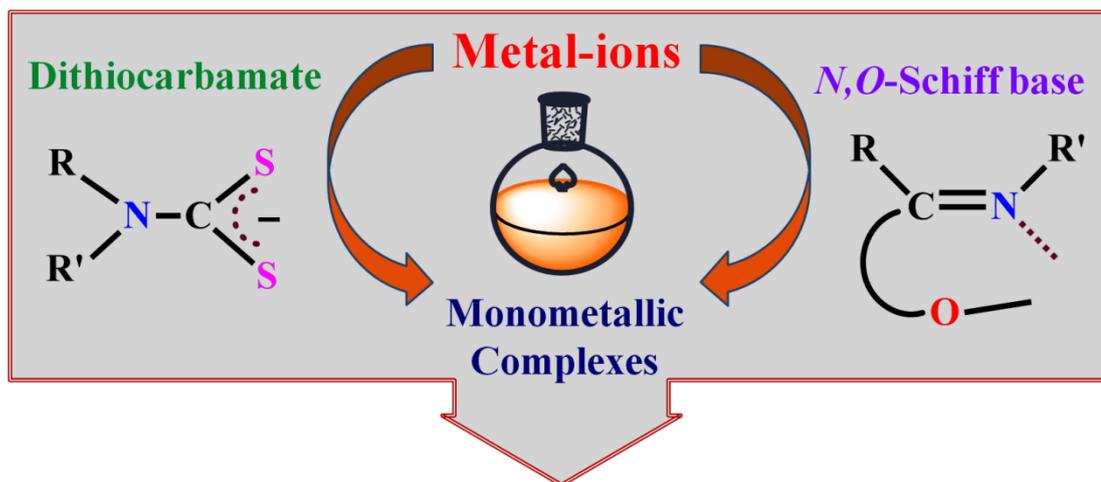


Introduction: Metal complexes bearing *N*, *O* or *S* binding ligands; Synthesis, characterization and properties

Abstract



A systematic exhaustive literature survey on 1,1-dithiocarbamate and *N, O*-Schiff base ligand systems and their versatile coordination chemistry with transition and non-transition metals in a variety of stoichiometries and properties has been comprised in this chapter. The exploitation of unique stereoelectronic properties of metal ions and dithiocarbamate/ *N,O*-Schiff base ligands in metal directed self-assembly process leads to discrete structures with fascinating physico-chemical properties and broad spectrum of applicability which are indeed highlighted in this section. The main objectives of the present work are also included at the end of this chapter.

1.1. Self-assembly

Self-assembly has greatly extended the scope of the chemistry intending the synthesis of diverse products with higher order and functions, extending chemical bonds to non-covalent interactions [1]. A marvelous number of molecular self-assemblies are present in nature, especially biological systems [2] which are so crucial for the function of a cell. Self-assembly forms the basis for many natural processes, including protein folding, DNA transcribing and hybridization, and the formation of cell membranes. This process of self-assembly in nature is governed by inter- and intra-molecular forces that drive the molecules into a stable, low energy state. These forces primarily include hydrogen bonding, electrostatic interactions, hydrophobic

interactions, and Van der Waals forces. For example, self-assembly of lipid forms the cellular membrane, whereas, that of proteins form quaternary structures responsible for enzyme activity. A number of biochemical processes and double helical DNA are formed through the well defined hydrogen bonding of the individual strands. These structures are better described as "self-organised" structures. Some examples of "self-organised" structures are shown in (Fig. 1).

