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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.

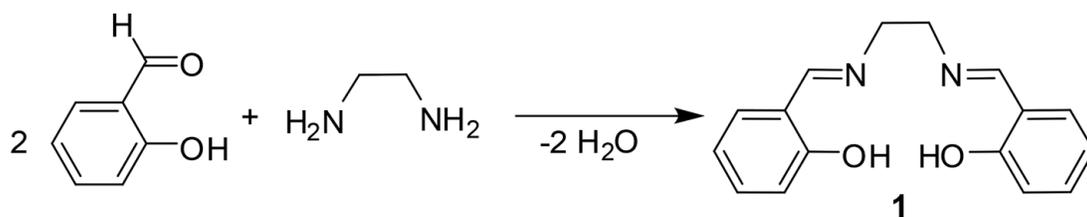


Figure 1.
Synthesis of salen ligand.

Salen ligand possess N₂O₂ 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

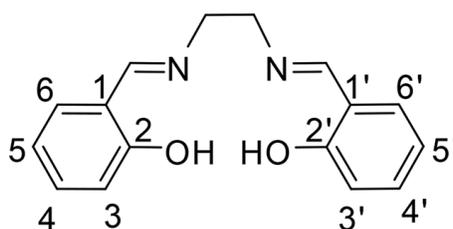
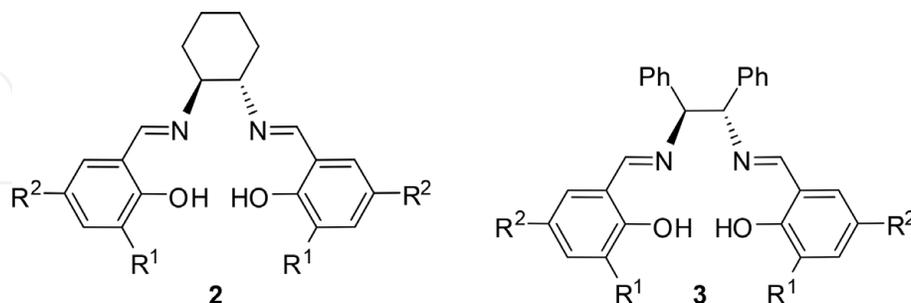
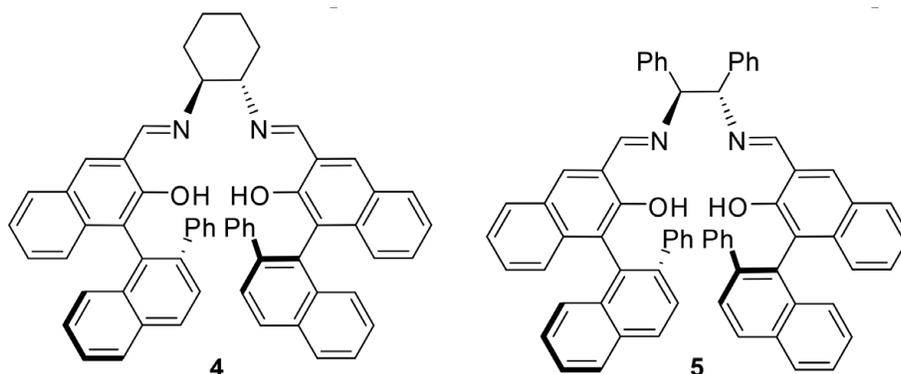


Figure 2.
Numbered positions in salen ligand.

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 C₂-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

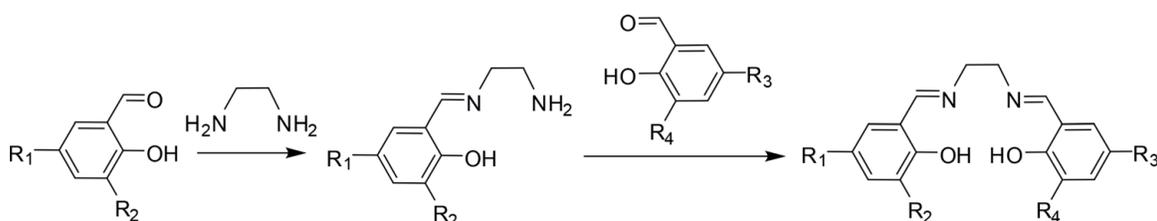


Figure 3.
Direct two step synthesis of nonsymmetrical salen ligand.

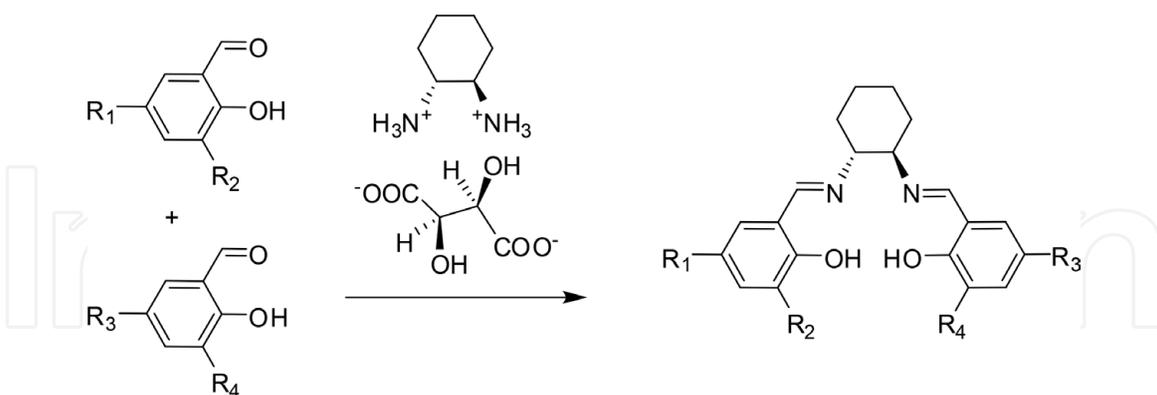


Figure 4.
Direct one step synthesis of nonsymmetrical salen ligand.

