Synthesis and antioxidant activities of Schiff bases and their complexes: a review

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Schiff bases, named after Hugo Schiff, are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by imine or azomethine group. They are widely used for industrial purposes and also have a broad range of applications as antioxidants. An overview of antioxidant applications of Schiff bases and their complexes is discussed in this review. A brief history of the synthesis and reactivity of Schiff bases and their complexes is presented. Factors of antioxidants are illustrated and discussed. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: Schiff bases; antioxidant; metal ions; imines; synthesis

Introduction

Schiff bases contain the imine group (–RC=N–) and are prepared by the condensation between primary amine (R–NH$_2$) and active carbonyl (RCOR') compounds, where R, R' is either an alkyl or aryl group. Schiff bases are known for their strong coordinative ability as a family of ligands.[1] The Schiff base class is very versatile, as these compounds can have a variety of different substituents and they can be unbridged or N,N'-bridged. Most commonly Schiff bases have NO or N$_2$O$_2$ donor atoms but oxygen can be replaced by sulfur, nitrogen or selenium atoms.[2]

It has been found that, depending on the solvent, in the absence of dioxygen, cobalt(II) Schiff base complexes may be four, five or six coordinate. In addition, in a strongly coordinating solvent such as pyridine, both [Co(salen)pyr] and [Co(salen)$_2$Pyr] exist, whilst in chloroform the major species is Co.(salen) (Fig. 1). Irrespective of the solvent, the rate of dioxygen uptake is shown to be similar; however, the product obtained may be a 1:1 (IV) or a 2:1 (V) (oxygen-bridged) complex (Fig. 1).[3,4]

Schiff base compounds constitute an important class of ligands which have been studied in coordination chemistry. Schiff base complexes are also known for their significant biological activities such as in photosynthesis and transport of oxygen in mammalian and other respiratory systems.[5] A wide variety of cobalt(II) complexes are known to bind dioxygen, more or less reversibly, and therefore are frequently studied as model compounds for natural oxygen carriers and for their use in oxygen storage as well as in organic synthesis due to their catalytic properties under mild conditions.[6] Metal Schiff base complexes are well known catalysts, in both heterogeneous and homogeneous systems. Other applications of these complexes are reported, such as stereoselective alkene epoxidation,[7–9] liquid–liquid extraction,[10–12] liquid membrane transport of metal cations,[13] the asymmetric addition of organometallic reagents to aldehydes[14] and asymmetric hetero Diels–Alder reactions.[15]

Dioxygen Coordination

Synthetic dioxygen carriers are extensively studied and, for example, tertiary phosphine, salen, porphyrin and phthalocyanine complexes of Co., Mn, Fe, Mo and Cu have been found to coordinate to dioxygen reversibly.[16,17] The activation of molecular oxygen with salen-type complexes was observed in the 1930s by Tsumaki.[18]

Dioxygen coordination involves an electron-seeking oxidative attack and its reversibility and rate depend significantly on the steric and electronic properties of the complexes.[19,20] For example, in bridged Schiff bases an alkylene bridge between the imine moieties results in complexes that coordinate dioxygen more easily than complexes with a phenylene bridge or a tetramethylated ethylene bridge.[21]

Planar complexes have a high affinity for oxygen.[22] The electron density-donating substituents, such as alkyl, alkoxy and halides, increase the coordination rate, whereas substituents withdrawing electron density, such as alkyl, carboxylic and nitro groups, decrease it because they induce a lower charge density of the central ion which in turn results in more difficult oxidation of the ion.[23–25] However, Co. salen-type complexes with *tert*-butyl groups in the salicylidene moieties have been reported to have a good affinity for dioxygen when the cyclohexyl bridge between the imine moieties is functionalized with OH groups hydrogen bonded to the coordination dioxygen.[26]

The dioxygen coordination can occur via different modes, the preferred mode in each particular case depending on the ligand, and the species present in solution if the complexes are studied in solution.[27] For example, Co.(salen) and salophen (chemical formula C$_{15}$H$_{13}$NO$_4$) complexes can form monomeric (superoxo) or dimeric (μ-peroxo) adducts with dioxygen in neutral solution or in solid form. The presence of a suitable donor solvent, such as dimethylformamide or dimethylsulfoxide, or of a monodentate

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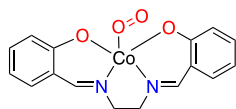b Department of Chemistry, College of Science for Women, Baghdad University, Baghdad, Iraq

Figure 1. Chemical structure of the metal complex Co.(salen) with dioxygen.

base, all of which act as axial ligands, facilitates dioxygen coordination.[19] The base can be an aliphatic or aromatic amine, but pyridine and substituted pyridines are mostly used.[20] The axial base (solvent) provides an additional stabilization of the Co.–O_2 bond through an increase in electron density.[21]

In addition, in the salen and salophen complexes, which prefer square-planar geometry, dioxygen is coordinated in one axial position and the other axial position is occupied by base or solvent molecule.[22] The coordinated dioxygen is easily removed from the complexes by heating, both in solution and solid state, in a stream of inert gas.[23] Though numerous Co.(salen) complexes (Fig. 2) activate dioxygen reversibly, there are still complexes, for instance (bis(salicylaldehyde)methylene-p,p′-diphenylenediaminato)–Co.(II), (di(salicylal)-3,3-diimino-di-n-propylamine)–Co.(II) and rac- and meso-butane-2,3-diylbis(salicylideneiminato)–Co.(II), that have an irreversible dioxygen coordination.[24] In addition, some complexes, for example di(o-hydroxyacetophenone)ethylenediimine–Co.(II), do not show any affinity for dioxygen.[24]

Cedeno et al. have reported the catalytic oxidation of models of guaiacyl (G) and syringyl (S) subunits in lignin to their corresponding p-quinones in the presence of molecular oxygen. The oxidation of syringyl-like phenols readily occurred with five-coordinate cobalt catalysts in which one of the ligands is a monodentate pyridine or imidazole base that coordinates axially to the metal. Formation of p-quinones with this system depends on the coordination of the axial ligand to the metal as influenced by its pK_a and its size. The yield of p-quinones from guaiacyl models was markedly improved by the addition of a sterically hindered aliphatic nitrogen base that does not coordinate to the catalyst.[27]