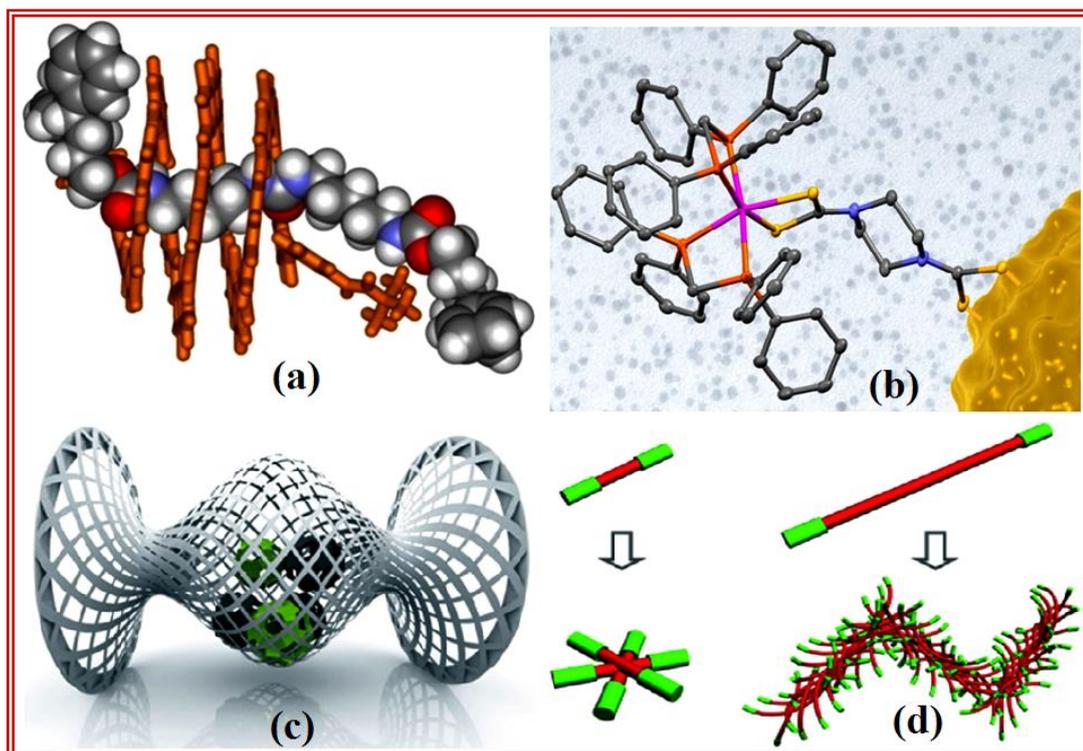


Fig. 1. Some *static* (a, b) and *dynamic* (c, d) self-assembly

The beauty and complexity of self-assembly processes occurring in the nature have inspired synthetic chemists to impersonate such structures at a molecular level. The metal-directed self-assembly has emerged as one of the most efficient approaches towards the design and synthesis of diversified supramolecular architectures like one-, two-, and three-dimensional infinite organic /inorganic hybrid frameworks such as filament, rod, ladder, rack, cylinder, brick wall, box, square grid, honeycomb, parquet, helical, diamondoid, etc. This means *coordination chemistry* has been successfully used to construct discrete structures with fascinating physicochemical properties [3] (Fig. 2 and Fig. 3)

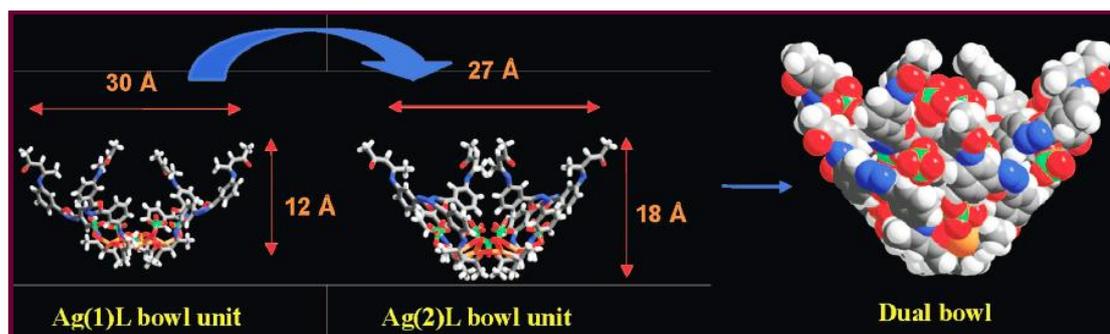


Fig. 2. Coordination chemistry used in construction of diverse molecular architectures.