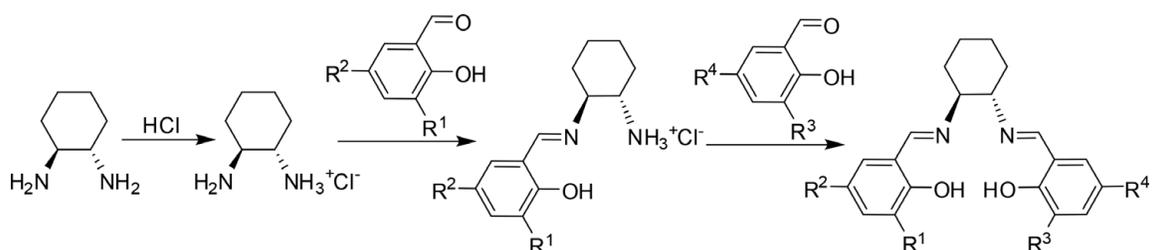
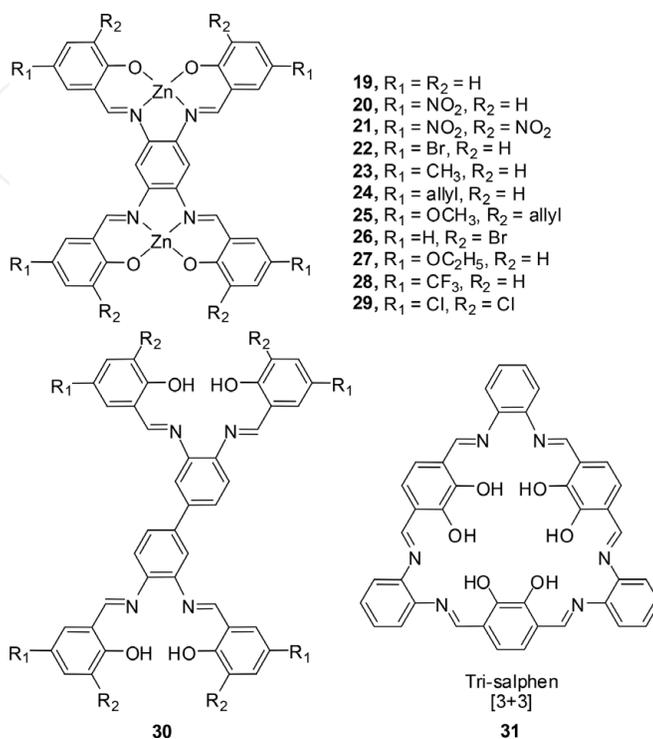


Figure 5.
Protection-deprotection method for the synthesis of nonsymmetrical salen ligand.

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 exist 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 H₂O₂ 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.

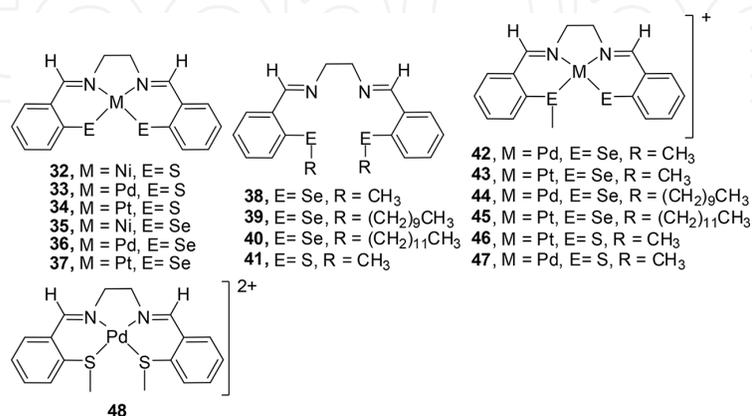
Kleij et al. found the unique self-aggregation nature of bis-Zn(salophen) [14, 15, 56, 57]. They have secure self-assembly behaviour through linking coordination motifs that are fundamentally different from those usually found for the self-assembly of mononuclear Zn-salophens [58]. This takes place on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

of Zn(salphen) which form dimeric structures having a classical Zn_2O_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 N_2O_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 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

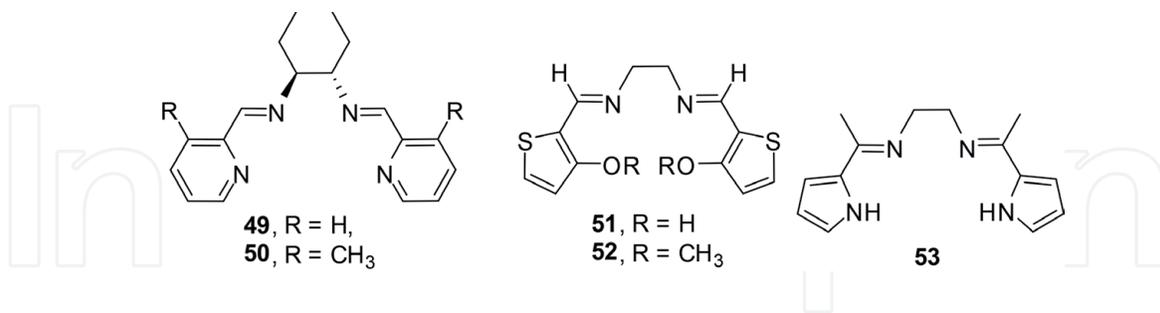
Due to the extended applications of salen ligand systems, their various analogues have been developed and studied. Chalcogen analogues of salen include sulphur and selenium derivatives as thiasalen and selenasalen. However, the sulphur and selenium analogues are relatively less explored because of the 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], COdehydrogenase [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 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 B₁₂ [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 α -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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References