Oxo-molybdenum chemistry is of great interest since such units are found in the active sites of a majority of molybdo-enzymes. In order to mimic the biological systems, a number of oxo-molybdenum complexes have been synthesized and studied. The coordination geometry around the molybdenum center in these complexes can be best described as a distorted octahedron in which the ONO tridentate ligand occupies a meridional position with two anionic oxygen donors mutually trans and cis to the oxygen centers of the cis-dioxo group. Most applications of cis-MoO_2(ONO)-type complexes reported in the literature involve oxo transfer reactions like epoxidation, sulfoxidation and phosphine oxidation reactions.[28]
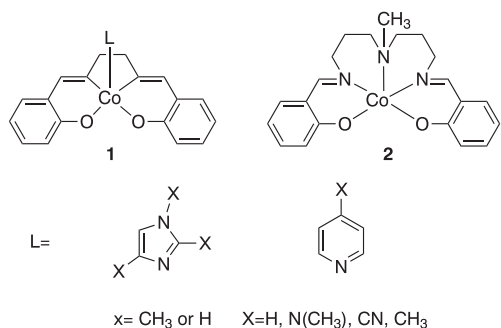
Studies have indicated that four-coordinated Co.(II) complexes are very poor dioxygen binders whereas the corresponding five-coordinated complexes readily bind it at ambient pressure. Punniyamurthy et al. have studied cobalt(II) Schiff base complexes **1**, **2** and **3** (Fig. 3) that catalyze the oxidation of a wide range of organic substrates in the presence of carbonyl compounds and dioxygen. Electron paramagnetic resonance (EPR) studies of **1** indicate that these reactions proceed via Co.(III) superoxo complexes formed under the aegis of carbonyl compounds and dioxygen. Catalysts **1**–**3** exhibit diverse reactivity profiles, which has been attributed to the nature of the ligand around cobalt which causes the formation of different active species from dioxygen. These studies revealed that aliphatic aldehydes and cyclic β-ketoesters also act as good ligands to cobalt(II) Schiff base complex **1** (**2**) in promoting the formation of monomeric cobalt(III)–dioxygen species. Theses carbonyl compounds not only help in the formation of cobalt(II)–dioxygen species but also act as the reducing agent during oxygen atom transfer to organic substrates.[27]

Salicylaldehyde, 2-hydroxyacetophenone and 3,5-dichlorosalicylaldehyde react with 1,2-diaminoethane to give three symmetrical Schiff bases H_2L^1, H_2L^2 and H_2L^3, respectively. With Ru(III) ions, these ligands lead to three complexes: Ru(III)ClL^1 (1), Ru(III)ClL^2 (2) and Ru(III)ClL^3 (3). The purity of these compounds was estimated using TLC and microanalysis while their structures were supported by the usual spectroscopic methods such as ^{13}C NMR, ^{1}H NMR, infrared (IR) and UV–visible electronic spectroscopies. Under the same experimental conditions, it was proved that the ruthenium is coordinated in the three complexes 1, 2 and 3 giving quasi-reversible redox systems. The behavior of these complexes and their comparison with cytochrome P450 (belonging to the superfamily of proteins) were investigated, using them as catalysts in the presence of molecular oxygen with an apical nitrogen base: 1- or 2-methylimidazole.[28]

The reactions between bis(acetylacetonato)dioxomolybdenum (VI) and Schiff base ligands derived from 5-chlorosalicylaldehyde or 3-ethyoxysalicylaldehye, and 3-methoxybenzoic hydrazide (m-anisi hydrazide), 2-furoic hydrazide or 2,4-dihydroxybenzoic hydrazide yielded cis-dioxomolybdenum(VI) complexes with the general formula $MoO_2L(D)$, where L = tridentate Schiff ligand and D = dimethylsulfoxide, hexamethylphosphoramide, dimethylformamide, imidazole or methanol (Fig. 4). The complexes were characterized by elemental analysis, electronic IR, ^{1}H NMR and ^{13}C NMR spectroscopies, thermogravimetric analysis and cyclic voltammetry, and the molecular structures of five of the dioxomolybdenum complexes were elucidated using single-crystal X-ray diffraction studies. In general, the complexes adopt an octahedral environment around the Mo center with a cis-oxo configuration. The other coordination sites are occupied by the imino nitrogen, phenoxyl oxygen and hydroxyl oxygen of the tridentate Schiff base and the donor atom of the solvent molecule. The structural data revealed that the labile coordination site, which is
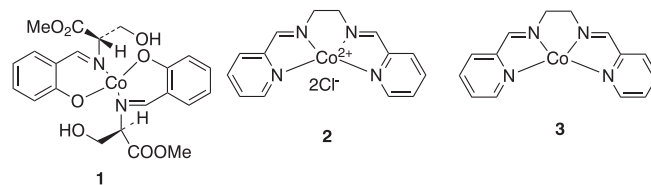

x= CH$_3$ or H   X=H, N(CH$_3$), CN, CH$_3$

Figure 2. Structural formulae of metal complexes.