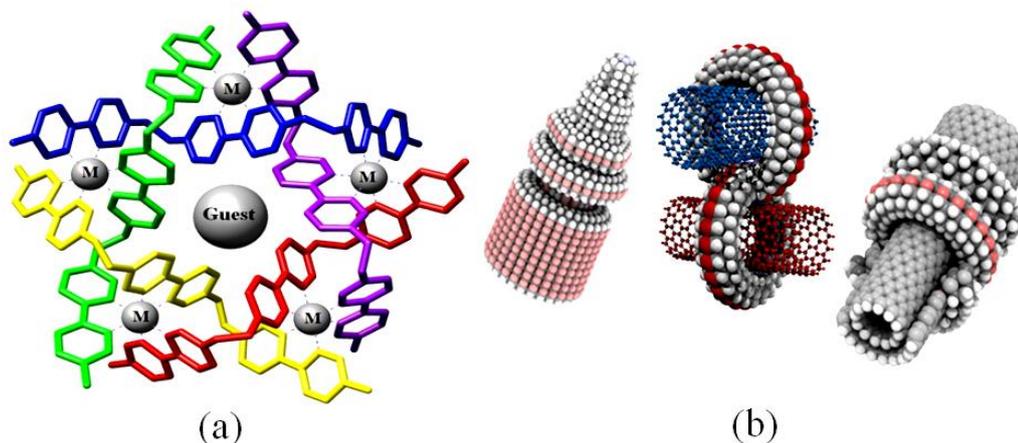


Fig. 3. Supramolecular self-assembly in different fashions shown in (a) and (b)

Thus coordination-driven self-assembly has been emerging as an active research area of chemistry in recent years [4]. It offers an additional scope for fine tuning of the electronic and structural properties of such structures through imaginative modification in ligand system and judicious choice of metal ions [5].

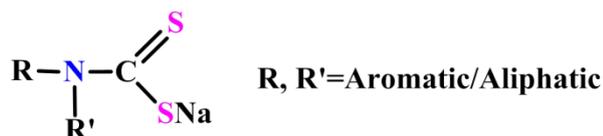
Metal-directed self-assembly presents several advantages over conventional covalent syntheses [6,7]. This involves only a few basic subunits which can be assembled in just one or a few steps. The building process can be readily controlled because it employs reversible bonds. This allows for error healing and structural changes according to environment. Moreover, metal ions provide a range of coordination geometries, binding strengths/ labilities and photochemical/ redox behaviors which can be utilized in self-assembly.

1.2. 1,1-dithio ligands

The coordination chemistry of 1,1-dithio ligands, especially dithiocarbamate ligand has been extensively documented, [8] but its application in the field of self-assembly has only recently been reported [9]. This is surprising, given the qualities of the dithiocarbamate motif. For example, dialkyldithiocarbamates form

complexes with a wide variety of transition metals and it offers plenty of scope for introducing different metals into the molecular framework. Secondly, the optical and electrochemical properties of dithiocarbamate complexes can be used to construct sensors for guest molecules [9a,b] Thirdly, dithiocarbamates are known to stabilize unusually high oxidation states of metal ions [10]. This suggests that complex geometry could be manipulated by adjusting the metal oxidation state. Thus, dithiocarbamate (DTC) with broad pharmacological properties has been a subject of major research area.. Coordinating these ligands with transition metals may produce compounds with enhanced biological properties and this can be a basis for novel compounds. Prof. Paul D. Beer University of Oxford, UK is the foremost person in the field of dithiocarbamate chemistry.

Dithiocarbamates (DTCs) belongs to the class of compounds known as the 1,1-dithiolates [11-13]. This is considered as a analog of carbamate in which both oxygen atoms are replaced by sulfur atoms or and semi-amides of dithiocarbonic acid [14].



