with substituted salicylaldehyde (**Figure 3**) [25–27]. This method do not need any

protection of group or presence of special reagent, but the main drawback of this method is that the stepwise coupling is not much favourable due to the formation of symmetrical product in first step and lability of imine bonds towards hydrolysis which reduces the yield of desirable unsymmetrical product drastically. Jacobsen et al. exhibited another way to prepare nonsymmetrical salen ligand directly by the reaction of two different salicylaldehyde derivatives and (1R,2R)-(+)-1,2-diaminocyclohexane L-tartrate in 1:1:1 molar ratio in single spot, but in moderate yield (**Figure 4**) [28, 29]. Another approach for the synthesis of non-symmetrical salen is selective protection of one of the amine groups of diamine compound followed by Schiff base coupling of another amine group with salicylaldehyde, then the protected amine group is deprotected and coupled with distinct salicylaldehyde (**Figure 5**) [30, 31].

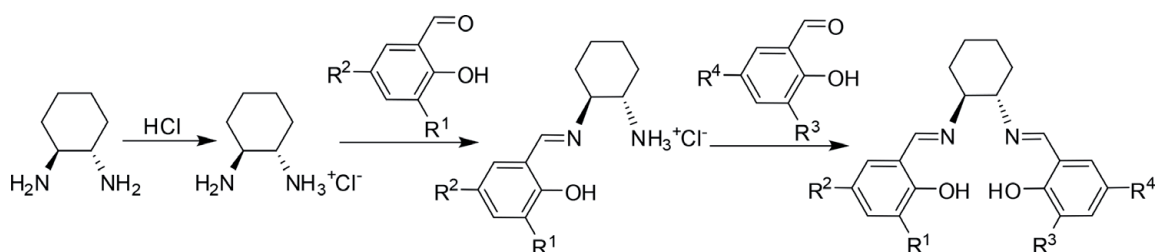
Silica- and polymer-immobilised Co(III)-salen non-symmetrical complexes (**6**) have also been developed and successfully used as catalysts for hydrolytic kinetic resolution of terminal epoxides with better rate, enantioselectivity and recyclability [32, 33]. Similar Mn(III)-salen non-symmetrical complexes have also been designed and studied [7]. Rigamonti et al. reported the synthesis of nonsymmetrical salen-Cu(II) complexes (**7–14**) by the reaction of salicylaldehyde/5-nitrosalicylaldehyde