- [1] Pfeiffer P, Breith E, Lubbe E, Tsumaki T. Tricyclische orthokon-densierte Nebervalenzringe. *Justus Liebigs Annalen der Chemie*. 1933;**503**:84
- [2] Clarke RM, Storr T. The chemistry and applications of multimetallic salen complexes. *Dalton Transactions*. 2014;**43**:9380
- [3] Atwood DA, Harvey MJ. Group 13 compounds incorporating salen ligands. *Chemical Reviews*. 2001;**101**:37
- [4] Karmakar M, Chattopadhyay S. A comprehensive overview of the orientation of tetradentate N₂O₂ donor Schiff base ligands in octahedral complexes of trivalent 3d metals. *Journal of Molecular Structure*. 2019;**1186**:155
- [5] Pessoa JC, Correia I. Salen vs. salen metal complexes in catalysis and medicinal applications: Virtues and pitfalls. *Coordination Chemistry Reviews*. 2019;**388**:227
- [6] Yuan G, Jiang H, Zhang L, Liu Y, Cui Y. Metallosalen-based crystalline porous materials: Synthesis and property. *Coordination Chemistry Reviews*. 2019;**378**:483
- [7] Baleizão C, Garcia H. Chiral salen complexes: An overview to recoverable and reusable homogeneous and heterogeneous catalysts. *Chemical Reviews*. 2006;**106**:3987
- [8] Cozzi PG. Metal–salen Schiff base complexes in catalysis: Practical aspects. *Chemical Society Reviews*. 2004;**33**:410
- [9] Bennani YL, Hanessian S. Trans-1,2-diaminocyclohexane derivatives as chiral reagents, scaffolds, and ligands for catalysis: Applications in asymmetric synthesis and molecular recognition. *Chemical Reviews*. 1997;**97**:3161
- [10] Lucet D, Le Gall T, Mioskowski C. The chemistry of vicinal diamines. *Angewandte Chemie, International Edition*. 1998;**37**:2580
- [11] Che C-M, Huang J-S. Metal complexes of chiral binaphthyl Schiff-base ligands and their application in stereoselective organic transformations. *Coordination Chemistry Reviews*. 2003;**242**:97
- [12] Nishikori H, Katsuki T. Catalytic and highly enantioselective aziridination of styrene derivatives. *Tetrahedron Letters*. 1996;**37**:9245
- [13] Belokon Y, Moscalenko M, Ikonnikov N, Yashkina L, Antonov D, Vorontsov E, et al. Asymmetric trimethylsilylcyanation of benzaldehyde catalyzed by (salen) Ti(IV) complexes derived from (R)- and/or (S)-4-hydroxy-5-formyl[2.2] paracyclophane and diamines. *Tetrahedron: Asymmetry*. 1997;**8**:3245
- [14] Cort AD, Mandolini L, Pasquini C, Schiaffino L. Inherently chiral uranyl-salophen macrocycles: Computer-aided design and resolution. *The Journal of Organic Chemistry*. 2005;**70**:9814
- [15] Ciogli A, Cort AD, Gasparri F, Lunazzi L, Mandolini L, Mazzanti A, et al. Enantiomerization of chiral uranyl-salophen complexes via unprecedented ligand hemilability: Toward configurationally stable derivatives. *The Journal of Organic Chemistry*. 2008;**73**:6108
- [16] Jacobsen EN, Pfaltz A, Yamamoto H. *Comprehensive Asymmetric Catalysis*. Vol. 2. Berlin, Germany: Springer-Verlag; 1999
- [17] Katsuki T. Some recent advances in metallosalen chemistry. *Synlett*. 2003;**3**:281
- [18] Kokubo C, Katsuki T. Highly enantioselective catalytic oxidation

of alkyl aryl sulfides using Mn-salen catalyt. *Tetrahedron*. 1996;**52**:13895

[19] Fujisaki J, Matsumoto K, Matsumoto K, Katsuk T. Catalytic asymmetric oxidation of cyclic dithioacetals: Highly diastereo- and enantioselective synthesis of the S-oxides by a chiral aluminum(salalen) complex. *Journal of the American Chemical Society*. 2011;**133**:56

[20] Kleij AW. Nonsymmetrical salen ligands and their complexes: Synthesis and applications. *European Journal of Inorganic Chemistry*. 2009;**2**:193

[21] Breinbauer R, Jacobsen EN. Cooperative asymmetric catalysis with dendrimeric [Co(salen)] complexes. *Angewandte Chemie, International Edition*. 2000;**39**:3604

[22] Sellner H, Karjalainen JK, Seebach D. Preparation of dendritic and non-dendritic styryl-substituted salens for cross-linking suspension copolymerization with styrene and multiple use of the corresponding Mn and Cr complexes in enantioselective epoxidations and hetero-Diels–Alder reactions. *Chemistry—A European Journal*. 2001;**7**:2873