Figure 3. Proposed structural formulae of metal complexes (**1**, **2**, **3**) as oxidation catalysts for organic substrates in the presence of carbonyl compounds and dioxygen.
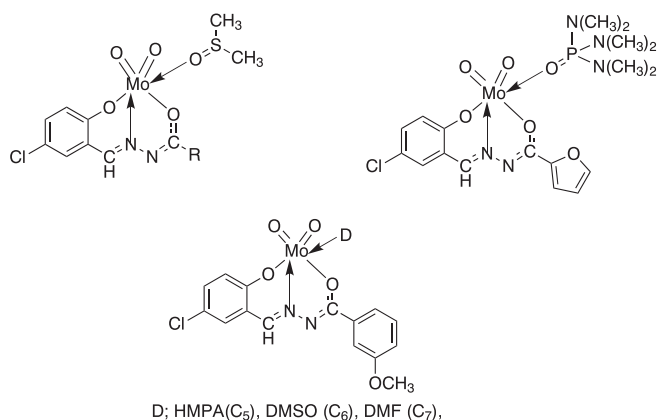
Figure 4. Dioxomolybdenum(VI) complexes with tridentate Schiff base in the presence of various solvent molecules.

occupied by N or O atoms from the donor solvents, has a longer Mo–O or Mo–N bond distance.[29]

Complexes of Co.(II) involving derivatives of salicylaldehyde and primary amines have received considerable attention because of their similarity to biological dioxygen carriers, as well as being catalysts for the insertion of oxygen into organic substrates. In particular, the dioxygen adducts of [Co(salen)] and their ring-substituted analogues have been much investigated. Only limited studies have been made of [Co(napen)] (H₂napen is N,N'-ethylenebis(1-hydroxy-2-naphthylmethyleneimine)) and its dioxygen adduct. Marinescu *et al.* have reported the preparation of two new complexes of Co.(II) and Co.(III) with the Schiff base derived from 1-formyl-2-naftol and ethylenediamine(H₂L) on the basis of elemental chemical analysis and electronic and IR spectra. The complexes were formulated as mononuclear species, [CoL(H₂O)₂], and its mononuclear adduct with dioxygen [CopyO₂] (where L is the dianion of the Schiff base). An electrochemical study supports the formulation of the mononuclear superoxo adduct of Co.(III) ion.[30–34]

The numerous molybdenum(VI) Schiff base complexes have been extensively investigated for over twenty years. Owing to their importance in the domains of stereochemistry[35] and structural[36] and analytical chemistry[37] and as model systems for the interaction of organic substrates with catalytic oxide surfaces,[38] some of them are also interesting due to their ability to oxidize thiols, hydrazines, polyketones and tertiary phosphines.[39–41] Their oxygen atom transfer properties play a significant role in investigating the functioning mechanism of molybdenum oxotransferase.[42,43] Although a number of literature reports deal with the mononuclear dioxomolybdenum(VI) complexes of bi-, tri- or tetradentate Schiff base ligands,[44–50] complexes containing monodentate-coordinated Schiff base derivatives as zwitterionic ligands are extremely rare.

Cindric *et al.* have reported the synthesis of two monomeric molybdenum(VI) Schiff base complexes derived from N-phenyl-2-naphthaldimine and N-benzyl-2-hydroxy-1-naphthaldimine, namely [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₆H₅)] (**I**) and [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHCH₂C₆H₅)] (**II**). These are the first examples in which potentially bidentate Schiff bases are monodentately bonded to molybdenum as zwitterionic. The structure of complex **I** was determined using X-ray analysis. Within the same ligand, the hydrogen atom attached to nitrogen forms an intramolecular hydrogen bond of 2.548(2) Å with the oxygen atom coordinated to molybdenum. The octahedral coordination of

molybdenum is completed by two oxo-oxgyens, two acetylacetonato oxygens and one methoxy oxygen.[51]

Ourari *et al.* have reported the reaction salicylaldehyde, 2-hydroxyacetophenone and 3,5-dichlorosalicylaldehyde with 1,2-diaminothane to give symmetric Schiff bases H₂L¹, H₂L² and H₂L³, respectively (Fig. 5). With Ru(III) ions, these ligands lead to three complexes: Ru(III)ClL¹ (**1**), Ru(III)ClL² (**2**) and Ru(III)ClL³ (**3**). The purity of these compounds was estimated using TLC and microanalysis while their structures were supported by data from the usual spectroscopic methods such as NMR, IR and electronic spectroscopies. Under the same experimental conditions, it was proved that the ruthenium is coordinated in the three complexes **1**, **2** and **3** showing quasi-reversible redox systems. The behavior of these complexes and their comparison with cytochrome P450 are investigated using them as catalysts in the presence of molecular oxygen with an apical nitrogen base: 1- or 2-methylimidazole.[52]

In previous studies it was found that in the case where complexes do not have an axial base, the reduction wave of the Ru(III)/Ru(II) redox couple appears as two successive waves E_{pc1} and E_{pc2} indicating the electroreduction of two species. This may be explained by the following equations:

$$L''Ru(II) + O_2 \longrightarrow L''Ru(III)\text{-}O\text{-}O^\bullet \quad (C)$$
$$L''Ru(III)\text{-}O\text{-}O^\bullet + 1e^- \longrightarrow L''Ru(III)\text{-}O\text{-}O^- \quad (E)$$
$$LRu(III) + O_2 \longrightarrow L''Ru(IV)\text{-}O\text{-}O^\bullet \quad (C)$$
$$LRu(IV)\text{-}O\text{-}O^\bullet + 2e \longrightarrow L''Ru(III)\text{-}O\text{-}O^- \quad (E)$$

The chemical steps involving the reversible reactions with oxygen are (2) and (4) whereas the electrochemical ones such as the reduction waves E_{pc1} and E_{pc2} may result from electroreduction of two different species as represented by (3) for E_{pc1} (Fig. 6, way (a)) and (5) for E_{pc2} (Fig. 6, way (b)). The second one, E_{pc2}, appearing at more cathodic potentials, was assigned to the bielectronic transfer on the metallic center of LnRu(IV)–O–O• (5) giving the LnRu(III)–O–O– species, which are simultaneously produced by (3) according a monoelectronic transfer.[52]