**Figure 3.**  
Direct two step synthesis of nonsymmetrical salen ligand.

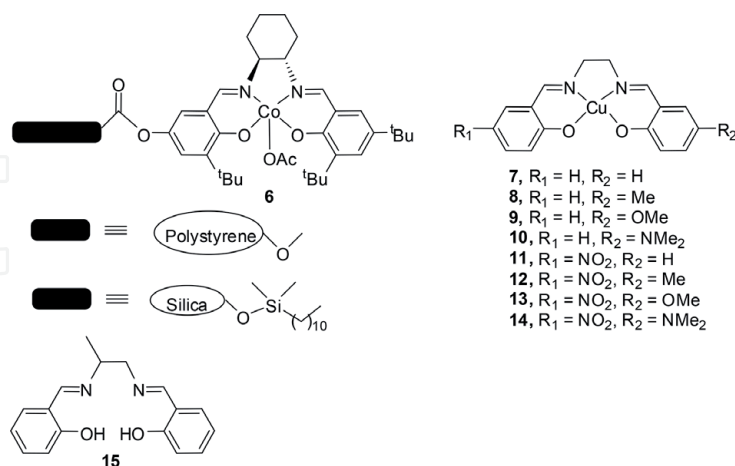


**Figure 4.**  
Direct one step synthesis of nonsymmetrical salen ligand.



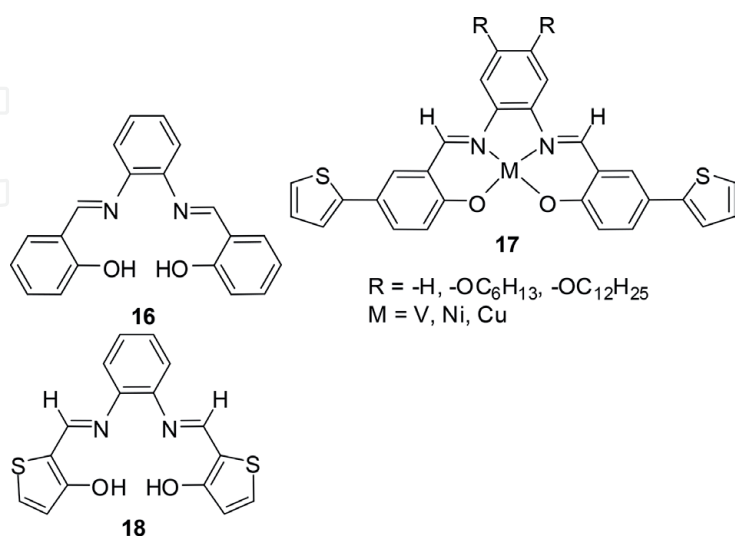
**Figure 5.**  
Protection-deprotection method for the synthesis of nonsymmetrical salen ligand.

and ethylenediamine/propylenediamine in 1:1 molar ratio in presence of Cu(II) ion and pyridine followed the addition of differently substituted salicylaldehyde and their nonlinear optical properties were studied and correlated with the structural diversities [34]. Salen ligand with methyl group at ethylene backbone is known as “salpn” (15). Salpn and its complexes have been used as additive in engine oil [35].



## 2.2 Conjugated salen

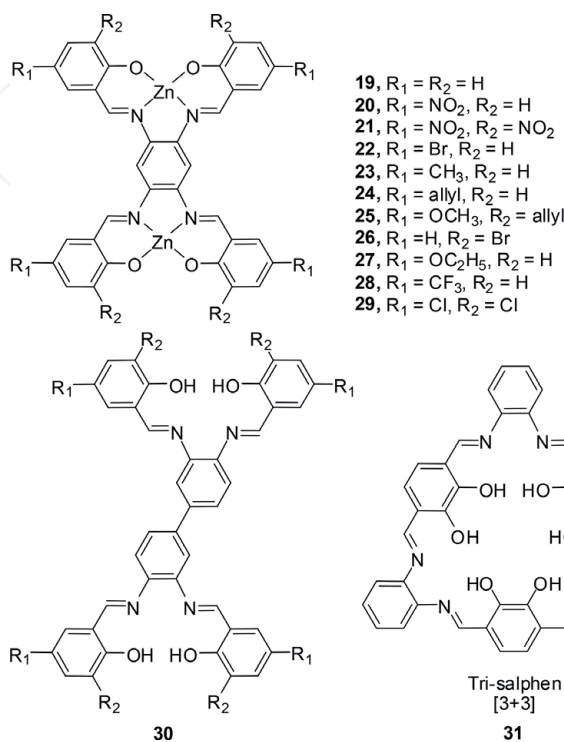
When phenylenediamine (phen) is taken in place of ethylenediamine during the reaction, the ligand formed is known as “Salphen” or sometimes “Salophen” (16). Salphen has extended conjugation with rigid planarity when coordinated with metal ion in square planar, octahedral or square pyramidal geometry, which is a very important criterion for material applications. Their photophysical properties can be fine-tuned by putting suitable substituents. Pietrangelo et al. synthesised thiophene capped salen ligands and their V, Ni and Cu copper complexes (17) and electrochemically polymerised them [36]. Asatkar et al. reported the synthesis of thiophene analogue of salphen (18) by taking 2-formyl-3-hydroxythiophene in place of salicylaldehyde and their Cu(II) and Zn(II) complexes [37]. However, the complexes could not be electrochemically polymerised as thiophene capped salphen did.