[23] Kim G-J, Shin J-H. Application of new unsymmetrical chiral Mn(III), Co(II,III) and Ti(IV) salen complexes in enantioselective catalytic reactions. *Catalysis Letters*. 1999;**63**:83

[24] Renehan MF, Schanz H-J, McGarrigle EM, Dalton CT, Daly AM, Gilheany DG. Unsymmetrical chiral salen Schiff base ligands. *Journal of Molecular Catalysis A*. 2005;**231**:205

[25] Atkins R, Brewer G, Kokot E, Mockler GM, Sinn E. Copper(II) and nickel(II) complexes of unsymmetrical tetradentate Schiff base ligands. *Inorganic Chemistry*. 1985;**24**:127

[26] Huber A, Müller L, Elias H, Klement R, Valko M. Cobalt(II)

complexes with substituted salen-type ligands and their dioxygen affinity in N,N-dimethylformamide at various temperatures. *European Journal of Inorganic Chemistry*. 2005;**1459**

[27] Boghaei DM, Mohebi S. Non-symmetrical tetradentate vanadyl Schiff base complexes derived from 1,2-phenylene diamine and 1,3-naphthalene diamine as catalysts for the oxidation of cyclohexene. *Tetrahedron*. 2002;**58**:5357

[28] Konsler RG, Karl J, Jacobsen EN. Cooperative asymmetric catalysis with dimeric salen complexes. *Journal of the American Chemical Society*. 1998;**120**:10780

[29] Mazet C, Jacobsen EN. Dinuclear {(salen)Al} complexes display expanded scope in the conjugate cyanation of α,β -unsaturated imides. *Angewandte Chemie, International Edition*. 2008;**47**:1762

[30] Daly AM, Dalton CT, Renehan MF, Gilheany DG. Enantioselective rhodium catalyzed hydroboration of olefins using chiral bis(aminophosphine) ligands. *Tetrahedron Letters*. 1999;**40**:3617

[31] Campbell EJ, Nguyen ST. Unsymmetrical salen-type ligands: High yield synthesis of salen-type Schiff bases containing two different benzaldehyde moieties. *Tetrahedron Letters*. 2001;**42**:1221

[32] Annis DA, Jacobsen EN. Polymer-supported chiral co(salen) complexes: Synthetic applications and mechanistic investigations in the hydrolytic kinetic resolution of terminal epoxides. *Journal of the American Chemical Society*. 1999;**121**:4147

[33] Anyanwu UK, Venkataraman D. Effect of spacers on the activity of soluble polymer supported catalysts for the asymmetric addition of diethylzinc

to aldehydes. *Tetrahedron Letters*. 2003;**44**:6445

[34] Rigamonti L, Demartin F, Forni A, Righetto S, Pasini A. Copper(II) complexes of salen analogues with two differently substituted (push-pull) salicylaldehyde moieties. A study on the modulation of electronic asymmetry and nonlinear optical properties. *Inorganic Chemistry*. 2006;**45**:10976

[35] Dabelstein W, Reglitzky A, Schutze A, Reders K. Automotive fuels. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH; 2007

[36] Pietrangelo A, Sih BC, Boden BN, Wang Z, Li Q, Chou KC, et al. Nonlinear optical properties of Schiff-base-containing conductive polymer films electro-deposited in microgravity. *Advanced Materials*. 2008;**20**:2280

[37] Asatkar AK, Senanayak SP, Bedi A, Panda S, Narayan KS, Zade SS. Zn(II) and Cu(II) complexes of a new thiophenebased salphen-type ligand: Solution-processable high-performance field-effect transistor materials. *Chemical Communications*. 2014;**50**:7036

[38] Whiteoak CJ, Salassa G, Kleij AW. Recent advances with p-conjugated salen systems. *Chemical Society Reviews*. 2012;**41**:622

[39] Kuo K-L, Huang C-C, Lin Y-C. Synthesis and photophysical properties of multinuclear zinc-salophen complexes: Enhancement of fluorescence by fluorene termini. *Dalton Transactions*. 2008;**3889**

[40] Kleij AW, Tooke DM, Kuil M, Lutz M, Spek AL, Reek JNH. ZnII-salphen complexes as versatile building blocks for the construction of supramolecular box assemblies. *Chemistry—A European Journal*. 2005;**11**:4743

[41] Ada'n ECE, Belmonte MM, Martin E, Salassa G, Buchholz JB, Kleij AW. A short desymmetrization protocol for the coordination environment in bis-salphen scaffolds. *The Journal of Organic Chemistry*. 2011;**76**:5404

[42] Kleij AW. New templating strategies with salen scaffolds (salen=N,N'-bis(salicylidene)ethylenediamine dianion). *Chemistry—A European Journal*. 2008;**14**:10520

[43] Castilla AM, Curreli S, Belmonte MM, Ada'n ECE, Buchholz JB, Kleij AW. Modular synthesis of heterobimetallic salen structures using metal templation. *Organic Letters*. 2009;**11**:5218

[44] Akine S, Taniguchi T, Nabeshima T. Synthesis and crystal structure of a novel triangular macrocyclic molecule, tris(H₂saloph), and its water complex. *Tetrahedron Letters*. 2001;**42**:8861

[45] Akine S, Nabeshima T. Cyclic and acyclic oligo(N₂O₂) ligands for cooperative multi-metal complexation. *Dalton Transactions*. 2009:10395

[46] Jiang J, MacLachlan MJ. Unsymmetrical triangular Schiff base macrocycles with cone conformations. *Organic Letters*. 2010;**12**:1020