Cindric *et al.* have reported the synthesis of two monomeric Mo(VI) Schiff base complexes derived from N-phenyl-2-hydroxy-1-naphthaldimine and N-benzyl-2-hydroxy-1-naphthaldimine: [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₆H₅)] (**I**) and MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHCH₂C₆H₅)] (**II**) (Fig. 7). These are the first examples in which potentially bidentate Schiff bases are monodentately bonded to molybdenum as zwitterionic. Within
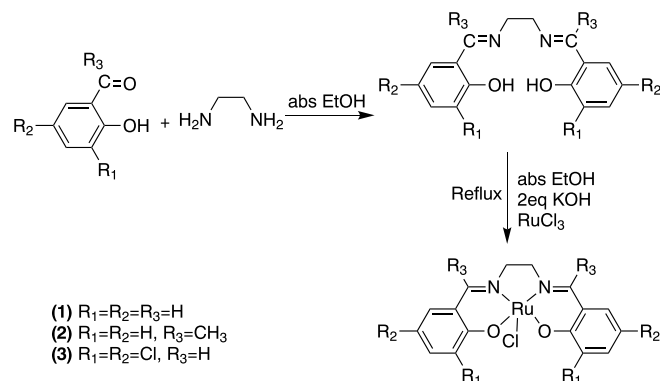

(1) R₁=R₂=R₃=H
(2) R₁=R₂=H, R₃=CH₃
(3) R₁=R₂=Cl, R₃=H

Figure 5. Suggested structures of Schiff base ligand and its metal complexes with Ru(III).
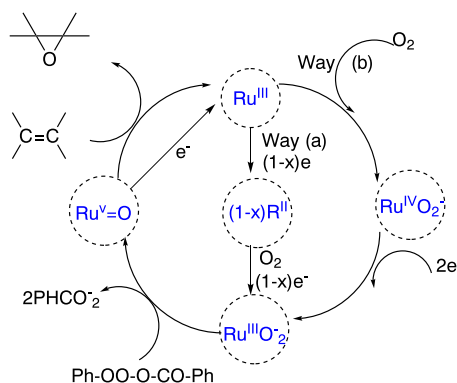
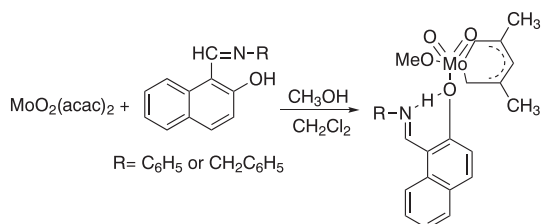**Figure 6.** Proposed scheme for the electrocatalytic epoxidation of olefins or oxidation of hydrocarbons.

Figure 7. Reaction scheme for synthesis of complexes $[MoO_2(C_5H_7O_2)(OCH_3)(2.OC_{10}H_6CH{=}NHC_6H_5)]$ and $[MoO_2(C_5H_7O_2)(OCH_3(2.OC_{10}H_6CH_2C_6H_5)]$.

the same ligand, the hydrogen atom attached to nitrogen forms an intramolecular hydrogen bond of 2.548 Å with the oxygen atom coordinated to molybdenum. The octahedral coordination of molybdenum is completed by two oxo-oxgyens, two acetylacetonato oxygens and one methoxy oxygen. The compounds were characterized using chemical analysis, IR spectroscopy and single-crystal structure determination.[53] Some of the molybdenum(VI) Schiff base complexes are also interesting due to their ability to oxidize thiols, hydrazines, polyketones and tertiary phosphines.[54–56] Their oxygen atom transfer properties play a significant role in investigating the functioning mechanism of molybdenum oxo-transferase.[57,58]

The synthetic oxygen carriers have a potential application in the fields of dioxygen separation, industry, agriculture, medicine and biology. The imine complexes which can adsorb molecular oxygen are important in the fields of coordination organic chemistry and physical chemistry and have broad application in the fields of analytical chemistry, stereochemistry, electrochemistry, spectroscopy, biochemistry, catalysis, materials science, nuclear chemistry, extraction, active transport and so on. The recent application status and research and development of imine complexes in the context of oxygen carriers were briefly introduced and prospects for oxygen carrying were reviewed.[59]

Bioinorganic Chemistry: Synthesis of Oxygen-Carrying Co. Complexes

Naturally occurring oxygen carriers and storage proteins contain a transition metal ion to which molecular oxygen can reversibly bind, typically iron (in the form of ferrous heme in proteins such as myoglobin and hemoglobin) or copper (hemocyanin) (Fig. 8).

The study of complexes capable of reversible binding of molecular oxygen, known as oxygen carriers, has received a great deal of attention. Such systems are utilized biologically in the transport and storage of molecular oxygen.[59–63]

When Co.(salen) was first prepared, it was observed that the red-brown crystals darkened on exposure to air. However, it was not until five years later that it was established that the color change was due to reversible uptake of molecular oxygen. SalenH2 (Fig. 9) is a Schiff base ligand formed by the condensation of two molecules of salicylaldehyde (sal) with ethylenediamine (en)[64] (Fig. 9).

Later, it was found that different crystalline forms existed depending on the solvent used in the preparation, and that these crystalline forms had varying capacity for oxygenation in the solid state. This variation in oxygenation has been related to the presence of voids in the crystal lattice, sufficient to allow the passage of molecular oxygen. This suggestion is supported by the X-ray structure determination of the so-called 'inactive' form which shows that the structure consists of the dimeric units $[Co(salen)]_2$. The active forms of Co.(salen) are presumed to contain dimeric units with a more open lattice packing relative to the inactive form (Fig. 10).[65]

In anaerobic solution, it has been found that the cobalt(II) may be four, five or six coordinate, depending on the solvent. For example, in a strongly coordinating solvent such as pyridine (py; C_5H_5N) both $[Co(salen)(py)]$ and $[Co(salen)(py)_2]$ exist, while in chloroform the only species is Co.(salen). When five- or six-coordinate species can exist, molecular oxygen will form a complex with Co.(salen). The oxygenated product may be a 1:1 ($Co:O_2$) or a 2:1 ($2Co:O_2$) complex. It is thought that molecular oxygen becomes the sixth ligand to a five-coordinate complex, or replaces one of the coordinating
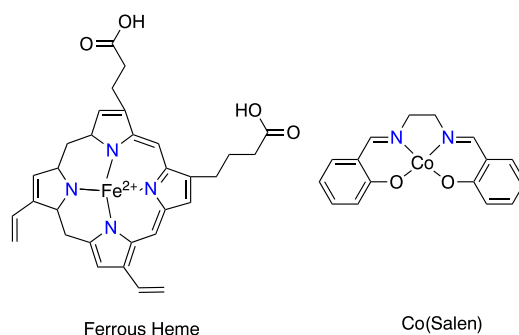