Even more complicated salphen have been developed by linking/merging two or more such units either through phenylene or salicylaldehyde [38] Bis-salphen scaffold ligand can be prepared by the reaction of four equivalents of salicylaldehyde and one equivalent of 1,2,4,5-benzenetetramine and its derivatives can also be developed in similar way [39, 40]. Kleij et al. reported the synthesis of unsymmetrical



bis-metal-salphen scaffold complexes by partial hydrolysis of parent symmetrical bis-zinc-salphen scaffold complex followed by Schiff-base coupling with differently substituted salicylaldehyde derivatives (**19–29**) [41]. Similarly, another bis-salphen symmetrical and unsymmetrical ligands (**30**) are prepared using one equivalent of 3,3'-diaminobenzidine and four equivalents of salicylaldehyde [42, 43]. Salphen based tri [3+3] (**31**), tetra [4+4] and hexa [6+6] macrocycles have also been prepared using 2,3-dihydroxybenzene-1,4-dicarbaldehyde and 1,2-phenylenediamine [44–47].



### 2.3 Salen based metal organic framework

Metal-organic frameworks (MOFs), is a fascinating classification of porous materials that can exits as self-assembled *via* coordination of metal aggregation/ions with organic linkers [48–50]. Shultz et al. synthesised MOF using pyridine functionalized Salen-Mn complex and tetrakis(4-carboxyphenyl)benzene [51]. The MOF was further used to prepare new MOFs with change in metal ion. The Mn-MOF was demetalated first using  $H_2O_2$  then remetalated with Cr(II), Co(II), Ni(II), Cu(II) and Zn(II) ions [52]. Lin et al. reported MOFs using chiral Mn-Salen functionalized with variable size dicarboxylic acid linkage. The MOFs exhibited asymmetric epoxidation catalysis with enantiomeric excess as high as 92% [53]. Jeon et al. reported infinite coordination particles based on carboxylic acid functionalized Salen-Zn complex and studied the gas absorption capacity. The amorphous material showed excellent hydrogen gas intake capability [54]. Roesky et al. used carboxylic acid functionalized Salen-Ni complex and lanthanides to synthesise MOFs [55]. Shape of the framework was found to be dependent of size of lanthanides.

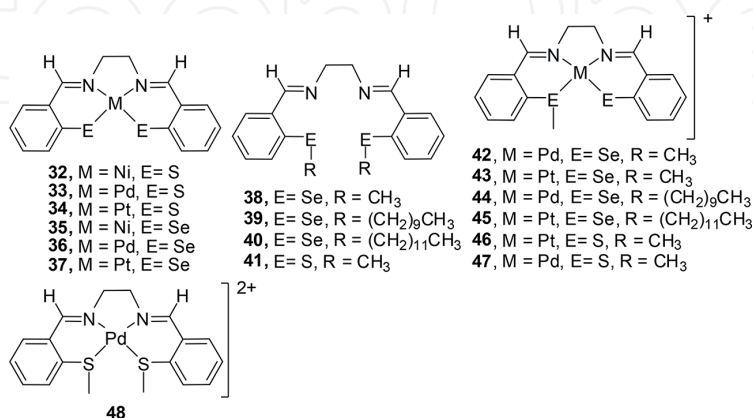
Kleij et al. found the unique self-aggregation nature of bis-Zn(salophen) [14, 15, 56, 57]. They have secure self-assembly behaviour through linking coordination motifs that are fundamentally different from those usually found for the self-assembly of mononuclear Zn-salophens [58]. This takes place on both at the interface of solid-liquid as well in solution. Oligomeric  $(Zn-O)_n$  coordination moiety are accumulated inside the assembly and this is quite distinct from mononuclear analogues

of Zn(salphen) which form dimeric structures having a classical  $\text{Zn}_2\text{O}_2$  central unit [59]. Multimetallic salen frameworks have been revealed to act as metallohosts forming adduct complexes with further structural ordering upon substrate binding [38]. Nabeshima et al. employed a linear metallohost containing two  $\text{N}_2\text{O}_2$  binding units [60]. Upon metalation with Zn(II) a 1:3 ligand to metal complex forms *via* a highly cooperative process. One Zn(II) ion is situated in a C-shaped  $\text{O}_6$  site in the centre of the helical complex. Guest exchange was shown to occur through substitution of the central Zn(II) with rare earth metal and lanthanide cations. Excitingly, the helicity of the complex is relying on the size of the central guest cation.