Further, this group of compounds also includes (Chart 1) the dithiophosphates, dithiophosphinates, dithiocarbimates and other related compounds.

Composition	Structure	Name
R_2NCS_2^-		Dithiocarbamate
OCS_2^{2-}		Dithiocarbonate
CS_3^{2-}		Trithiocarbonate
RCS_2^-		Dithiocarboxylate
ROCS_2^-		Xanthate
$(\text{RO})_2\text{PS}_2^-$		Dithiophosphate

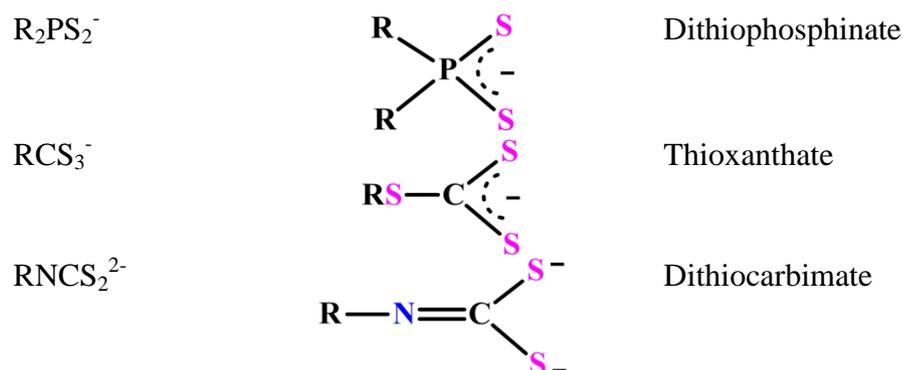
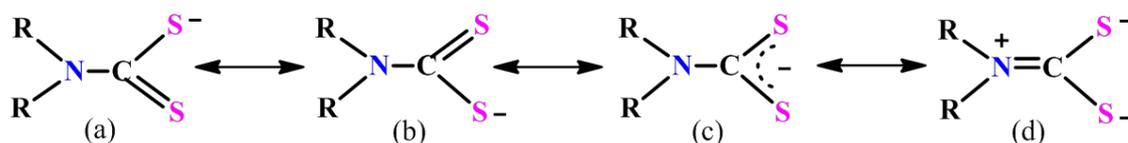


Chart 1: Group of compounds comprises 1,1-dithio ligands

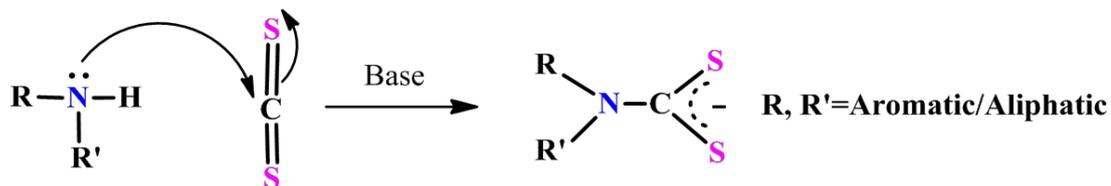
The structure of these monoanionic 1,1-dithio ligands [15] can be described by four resonance structures (Scheme 1). The contribution of structure (d) is significant in the description of the overall structure of dithiocarbamates based on the IR band in the region $1450\text{-}1550\text{cm}^{-1}$ assigned to the $\nu(\text{C}=\text{N})$ bonds. [16-17]



Scheme 1: Canonical forms of the dithiocarbamate ligand

1.2.1. Preparation of the dithiocarbamate ligand

The dithiocarbamate ligand (dtc) was first identified during the early days of organosulfur chemistry, by the nucleophilic attack of primary or secondary amines with carbon disulfide in basic solution. Free dithiocarbamic acids (R_2NCS_2H) are highly unstable and the ligands are therefore usually isolated as their alkali metal salts. One important feature of dithiocarbamate ligands is their ability to stabilise high formal oxidation states, this result the delocalisation that the ligand provides the consequential high electron density the sulfur donors present.