Ferrous Heme   Co(Salen)

Figure 8. Ferrous heme is the factor that binds O_2 reversibly in hemoglobin and myoglobin. Co.(salen) is a coordination compound that can also bind O_2 reversibly.
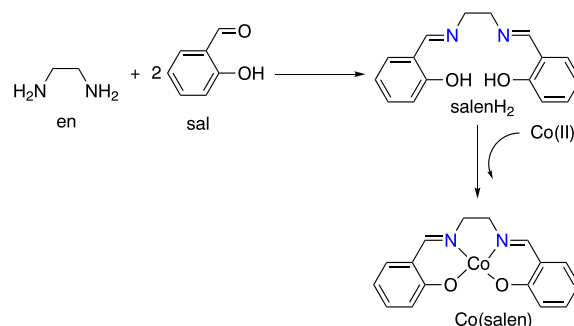

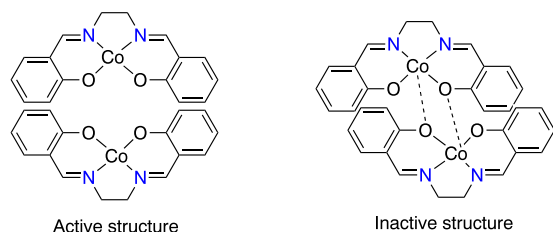**Figure 9.** Synthetic scheme for the formation of Co.(salen).

Figure 10. Structure of active and inactive Co.(salen) in the solid state.

R= -(CH₂)₂)-, -(C₂H₄)NH(C₂H₄)-,
X= Cl, Im, 2MeIm. N of R

R= -(C₆H₄)-, -(CH₂)₂-, -(C₂H₄)NH(C₂H₄)-
X= Im, 2MeIm, Cl, 2MeIm, N of R

Figure 12. Two possible structures of a complex.

solvent molecules. The final structure may be either a six-coordinate 1:1 complex or a six-coordinate 2:1 complex. It is worth noting that the conventional way to view the formation of an O₂ adduct is as a redox process, in which molecular oxygen accepts one electron from Co.(II), thereby forming superoxide, molecular oxygen bound to Co.(III) (Fig. 11).[66]

The synthesis and dioxygen affinities of some Ru(III) Schiff base complexes in dimethylformamide solution in the presence of various axial bases have been reported. The ligands used are bis(salicylaldehyde)-*o*-phenylenediimine (picoph), bis(picolinaldehyde)ethylenediimine (picen) and bis(picolinaldehyde)diethylenetriimine (picdien). The axial ligands employed are chloride (Cl⁻), imidazole (Im) and 2-methylimidazole (2-MeIm). From the oxygenation constants it is found that electron-donating substituents on the Schiff bases increase the affinity for dioxygen. Equilibrium dioxygen uptake measurements at 278, 288 and 303 K provide values of $H°$ and $S°$ of oxygenation that fall in the range -6.1 to -13.3 kcal mol⁻¹ for $H°$ and -10 to -31 cal deg.⁻¹ mol⁻¹ for $S°$. The dioxygen adducts of Ru(III) were characterized using electrochemistry, UV–visible, IR and EPR techniques as Ru(IV) superoxo complexes (Fig. 12).[67]

Studies of the interactions of axial ligands and molecular oxygen with Co.(II) porphyrin and Schiff base complexes have revealed a number of interesting and significant features regarding the nature of such interactions. The binding of a first axial ligand to cobalt(II) octamethyltetrabenzoporphyrin (CoOMBP) occurs with greater ligand affinity than is observed for other Co.(II) porphyrin (CoP) complexes. Also, LCoOMBP is shown by visible spectroscopy to completely bind a second axial ligand at high ligand concentrations in several cases, while other LCoP complexes do not under similar conditions.[67]

These binding properties are attributed to the very weak σ-basicity of OMBP causing approaching axial ligands to see a metal center with more positive charge. In contrast, molecular oxygen binds more strongly to LCoOMBP complexes than would be predicted from the σ-basicity properties of OMBP. This observation is explained in terms of the strong π-donating abilities of OMBP
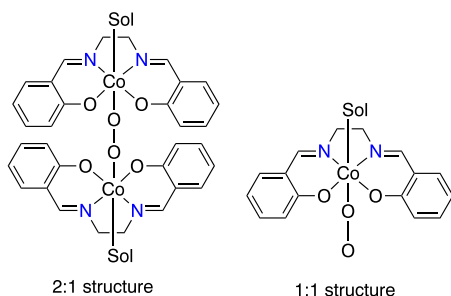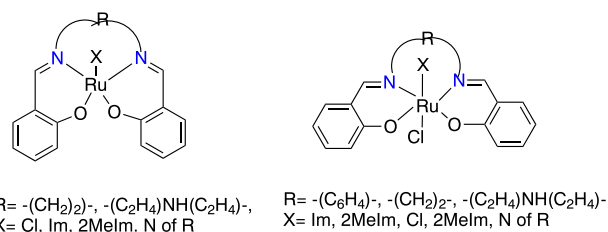
enhancing the affinity of the Co.(II) complex for dioxygen; thus good evidence is obtained for coordinated dioxygen being able to accept Tr-electron density. The π-donating abilities of OMBP are also invoked to explain the observed similarities in ΔH values associated with K_1 and K_2; it is suggested that the π-interactions inhibit metal center displacement from the porphyrin plane upon the formation of a five-coordinate adduct.[67]