### 3. Analogues of salen

Due to the extended applications of salen ligand systems, their various analogues have been developed and studied. Chalcogen analogues of salen include sulphur and selenium derivatives as thiasalen and selenasalen. However, the sulphur and selenium analogues are relatively less explored because of the volatile nature, instability, synthetic complications, unpleasant smell and adverse effect of thiol and selenol compounds. To synthesise the metal-thiasalen/selenasalen complexes, template synthesis is often used.

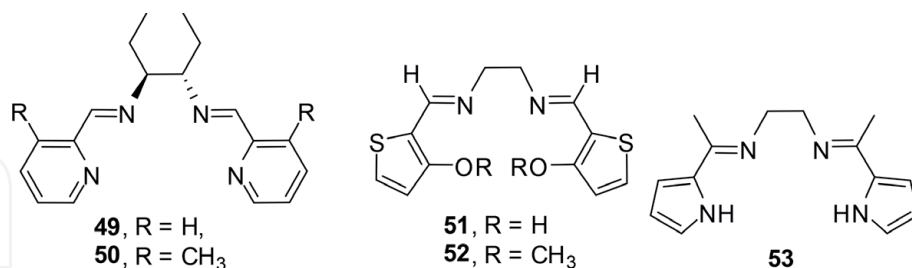
Dutta et al. reported the one pot synthesis of thia/selena analogues of salen-metal complexes (32–37) *via* oxidative addition of zero valent group ten metals (Ni(0), Pd(0) and Pt(0)) to S-S/Se-Se bond of bis(o-formylphenyl)disulphide/–diselenide followed by *in situ* coupling with ethylenediamine [61]. Panda et al. reported the synthesis of bis(alkylseleno)salen ligands (38–41) by the reaction of 2-(alkylthio/seleno)benzaldehyde and ethylenediamine [62]. Their complexation with Pd(II) and Pt(II) ions exhibited very interesting results. Complexation of 2-(alkylseleno)benzaldehyde with Pd(II) and Pt(II) ion yielded the formation of unsymmetrical complexes with the cleavage of one of the alkyl groups from Se-C(alkyl) bonds. However, the complexation with Pd(II) ions Complexation of 2-(methylthio)benzaldehyde with Pt(II) ion, reported by Dutta et al., yielded similar unsymmetrical complex (42–46) while the same with Pd(II) ion yielded time dependent product [63]. When the reaction mixture was refluxed for 5 min the symmetrical complex (48) with both the methyl groups intact was obtained, but when it was refluxed for 4 h the unsymmetrical complex (47) was obtained.



Benzene rings have also been replaced by other aromatic rings to design the new salen analogues. Jeong et al. reported the synthesis of pyridine based salen type chiral ligands (49–50) and their complexes and used them as enantioselective catalysts in Henry reaction [64]. Asatkar et al. reported the thiophene analogues (51–52)



of salen ligand system [65]. Interestingly, thiophene analogue of simple salen was found to exist in different tautomeric forms in solid and solution phases, unlike salen ligand. Its reaction with Cu(II) ion resulted in the dimeric complex. Another example of change in aromatic ring is pyrrole based salen type ligand (**53**), reported by Berube et al. along with its dimeric samarium(II) complex [66].



## 4. Applications of salen-metal complexes

M(salen) complexes have unique and exciting class of ligand based complexes with exceptionally versatile applications ranging from laboratory reaction to mass scale industries level. Interestingly, metal salen complexes gained popularity because of their roles in multiple areas few important of them are discussed below:

### 4.1 Catalysis

Metal-salen complexes appear as both homogeneous and heterogeneous catalyst and have been substantially investigated by researchers for multiple uses [5]. The most attracting feature of metal salen catalysts is that they can be recovered and reused. Usually found that the salen as catalyst possess high stability revealed by their high stability constants [7]. When metal salen are applied as catalyst, demetalation of the complex occurs because of competitive binding with reagents, solvent or products, may be associated with changes in the oxidation state of metal in catalytic cycle. Few important reactions catalysed by metal salen includes Meerwein-Ponndorf-Verley reductions (MPV) [67, 68], Friedel-Crafts Reactions [69], Oppenauer oxidation, Tishchenko reactions [70, 68], ene reaction [71], mixed-aldol condensation [72, 73], Diels-Alder reactions [71], dipolar cycloadditions, Claisen rearrangements [74] and the cyclotrimerization of isocyanates to isocyanurates [75].

Interestingly, Metal salen holds important role in many oxidation reactions like alkene epoxidation [76], asymmetric syntheses of cyanohydrins and amino acids [77], and oxidation of heteroatom-containing compounds [78]. In biological system they actively take part in catalytic oxidation of Ni(III) oxidised in the catalytic cycles of Ni-Fe hydrogenases [79–82], acetyl coenzyme A synthase (ACS) [83–85], CO dehydrogenase [86, 87], and methyl coenzyme M reductase [88]. Mirkhani et al. have found that the oxidation of diphenyl sulphide mediated by Mn(III)-salphen and Mn(III)-salen employing terminal oxidant as sodium periodate. The Mn(III)-salphen complex yields a product mixture of sulfoxide and sulfone (4, 1 ratio) in 100% transformation under mild conditions [89]. This is in contrast to the analogous Mn(III)salen complex which only led 18% (ratio of sulfoxide and sulfone, 2:1). Mn(III)-salphen catalytic system was also successfully applied towards a variety of other sulphides and also furnished 100% yields.

Salen complex of heterobimetallic origin have been exclusively examined for many asymmetric catalytic synthesis [90]. Salen ligands are prepared from diamines and salicylaldehydes [91], configuration of both of these constituents can

easily be changed, sterically modified as per desirable physical and electronically altered which makes it possible for the synthesis of recyclable and immobilised salen complexes [7, 92–96]. Shibasaki et al. have used chemoselective complexation of transition metals at  $N_2O_2$  coordination core while the rare earth metal utilised  $O_2O_2$  core of same ligand. However, the key role for selectivity and reactivity of these multimetallic catalysts is based on metal ions e.g., coupling of Cu(II) and Sm(III) yields 66–99% enantiomeric excess (ee) in Mannich-type reactions [97] whereas Pd(II) and La(III) is the best combination for the asymmetric synthesis in Henry reaction, yielding product in 72–92% ee [98].

## 4.2 Molecular magnetism

Magnetic linkage of paramagnetic metal centres with some non-innocent ligands, in multimetallic salen complexes has produced essential information on spin interaction mechanisms. The extent of magnetic interaction (whether it be antiferromagnetic or ferromagnetic) is dependent on a number of factors including the distance between the paramagnetic centres and comparative orientation of the related magnetic orbitals. The relative ease of synthesis and the distance between the paramagnetic centres. Single molecule magnets have gained much research attention since the discovery of spontaneous magnetization below a critical temperature [99, 100]. By applying proper ligand scaffolds, ferromagnetic interactions can be enforced between metal centres in multimetallic complexes [101]. Glaser et al. investigated phloroglucinol as a linker between paramagnetic metal salen units [102–104]. At the time, *m*-phenylene linkers had been well established in the organic radical community as an efficient ferromagnetic coupler and had been used extensively as a means to produce high spin organic radicals [105]. First row of transition metal V(IV)=O [106], Mn(III) [107], Fe(III) [108], Ni(II) [109] and Cu(II) [110] are best fitted coordinating with triple salen.