Scheme 2: Nucleophilic addition of amine with carbon disulfide (CS_2)

Dithiocarbamate salts are generally prepared from nucleophilic addition reactions of N-nucleophiles with carbon disulfide (CS_2) as given in Scheme 2. Reactions are generally carried out in triethyl amine, acetonitrile, water, methanol or ethanol in presence of base such as sodium hydroxide (NaOH) or potassium

hydroxide (KOH). Strong bases such as sodium hydride (NaH) also can be used to prepare dithiocarbamate salts of aromatic amines react less readily with carbon disulfide. These reactions are best carried out at lower temperatures and are rapid, good yielding and without side products. However at high temperature sometimes gives undesirable products (Scheme 3).



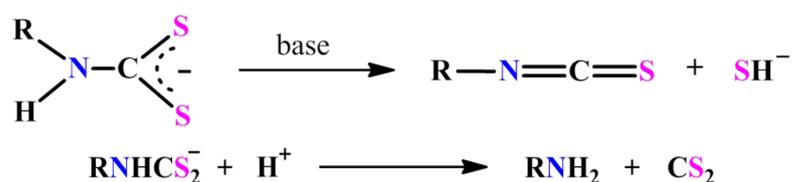
Where M = K or Na

Scheme 3: General method for the preparation of dithiocarbamate ligands

The synthesis of S-alkyl substituted dithiocarbamate has been reported with excellent yields and complete regiospecificity by employing a highly efficient, one-pot and three component reactions of amines and carbon disulfide with alkyl vinyl ethers via Markovnikov addition reaction in water under a mild and green method. [18]. Moreover, α , β -unsaturated compounds are also known to react efficiently in one-pot with amines and carbon disulfide in water under a mild and green procedure to yield dithiocarbamates [19].

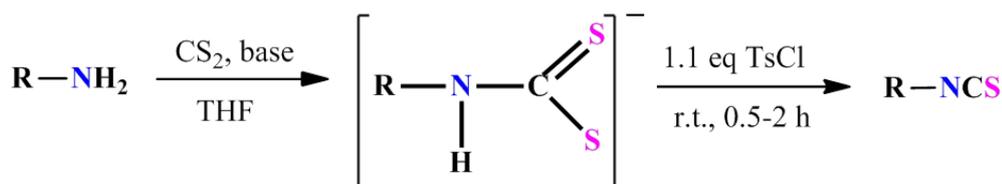
1.2.2. Properties of dithiocarbamates

The potassium and sodium salts are soluble in water and are relatively insoluble in common organic solvents. Where necessary, isolation is carried out in methanol, ethanol etc. Triethyl ammonium salt of dithiocarbamate can also be prepared and isolated. DTCs are stable under basic and neutral condition but those from primary amines readily decompose under basic condition to form isothiocyanates (Scheme 4). However most of the DTCs decompose under acidic conditions to an amine and carbon disulfide (Scheme 4). Dithiocarbamate ligands prepared from primary amines tend to be less stable, as they are susceptible to elimination reactions yielding isothiocyanates.



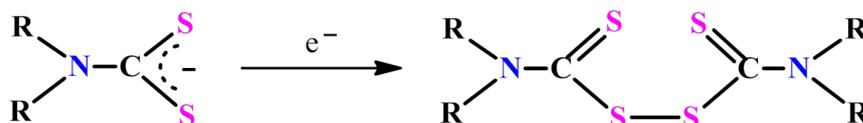
Scheme 4: Decomposition of dithiocarbamates

Isothiocyanates from tosyl chloride mediated decomposition of *in situ* generated dithiocarbamic acid salts, according to the following scheme 5 has also been reported [20].



Scheme 5: Decomposition of dithiocarbamates

Dithiocarbamates undergo oxidation to form thiuram disulfide quite easily (Scheme 6). This reaction is high yielding and in presence of iodine, hydrogen peroxide, bromine and potassium ferricyanide oxidation takes place.