A series of quinazolinone-derived Schiff base derivatives (Fig. 13) were synthesized and analyzed as novel antioxidants and anti-inflammatory agents. The *in vitro* antioxidant activities of these compounds were evaluated and compared with those of commercial antioxidants ascorbic acid, gallic acid, butylated hydroxytoulene and butylated hydroxyanisole (BHA) employing 1,1-diphyenyl-2-picrylhydrazyl (DPPH) assay. The results revealed that IC₅₀ values of compounds were lower than those of standards in all three performed antioxidant assays indicating good activities of these compounds. Preliminary structure–activity relationship studies revealed that the compounds with electron-donating moiety (OH, OCH₃) were found to be excellent antioxidants and compounds with electron-withdrawing moiety (Cl, NO₂) were found to be excellent anti-inflammatory agents.[68]

A series of new cholesterol-based Schiff base derivatives, namely cholesteryl-*n*-(4-((*E*)-(4'-cyanobiphenylylimino)methyl)phenoxy) alkanoate (Fig. 14), have been analyzed and characterized using IR, NMR and mass spectral studies. *In vitro* antioxidant activities of these compounds were evaluated against superoxide anion radical, nitric oxide radical, DPPH radical and hydrogen peroxide and were compared with a standard natural antioxidant, ascorbic acid. The results showed excellent radical scavenging activities of these compounds.[69]

A series of nine new biologically active Schiff bases (Fig. 15) were synthesized by a condensation of 4-acyl-5-pyrazolones with aromatic diamines, and characterized using elemental analysis and mass spectroscopic data. All the compounds showed antibacterial activity against *Bacillus subtilis* and Escherichia coli, good antifungal

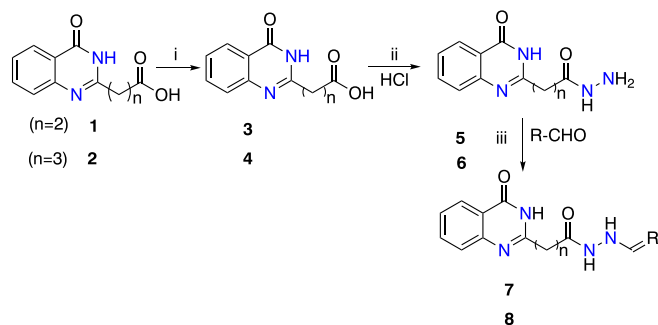
Figure 11. Two possible structures for the O₂ adduct of Co.(salen), in which 'Sol' represents a coordinating solvent molecule.

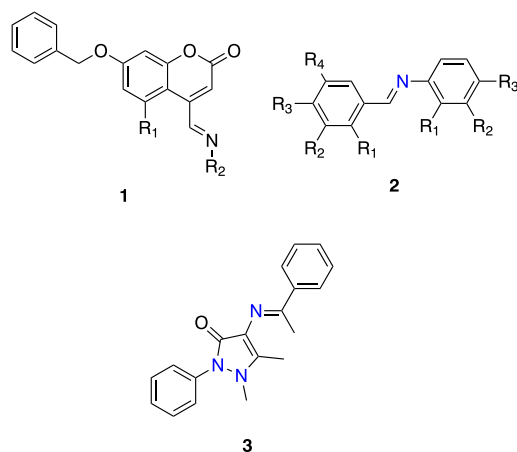**Figure 13.** Synthetic scheme of quinazolinone-derived Schiff base derivatives.

Figure 14. Examples of some Schiff bases: cholesteryl-*n*-(4-((*E*)-(4'-cyanobiphenylylimino)methyl)phenoxy)alkanoate.
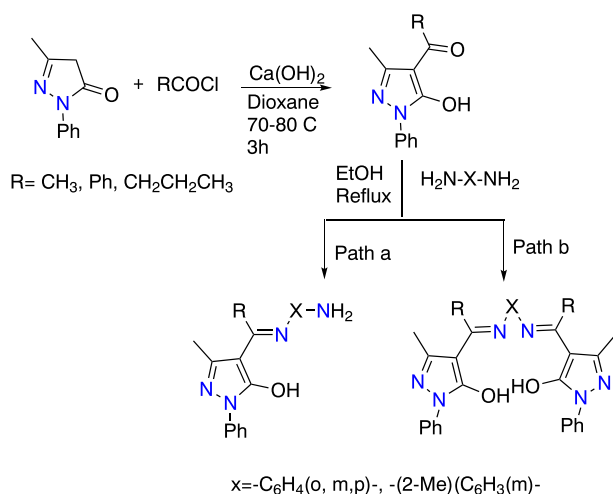

Figure 15. Synthetic scheme of Schiff bases from 4-acyl-5-pyrazolones with aromatic diamines.

activity against *Phytophthora infestanse* and *Aspergillus niger*, and ferric-reducing antioxidant power.[70]

Potentially pentadentate ONSNO donor Schiff bases were prepared by the condensation of thiocarbodihydrazide with 3,5-dibromosalicylaldehyde (H₃L1), 3-bromo-5-chlorosalicylaldehyde (H₃L2) and 3,5-dichlorosalicylaldehyde (H₃L3). The reactions between bis(acetylacetonato)dioxomolybdenum(VI) and Schiff bases in the presence of donor solvents yielded neutral *cis*-dioxomolybdenum(VI) complexes with the general formula [MoO₂HL(D)] (HL = tridentate ONS donor Schiff base ligand (HL1, HL2, HL3) and D = methanol, ethanol, dimethylsulfoxide, dimethylformamide, pyridine). All the compounds were characterized using elemental analysis and UV, IR and ¹H NMR spectroscopies. The synthesized compounds were screened for their antioxidant capacity using the cupric reducing antioxidant capacity (CUPRAC) method. *In situ* spectroelectrochemical studies were employed to determine the spectra of electrogenerated species of the complexes and to assign the redox processes. The fluorescence properties of the bisthiocarbohydrazone ligands and their

dioxomolybdenum(VI) complexes in dimethylsulfoxide solutions were investigated.[71]