## 4.3 Material applications

Metal salen based materials have drawn attraction of material scientists as well [111]. Metal organic framework (MOF) and zeolite encapsulated salen have porosity in their bulk material and thus exhibited gas storage properties and thus expected as gaseous fuel loading materials [6, 112]. Various lanthanide and transition metal-lanthanide complexes have been found to have excellent luminescence properties [113]. Yu et al. reported the Zn(II) complex of salen type ligand exhibiting blue photoluminescence with brightness of around  $37.2 \text{ cd m}^{-2}$  [114]. The LED material also showed excellent thermal stability and thin film coating property. Ni(II), Pd(II) and Pt(II) complexes of salphen derivatives have also shown LED uses [115, 116]. Cu(II) and Zn(II) complexes of thiophene analogue of salphen have been reported as semiconducting material for field-effect transistor with excellent hole mobilities [37]. Thiophene capped salen-metal (V, Ni and Cu) complexes, Pietrangelo et al., where electrochemically polymerised as thin film to get conducting polymers. The polymerised complex materials exhibited enhanced nonlinear optical properties [36].

## 4.4 Biological activities

Metallosalens exhibits many biological activities as antimicrobial activity, anti-oxidant activity [117] and anticancer propensity [118]. Their numerous applications have been seen in therapeutics and as biosensors. It has been found that the metal salen have functional enzyme mimic models as superoxide dismutase [119, 120], and Galactose oxidase mimics [121], Cytochrome P-450 mimics [122], Cytochrome

P-450 mimics [123], vitamin B<sub>12</sub> [124, 125]. Metallosalens are capable of inducing specific damage to DNA or RNA and have been recommended as footprinting agents [126, 127]. Salen complexes are versatile (biomimetic) catalysts for important organic transformations. Derivatives of diaryl-substituted amines linked with metal attached with salen as ligand were experimented in number of cancerous cell lines [128]. Aromatic ring substitution and structural orientation of salen complexes predict the cytotoxicity. Two labile titanium-salen complexes of *cis* configuration were discovered as antitumor agents due to its chelating ability as found in cis-platin [129, 130].

#### 4.5 Sensors

Metal salen complexes have shown the sensory properties for verities of metal ions and small molecules [2, 38]. Colorimetric and fluoremetric both types of responses have been observed depending on the sensor and sensing ions. Chan et al. reported the Pt(II)-salphen based polymeric sensors for the detection of Pd(II), Cd(II), Hg(II), Zn(II), Mg(II), Ca(II), Li(I) and K(I) ions [131, 132]. Wezenberg et al. reported Zn(II)-salphen complexes as metal ion sensors based on demetalation of complexes [133, 134]. Many multimetallic salen complexes have found to be potential sensory properties [2]. Song et al. reported chiral salen based fluorescent polymeric sensor for the enantioselective detection of  $\alpha$ -hydroxy carboxylic acids showing fluorescence quenching upon reaction [135]. The same group reported another chiral salen based fluorescent polymeric sensor for the detection of Zn(II) ion as turn-on fluorescence response [136]. Salen based chemosensors for the detection of Al(III) ion based on transmetalation mechanism have also been reported [137].

### 5. Conclusions

Researcher aims to design or synthesise a molecule with multidirectional use, for developing such a molecule endless work is needed with clarity of innovation leading to novelty. Salen is among those important creation, nevertheless molecule has unimaginable and multiple scope of application ranging from catalysis to biological activities, or as therapeutic use in many medicinal drugs. Salen and its derivatives have been extensively studied because the structural configuration of complex felicitates its importance in various chemical reactions. Widespread use enhances its reliability as catalyst in oxidation, reduction, asymmetric synthesis and many more. The nonsymmetrical salen derivatives have signify to be essential for the preparation of different polymer-supported catalysts that show improved properties (higher activities, catalyst recycling) as collate with parent mono-nuclear complexes. Metallic interference adhere tremendous approach in chemical reaction, presence of metallic centres promotes many specific reaction. Henry reaction, Mannich reaction, Diels-Alder reaction, alkene epoxidation and many such reactions encountered frequently employing salen as transitional part between reactant and product. Metal organic framework (MOF) using salen ligand is recent advancement in the field of macromolecule i.e., supramolecular structure attracting great attention in the field of catalysis and material science. Thus, it is assumed that in near future salen can escort a bloom in the field of catalysis, magnetism, sensors, medicinal areas and material sciences.

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