[47] Frischmann PD, Jiang J, Hui JK-H, Grzybowski JJ, MacLachlan MJ. Reversible-irreversible approach to Schiff base macrocycles: Access to isomeric macrocycles with multiple salphen pockets. *Organic Letters*. 2008;**10**:1255

[48] Furukawa H, Cordova KE, O'Keeffe M, Yaghi OM. The chemistry and applications of metal-organic frameworks. *Science*. 2013;**341**:1230444

[49] Liu TF, Feng D, Chen YP, Zou L, Bosch M, Yuan S, et al. Topology-guided design and syntheses of highly stable

mesoporous porphyrinic zirconium metal–organic frameworks with high surface area. *Journal of the American Chemical Society*. 2015;**137**:413

[50] Mo K, Yang Y, Cui Y. A homochiral metal–organic framework as an effective asymmetric catalyst for cyanohydrin synthesis. *Journal of the American Chemical Society*. 2014;**136**:1746

[51] Shultz AM, Farha OK, Adhikari D, Sarjeant AA, Hupp JT, Nguyen ST. Selective surface and near-surface modification of a noncatenated, catalytically active metal-organic framework material based on Mn(salen) struts. *Inorganic Chemistry*. 2011;**50**:3174

[52] Shultz AM, Sarjeant AA, Farha OK, Hupp JT, Nguyen ST. Post-synthesis modification of a metal–organic framework to form metallosalen-containing MOF materials. *Journal of the American Chemical Society*. 2011;**133**:13252

[53] Song F, Wang C, Falkowski JM, Ma L, Lin W. Isorecticular chiral metal–organic frameworks for asymmetric alkene epoxidation: Tuning catalytic activity by controlling framework catenation and varying open channel sizes. *Journal of the American Chemical Society*. 2010;**132**:15390

[54] Jeon Y-M, Armatas GS, Heo J, Kanatzidis MG, Mirkin CA. Amorphous infinite coordination polymer microparticles: A new class of selective hydrogen storage materials. *Advanced Materials*. 2008;**20**:2105

[55] Roesky PW, Bhunia A, Lan Y, Powell AK, Kureti S. Salen-based metal–organic frameworks of nickel and the lanthanides. *Chemical Communications*. 2011;**47**:2035

[56] Cort AD, Murua JIM, Pasquini C, Pons M, Schiaffino L. Evaluation of chiral recognition ability of a novel

uranyl–salophen-based receptor: An easy and rapid testing protocol. *Chemistry—A European Journal*. 2004;**10**:3301

[57] Bera MK, Chakraborty C, Malik S. How the stereochemistry decides the selectivity: An approach towards metal ion detection. *New Journal of Chemistry*. 2015;**39**:9207

[58] Salassa G, Coenen MJJ, Wezenberg SJ, Hendriksen BLM, Speller S, Elemans JAAW, et al. Extremely strong self-assembly of a bimetallic salen complex visualized at the single-molecule level. *Journal of the American Chemical Society*. 2012;**134**:7186

[59] Leoni L, Cort AD. The supramolecular attitude of metal–salophen and metal–salen complexes. *Inorganics*. 2018;**6**(42):1

[60] Akine S, Taniguchi T, Nabeshima T. Helical metallohost–guest complexes via site-selective transmetalation of homotrimeric complexes. *Journal of the American Chemical Society*. 2006;**128**:15765

[61] Dutta PK, Asatkar AK, Zade SS, Panda S. Oxidative addition of disulfide/diselenide to group 10 metal(0) and in situ functionalization to form neutral thiasalen/selenasalen group 10 metal(II) complexes. *Dalton Transactions*. 2014;**43**:1736

[62] Panda S, Krishna GR, Reddy CM, Zade SS. Synthesis, characterization and coordination properties of bis(alkyl)selenosalen ligands. *Dalton Transactions*. 2011;**40**:6684

[63] Dutta PK, Panda S, Krishna GR, Reddy CM, Zade SS. Reaction time dependent formation of Pd(II) and Pt(II) complexes of bis(methyl) thiasalen podand. *Dalton Transactions*. 2013;**42**:476