Five kinds of Schiff bases of chitosan and carboxymethyl chitosan (CMCTS) have been prepared according to a previous method and the antioxidant activity was studied using an established system, such as superoxide and hydroxyl radical scavenging. Obvious differences between the Schiff bases of chitosan and CMCTS were observed, which might be related to contents of the active hydroxyl and amino groups in the molecular chains.[72]

A study described the synthesis, crystal structure and antioxidant activity of managanese(III) complexes with Schiff base ligands obtained from condensation of pyridoxal with alkyl diamines: [Mn(pyr₂en)(H₂O)₂]Cl·4H₂O, [Mn(pyr₂en)(H₂O)(CH₃OH)]Cl, [Mn(pyr₂pn)(H₂O)₂]ClO₄ and [Mn₂(pyr₂bn)₃]·4H₂O, where H₂pyr₂en = 1,2-bis(pyridoxylidenamino)ethane, H₂pyr2pn = 1,3-bis(pyridoxylidenamino)propane and H₂pyr₂bn = 1,4-bis(pyridoxylidenamino)butane. The four complexes catalyze the dismutation of superoxide efficiently with IC₅₀ values in the range 1.22–2.15 μM, evaluated through the nitro blue tetrazolium photoreduction inhibition superoxide dismutase assay, in aqueous solution of pH = 7.8. The length of the alkyl spacer in the diamine fragment plays a key role in the antioxidant activity of these complexes, with [Mn(pyr₂pn)(H₂O)₂]ClO₄ showing the lowest IC₅₀ value.[73]

A new imidazole-based Schiff base, 2-((1*H*-imidazol-4-yl)methyleneamino)benzyl alcohol (HL), and corresponding analogous bis(2-((1*H*-imidazol-4-yl)methyleneimino)benzyl alcohol) metal(II) perchlorates (M: Co. (**1**), Ni (**2**), Cu (**3**)) have been prepared and characterized using elemental analyses, ESI-MS, IR, UV–visible spectroscopies and conductivity measurements. X-ray single-crystal structures of **1** and **2** have been also determined. Radical scavenging activities of the complexes have been evaluated using DPPH•, DMPD•⁺ and ABTS•⁺ assays. SC₅₀ values (μg ml⁻¹) of the complexes and standards on DPPH•, DMPD•⁺ and ABTS•⁺ follow the sequences BHA (9.06 ± 0.33) > CMPD3 (15.62 ± 0.52) > CMPD2 (17.43 ± 0.29) > Rutin (21.65 ± 0.60) > CMPD1 (25.67 ± 0.51) > Trolox (28.57 ± 0.37); Rutin > BHA > CMPD3 > CMPD2 > Trolox > CMPD1; and Trolox > BHA > CMPD3 > CMPD2 > Rutin > CMPD1, respectively.[74]

Pramanik *et al.* have reported the synthesis and characterization of six mixed ligand complexes, namely [Co(acac)L¹], [Fe(acac)L¹], [Co(acac)L²], [Fe(acac)L²], [Co(acac)L³] and [Fe(acac)L³] (H₂L¹ = *N,N*'-bis(salicylidene)-*trans*-1,2-diaminocyclohexane, H₂L² = *N,N*'-bis(salicaylidene)-1,2-phenylenediamine, H₂L³ = *N,N*'-bis(salicylidene)-4-methyl-1,2-phenylenediamine), using elemental analysis, IR spectra, UV–visible spectra, mass spectra, magnetic susceptibility measurements and ¹H NMR and ¹³C NMR spectra and thermogravimetric analysis. Antioxidant activity of the complexes was studied using the DPPH scavenging method.[75]

The amino acid [1-(aminomethyl)cyclohexyl]acetic acid was reacted with 2-hydroxynaphthaldehyde to produce the Schiff base ligand [1-({[(*Z*)-(2-hydroxynaphthalen-1-yl)methylidene]amino}methyl)cyclohexyl]acetic acid (H-HMAC) which was fully characterrized spectroscopically and by single-crystal diffraction. It was reacted with metal ions to produce compounds with composition [M(HMAC)₂] (M = Co.(II), Ni(II), Cu(II) and Zn(II)), which were characterized spectroscopically, and which were found to have distorted tetragonal geometries assigned based on spectroscopic and B3LYP theoretical studies. The coordination compounds were also screened for their free radical scavenging properties using DPPH free radicals and xanthine oxidase inhibitory activities.[76]

Because of their potential applicability as selective receptors in optical sensors, two novel azo Schiff base derivatives **I** and **II** were

synthesized and characterized with FT-IR, ^{1}H NMR and elemental analysis techniques. The optical response of azo groups of **I** and **II** towards Ni(II), Co.(II), Cu(II), Pb(II), Hg(II), Zn(II) and Cd(II) metal ions was studied in dimethylsulfoxide using UV–visible spectroscopy. Receptor **I** was highly specific for copper ions in dimethylsulfoxide solution. Finally, the study of antioxidant properties of **I** and **II** with the DPPH method revealed high and significant activities.[77]

The Schiff base 3-((5-chloro-2-phenyl-1*H*-indol-3-ylimino)methyl) quinoline-2-(1*H*)thione and its Cu(II), Co.(II), Ni(II), Zn(II) and Fe(III) complexes have been synthesized and characterized using elemental analysis, UV–visible, IR, ^{1}H NMR, ^{13}C NMR and mass spectra, molar conductance, magnetic susceptibility, EPR and thermogravimetric analysis. Antioxidant activity was investigated using DPPH, which was compared with that of standard drugs vitamin C and vitamin E, and DNA cleavage activity studied using calf thymus DNA.[78]

Baykara *et al.* have reported the synthesis a new Schiff base ligand by reaction of salicylaldehyde with 1,6-bis(4-chloro-2-aminophenoxy)hexane. Then the Schiff base complexes were synthesized using metal salts and the Schiff base. Antimicrobial and antioxidant studies, cyclic voltammetry of the complexes, and theoretical ^{1}H NMR and HOMO–LUMO energy calculations of the new bifunctional ligand were done.[79]