[64] Nguyen QT, Jeong JH. Synthesis and X-ray structure of a Cu(II) complex

- of N,N'-bis(2-pyridylmethylidene)-(R,R)-1,2-diaminocyclohexane and its catalytic application for asymmetric Henry reaction. *Polyhedron*. 2006;**25**:1787-1790
- [65] Asatkar AK, Panda S, Zade SS. Thiophene-based salen-type new ligands, their structural aspects and a dimeric Cu(II) complex. *Polyhedron*. 2015;**96**:25
- [66] Berube CD, Gambarotta S, Yap GPA, Cozzi PG. Di- and trivalent dinuclear samarium complexes supported by pyrrole-based tetradentate Schiff bases. *Organometallics*. 2003;**22**:434
- [67] Ooi T, Miura T, Maruoka K. Highly efficient, catalytic Meerwein-Ponndorf-Verley reduction with a novel bidentate aluminum catalyst. *Angewandte Chemie, International Edition in English*. 1998;**37**:2347
- [68] Ooi T, Itagaki Y, Miura T, Maruoka K. Simultaneous functional group manipulation in the Meerwein-Ponndorf-Verley reduction process catalyzed by bidentate aluminum reagent. *Tetrahedron Letters*. 1999;**40**:2137
- [69] Osamura Y, Terada K, Kobayashi Y, Okazaki R, Ishiyama Y. A molecular orbital study of the mechanism of chlorination reaction of benzene catalyzed by Lewis acid. *Journal of Molecular Structure*. 1999;**461-462**:399
- [70] Berberich H, Roesky PW. Homoleptic lanthanide amides as homogeneous catalysts for the Tishchenko reaction. *Angewandte Chemie, International Edition in English*. 1998;**37**:1569
- [71] Santelli M, Pons J-M. *Lewis Acids and Selectivity in Organic Synthesis*. New York: CRC Press; 1996
- [72] Saito S, Shiozawa M, Ito M, Yamamoto H. Conceptually new directed Aldol condensation using aluminum tris(2,6-diphenylphenoxide). *Journal of the American Chemical Society*. 1998;**120**:813
- [73] Nelson SG, Peelen TJ, Wan Z. Mechanistic alternatives in Lewis acid-catalyzed acyl halide aldehyde cyclocondensations. *Tetrahedron Letters*. 1999;**40**:6541
- [74] Yoon TP, Dong VM, MacMillan DWC. Development of a new Lewis acid-catalyzed Claisen rearrangement. *Journal of the American Chemical Society*. 1999;**121**:9726
- [75] Foley SR, Yap GPA, Richeson DS. Formation of novel tetrasulfido tin complexes and their ability to catalyze the cyclotrimerization of aryl isocyanates. *Organometallics*. 1999;**18**:4700
- [76] Dalton CT, Ryan KM, Wall VM, Bousquet C, Gilheany DG. Recent progress towards the understanding of metal-salen catalysed asymmetric alkene epoxidation. *Topics in Catalysis*. 1998;**5**:75
- [77] Achard TRJ, Clutterbuck LA, North M. Asymmetric catalysis of carbon-carbon bond-forming reactions using metal(salen) complexes. *Synlett*. 2005;**12**:1828
- [78] Venkataramanan NS, Kuppuraj G, Rajagopal S. Metal-salen complexes as efficient catalysts for the oxygenation of heteroatom containing organic compounds—Synthetic and mechanistic aspects. *Coordination Chemistry Reviews*. 2005;**249**:1249
- [79] Higuchi Y, Yagi T, Yasuoka N. Unusual ligand structure in Ni-Fe active center and an additional Mg site in hydrogenase revealed by high resolution X-ray structure analysis. *Structure*. 1997;**5**:1671
- [80] Higuchi Y, Ogata H, Miki K, Yasuoka N, Yagi T. Removal of the bridging ligand atom at the Ni-Fe

active site of [NiFe] hydrogenase upon reduction with H₂, as revealed by X-ray structure analysis at 1.4 Å resolution. *Structure*. 1999;**7**:549

[81] Spencer DJE, Marr AC, Schröder M. Structural mimics for the active site of [NiFe] hydrogenase. *Coordination Chemistry Reviews*. 2001;**219-221**:1055

[82] Volbeda A, Charon MH, Piras C, Hatchikian EC, Frey M, Camps JCF. Crystal structure of the nickel-iron hydrogenase from *Desulfovibrio gigas*. *Nature*. 1995;**373**:580

[83] Svetlitchnyi V, Dobbek H, Klauke WM, Meins T, Thiele B, Romer P, et al. A functional Ni-Ni-[4Fe-4S] cluster in the monomeric acetyl-CoA synthase from *Carboxydotherrmus hydrogenoformans*. *Proceedings of the National Academy of Sciences of the United States of America*. 2004;**101**:446

[84] Darnault C, Volbeda A, Kim EJ, Legrand P, Vernede X, Lindahl PA, et al. Ni-Zn-[Fe₄-S₄] and Ni-Ni-[Fe₄-S₄] clusters in closed and open subunits of acetyl-CoA synthase/carbon monoxide dehydrogenase. *Nature Structural Biology*. 2003;**10**:271

[85] Doukov TI, Iverson TM, Seravalli J, Ragsdale SW, Drennan CL. A Ni-Fe-Cu center in a bifunctional carbon monoxide dehydrogenase/acetyl-CoA synthase. *Science*. 2002;**298**:567

[86] Drennan CL, Heo JY, Sintchak MD, Schreiter E, Ludden PW. Life on carbon monoxide: X-ray structure of *Rhodospirillum rubrum* Ni-Fe-S carbon monoxide dehydrogenase. *Proceedings of the National Academy of Sciences of the United States of America*. 2001;**98**:11973

[87] Dobbek H, Svetlitchnyi V, Gremer L, Huber R, Meyer O. Crystal structure of a carbon monoxide

dehydrogenase reveals a [Ni-4Fe-5S] cluster. *Science*. 2001;**293**

[88] Ermler U, Grabarse W, Shima S, Goubeaud M, Thauer RK. Crystal structure of methyl-coenzyme M reductase: The key enzyme of biological methane formation. *Science*. 1997;**278**:1457

[89] Mirkhani V, Tangestaninejad S, Moghadam M, BaltorkIPM, KargarH. Efficient oxidation of sulfides with sodium periodate catalyzed by manganese(III) Schiff base complexes. *Journal of Molecular Catalysis A: Chemical*. 2005;**242**:251

[90] Shibasaki M, Kanai M, Matsunaga S, Kumagai N. Recent progress in asymmetric bifunctional catalysis using multimetallic systems. *Accounts of Chemical Research*. 2009;**42**:1117

[91] Walsh PJ, Kozlowski MC. *Fundamentals of Asymmetric Catalysis*. Sausalito: University Science Books; 2009

[92] Pozzi G, Shepperson I. Fluorous chiral ligands for novel catalytic systems. *Coordination Chemistry Reviews*. 2003;**242**:115

[93] Canali L, Sherrington DC. Utilisation of homogeneous and supported chiral metal(salen) complexes in asymmetric catalysis. *Chemical Society Reviews*. 1999;**28**:85

[94] Zulauf A, Mellah M, Hong X, Schulz E. Recoverable chiral salen complexes for asymmetric catalysis: Recent progress. *Dalton Transactions*. 2010;**39**:6911

[95] Leung ACW, MacLachlan M. Schiff Base complexes in macromolecules. *Journal of Inorganic and Organometallic Polymers and Materials*. 2007;**17**:57

[96] Madhavan N, Jones CW, Weck M. Rational approach

- to polymer-supported catalysts: Synergy between catalytic reaction mechanism and polymer design. *Accounts of Chemical Research*. 2008;**41**:1153
- [97] Handa S, Gnanadesikan V, Matsunaga S, Shibasaki M. Heterobimetallic transition metal/rare earth metal bifunctional catalysis: A Cu/Sm/Schiff base complex for Syn-selective catalytic asymmetric nitro-Mannich reaction. *Journal of the American Chemical Society*. 2010;**132**:4925
- [98] Handa S, Nagawa K, Sohtome Y, Matsunaga S, Shibasaki M. A heterobimetallic Pd/La/Schiff base complex for anti-selective catalytic asymmetric nitroaldol reactions and applications to short syntheses of β -adrenoceptor agonists. *Angewandte Chemie, International Edition*. 2008;**47**:3230
- [99] Miller JS, Calabrese JC, Epstein AJ, Bigelow RW, Zhang JH, Reiff WM. Ferromagnetic properties of one-dimensional decamethylferrocenium tetracyanoethylene (1:1): $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2]^{*+}[\text{TCNE}]^{\bullet-}$. *Journal of the Chemical Society, Chemical Communications*. 1986;**1026**
- [100] Miller JS, Calabrese JC, Rommelmann H, Chittipeddi SR, Zhang JH, Reiff WM, et al. Ferromagnetic behavior of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{*+}[\text{TCNE}]^{\bullet-}$. Structural and magnetic characterization of decamethylferrocenium tetracyanoethylene, $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{*+}[\text{TCNE}]^{\bullet-}\cdot\text{MeCN}$ and decamethylferrocenium pentacyanopropene, $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{*+}[\text{C}_3(\text{CN})_5]^-$. *Journal of the American Chemical Society*. 1987;**109**:769
- [101] Glaser T. Exchange coupling mediated by extended phloroglucinol ligands: Spin-polarization vs. heteroradialene-formation. *Coordination Chemistry Reviews*. 2013;**257**:140
- [102] Glaser T, Gerenkamp M, Fröhlich R. Targeted synthesis of ferromagnetically coupled complexes with modified 1,3,5-trihydroxybenzene ligands. *Angewandte Chemie, International Edition*. 2002;**41**:3823
- [103] Glaser T, Heidemeier M, Grimme S, Bill E. Targeted ferromagnetic coupling in a trinuclear copper(II) complex: Analysis of the $S = 3/2$ spin ground state. *Inorganic Chemistry*. 2004;**43**:5192
- [104] Glaser T, Heidemeier M, Fröhlich R, Hildebrandt P, Bothe E, Bill E. Trinuclear nickel complexes with tripesalen ligands: Simultaneous occurrence of mixed valence and valence tautomerism in the oxidized species. *Inorganic Chemistry*. 2005;**44**:5467
- [105] Ratera I, Veciana J. Playing with organic radicals as building blocks for functional molecular materials. *Chemical Society Reviews*. 2012;**41**:303
- [106] Theil H, von Richthofen C-GF, Stammler A, Bögge H, Glaser T. Ferromagnetic coupling by the spin-polarization mechanism in a trinuclear VIV tripesalen complex. *Inorganica Chimica Acta*. 2008;**361**:916
- [107] Mukherjee C, Stammler A, Bögge H, Glaser T. Trinuclear C₃-symmetric extension of Jacobsen's catalyst: Synthesis, characterization, and catalytic properties of a chiral trinuclear MnIII tripesalen complex. *Inorganic Chemistry*. 2009;**48**:9476
- [108] Mukherjee C, Stammler A, Bögge H, Glaser T. Do trinuclear tripesalen complexes exhibit cooperative effects? Synthesis, characterization, and enantioselective catalytic sulfoxidation by chiral trinuclear FeIII tripesalen complexes. *Chemistry—A European Journal*. 2010;**16**:10137
- [109] Theil H, von Richthofen C-G, Stammler A, Stammler A,