A novel series of metal complexes of the types [ML$_2$(H$_2$O)$_2$]Cl$_2$ and [ML$_2$]Cl$_2$ (M = Mn(II), **1**; Co.(II), **2**; Ni(II), **3**; Cu(II), **4**; and Zn(II), **5**) were synthesized by the interaction of ligand **L**, (*E*)-N-(furan-2-ylmethylene)quinolin-8-amine, derived from the condensation of 2-furaldehyde and 8-aminoquinoline. The synthesized ligand and its metal complexes were characterized on the basis of results obtained from elemental analysis, ESI-MS, XRD, SEM, TGA/DTA, magnetic moment, and FT-IR, UV–visible, ^{1}H NMR and ^{13}C NMR spectroscopic studies. EPR parameters were recorded in the case of complex **4**. The comparative *in vitro* antimicrobial activities against various pathogens with reference to known antibiotics and antioxidant activities against standard control at variable concentrations revealed that the metal complexes show enhanced antimicrobial and free radical scavenging activities in general as compared to free ligand. The complexes **1** and **5** showed best antioxidant activity among all the metal complexes.[80]

Abdel Aziz and Elbadawy have reported the synthesis four new air-stable low-spin Ru(III) complexes of the type [Ru(L$^{1-4}$)(H$_2$O)$_2$]Cl, with dianion of the tetradentate Schiff base ligands *N,N'*-bis(salicylaldehyde)-4,5-dimethyl-1,2-phenylendiamine (L^{1}H$_2$), *N,N'*-bis(salicylaldehyde)-4,5-dichloro-1,2-diphenylendiamine (L^{2}H$_2$), *N, N'*-bis(*o*-vanilline)-4,5-dimethyl-1,2-phenylendiamine (L^{3}H$_2$) and *N, N'*-bis(*o*-vanillin)-4,5-dichloro-1,2-phenylendiamine (L^{4}H$_2$). The complexes have been fully characterized using elemental analysis, IR spectroscopy, electronic spectroscopy, magnetic susceptibility and EPR spectroscopy. Elemental analyses and spectroscopic data showed that the stoichiometries of the complexes were 1:1 with an octahedral geometry for all the complexes. The antioxidant activity of the Ru(III) complexes against superoxide and hydroxyl radicals was evaluated using spectrophotometric methods *in vitro*. The experiments on antioxidant activity showed that the complexes possess potent antioxidant activity.[81]

The nickel(II), iron(III) and oxovanadium(IV) complexes (Fig. 16) of 3-hydroxysalicylidene-*S*-methylthiosemicarbazone were obtained from 3-hydroxysalicylaldehyde-*S*-methylthiosemicarbazone with R$_1$-substituted salicylaldehyde (R$_1$: H, 3-OH) in the presence of Ni (II), Fe(III) and VO(IV) as template ions. The ligand and its complexes were characterized using elemental analysis and electronic, UV–visible, ^{1}H NMR, EPR and IR spectroscopy. The free ligand and its metal complexes have been tested for *in vitro* antioxidant capacity by reduction of copper(II) neocuproine using the CUPRAC method. The ligand exhibited more potent *in vitro* antioxidant capacity than its complexes. The obtained trolox equivalent antioxidant capacity (TEAC) value of the iron(III) complex (TEAC$_{CUPRAC}$ = 3.27) was higher than those of the other complexes. Furthermore, the antioxidant activities of the free ligand and its complexes were determined by *in vitro* methods measuring the scavenging activity of reactive oxygen species including hydroxyl radical ($^\bullet$OH), superoxide anion radical (O$_2^{\bullet-}$) and hydrogen peroxide (H$_2$O$_2$), showing that especially the VO(IV) and Fe(III) complexes had significant scavenging activity for reactive oxygen species.[82]

A systematic and comparative study has been reported to define a correlation between the structure and function of a series of simple, biologically active small inorganic Schiff base copper complexes for the occurrence of a charge transfer phenomenon in calf thymus DNA using transient absorption spectroscopy corroborated with the magnetic field effect. Four copper(II) Schiff base complexes with differently substituted heterocyclic ligands with antioxidant activity were investigated.[83–85]

Conclusions

Schiff bases and their complexes have been widely explored for industrial applications. However, the antioxidant activities of this class of compounds deserve further investigation. This becomes clear when plant pathogens are considered. Although the research on this subject is incipient, the number of reports disclosing the effects of Schiff bases on pathogens of clinical interest has been increasing. Schiff base compounds and their complexes have been shown to be promising for design of more efficient chelates. Advances in this field will require analyses of the structure–activity relationships of the Schiff bases as well as the mechanism of action of these compounds.

The synthesis of new macrocyclic Schiff bases and their use as chelates will pave the way for applications of such antioxidants.

We have reviewed Schiff bases, which have an unusual capacity for the formation of complexes with metal ions, demonstrating that these Schiff bases and their complexes have antioxidant activity. Complexes of Schiff bases are excellent selective and efficient oxygen carriers.

[NiCl$_3$, FeCl$_3$, VOSO$_4$

Figure 16. Complexes of 3-hydroxysalicylidene-*S*-methylthiosemicarbazone.

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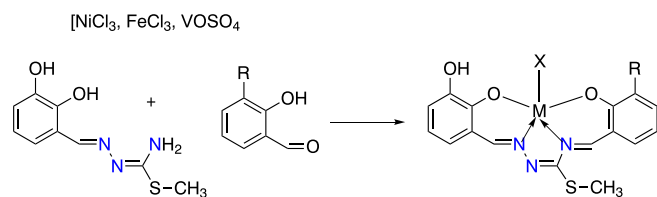[7] M. Calligaris, G. Nardin, L. Randaccio, *J. Chem. Soc.* **1973**, 419–24. *Dalton Trans*.

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