- Bögge H, Glaser T. From triplesalen to triplesalophen: Ferromagnetic interactions through spin-polarization in a trinuclear Ni-II triplesalophen complex. *European Journal of Inorganic Chemistry*. 2011;**49**
- [110] Glaser T, Heidemeier M, Strautmann JBH, Bögge H, Stammli A, Krickemeyer E, et al. Trinuclear copper complexes with triplesalen ligands: Geometric and electronic effects on ferromagnetic coupling via the spin-polarization mechanism. *Chemistry—A European Journal*. 2007;**13**:9191
- [111] Wezenberg SJ, Kleij AW. Material applications for Salen frameworks. *Angewandte Chemie, International Edition*. 2008;**47**:2354
- [112] Crane AK, MacLachlan MJ. Portraits of porosity: Porous structures based on metal salen complexes. *European Journal of Inorganic Chemistry*. 2012;**17**
- [113] Yang X, Jones RA, Huang S. Luminescent 4f and d-4f polynuclear complexes and coordination polymers with flexible salen-type ligands. *Coordination Chemistry Reviews*. 2014;**63**:273-274
- [114] Yu G, Liu Y, Song Y, Wu X, Zhu D. A new blue light-emitting material. *Synthetic Metals*. 2001;**117**:211
- [115] Lavastre O, Illitchev I, Jegou G, Dixneuf PH. Discovery of new fluorescent materials from fast synthesis and screening of conjugated polymers. *Journal of the American Chemical Society*. 2002;**124**:5278
- [116] Che C-M, Kwok C-C, Lai S-W, Rausch AF, Finkenzeller WJ, Zhu N, et al. Photophysical properties and OLED applications of phosphorescent platinum(II) Schiff Base complexes. *Chemistry—A European Journal*. 2010;**16**:233
- [117] Iranzo O. Manganese complexes displaying superoxide dismutase activity: A balance between different factors. *Bioorganic Chemistry*. 2011;**39**:73
- [118] Erxleben A. Transition metal salen complexes in bioinorganic and medicinal chemistry. *Inorganica Chimica Acta*. 2018;**472**:40
- [119] Barondeau DP, Kassmann CJ, Bruns CK, Tainer JA, Getzoff ED. Nickel superoxide dismutase structure and mechanism. *Biochemistry*. 2004;**43**:8038
- [120] Wuerges J, Lee J-W, Yim YI, Yim H-S, Kang S-O, Djinic Carugo K. Crystal structure of nickel-containing superoxide dismutase reveals another type of active site. *Proceedings of the National Academy of Sciences of the United States of America*. 2004;**101**:8569
- [121] Lyons CTL, Stack TDP. Recent advances in phenoxy radical complexes of salen-type ligands as mixed-valent galactose oxidase models. *Coordination Chemistry Reviews*. 2013;**257**:528
- [122] Cho K-B, Nam W, Hirao H, Shaik S. To rebound or dissociate? This is the mechanistic question in C–H hydroxylation by heme and nonheme metal–oxo complexes. *Chemical Society Reviews*. 2016;**45**:1197
- [123] Wollenweber E, Harborne JB, Mabry TJ, editors. *Flavonoids: Advances in Research*. London, New York: Chapman & Hall; 1982
- [124] Tsou TT, Loots M, Halpern J. Kinetic determination of transition metal-alkyl bond dissociation energies: Application to organocobalt compounds related to B12 coenzymes. *Journal of the American Chemical Society*. 1982;**104**:623
- [125] Halpern J, Ng FTT, Rempel GL. Metal-alkyl bond dissociation energies

in organocobalt compounds related to vitamin B12 coenzymes. *Journal of the American Chemical Society*. 1979;**101**:7124

[126] Herchel R, Sindelar Z, Travnicek Z, Zboril R, Vanco J. Novel 1D chain Fe(III)-salen-like complexes involving anionic heterocyclic N-donor ligands. Synthesis, X-ray structure, magnetic, ⁵⁷Fe Mössbauer, and biological activity studies. *Dalton Transactions*. 2009:9870

[127] Asatkar AK, Tripathi M, Panda S, Pande R, Zade SS. Cu(I) complexes of bis(methyl)(thia/selena) salen ligands: Synthesis, characterization, redox behavior and DNA binding studies. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*. 2017;**171**:18

[128] Saini AK, Kumari P, Sharma V, Mathur P, Mobin SM. Varying structural motifs in the salen based metal complexes of Co(II), Ni(II) and Cu(II): Synthesis, crystal structures, molecular dynamics and biological activities. *Dalton Transactions*. 2016;**45**:19096

[129] Gust R, Ott I, Posselt D, Sommer K. Development of cobalt(3,4-diarylsalen) complexes as tumor therapeutics. *Journal of Medicinal Chemistry*. 2004;**47**:5837

[130] Tzuberly A, Tshuva EY. Trans titanium(IV) complexes of salen ligands exhibit high antitumor activity. *Inorganic Chemistry*. 2011;**50**:7946

[131] Guo Z, Tong W-L, Chan MCW. Axially rotating (Pt-salphen)₂ phosphorescent coordination frameworks. *Chemical Communications*. 2009:6189

[132] Sun S, Tong W-L, Chan MCW. Alternating poly(Pt-salphen)-(p-phenyleneethynylene) as phosphorescent conjugated linear-rod and coilable sensory

materials. *Macromolecular Rapid Communications*. 2010;**31**:1965

[133] Wezenberg SJ, Escudero-Ada'n EC, Anselmo D, Buchholz JB, Kleij AW. Dimetallic activation of dihydrogen phosphate by Zn (salphen) chromophores. *European Journal of Inorganic Chemistry*. 2010;**4611**

[134] Wezenberg SJ, Ada'n ECE, Buchholz JB, Kleij AW. Colorimetric discrimination between important alkaloid nuclei mediated by a bis-salphen chromophore. *Organic Letters*. 2008;**10**:3311

[135] Song F, Wei G, Wang L, Jiao J, Cheng Y, Zhu C. Salen-based chiral fluorescence polymer sensor for enantioselective recognition of α -hydroxyl carboxylic acids. *The Journal of Organic Chemistry*. 2012;**77**(10):4759

[136] Song F, Ma X, Hou J, Huang X, Cheng Y, Zhu C. (R,R)-salen/salan-based polymer fluorescence sensors for Zn²⁺ detection. *Polymer*. 2011;**52**:6029

[137] Cheng J, Ma X, Zhang Y, Liu J, Zhou X, Xiang H. Optical chemosensors based on transmetalation of salen-based Schiff base complexes. *Inorganic Chemistry*. 2014;**53**(6):3210