Scheme 6: Oxidation of dithiocarbamates

The most characteristic feature of the dithiocarbamate ligands is their ability to stabilize metal ions with unusually high or low oxidation states. This property can be explained in terms of the two resonance forms, the dithiocarbamate and the thioureide form. In the thioureide form, the nitrogen atom carries a positive charge and each sulfur atom carries negative charge (Fig. 4). This allows DTC ligands to accommodate metal ions with high oxidation states. In addition, the dithiocarbamate ligand has the ability to delocalize the positive charge from the metal to the periphery of the complex.

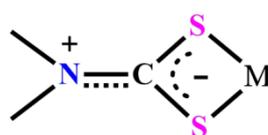


Fig. 4. Thioureide form of coordinated dithiocarbamate moiety.

1.2.3. Binding Modes

Dithiocarbamates are versatile ligands known to coordinate to metals in a variety of forms and their ligation forms are presented below (Fig. 5). One to four metal atoms can be accommodated by the ligand in different ways. The DTC moiety can form complexes where both sulphur atoms are coordinated to the same metal atom forming a four coordinated ring chelate.

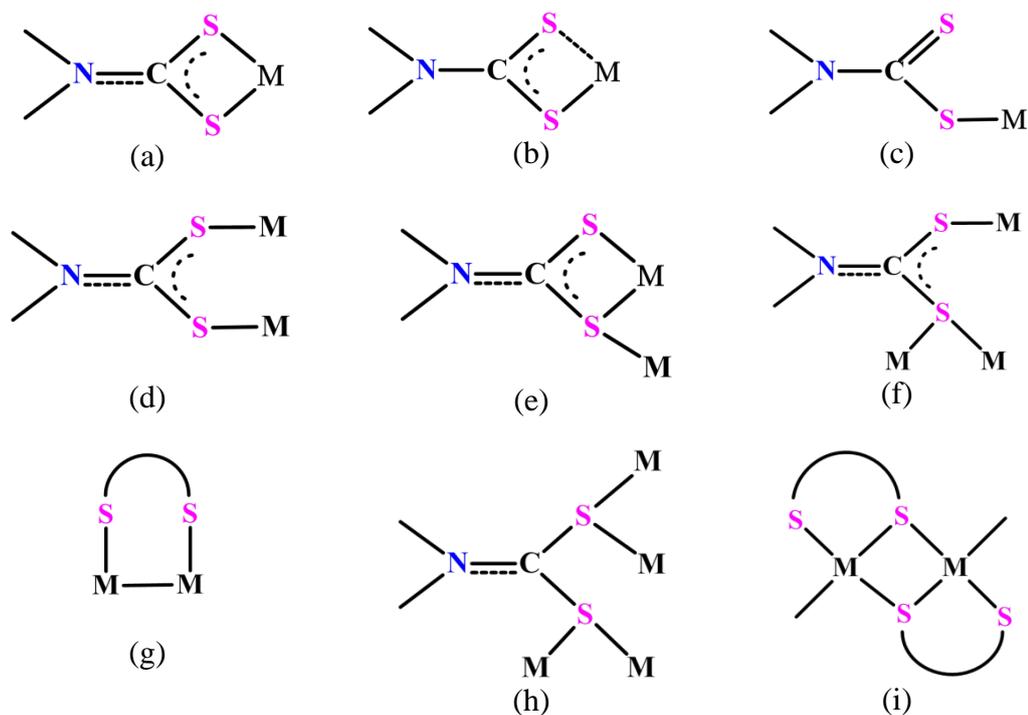


Fig. 5. Dithiocarbamate coordination modes shown as a-e.

Monodentate and bidentate coordination modes exhibited by some dithiocarbamate ligands are exemplified below. Monodentate binding mode of dithiocarbamate ligands is known to be formed with the metal ions where there is no possibility for the bidentate coordination (Fig. 6).

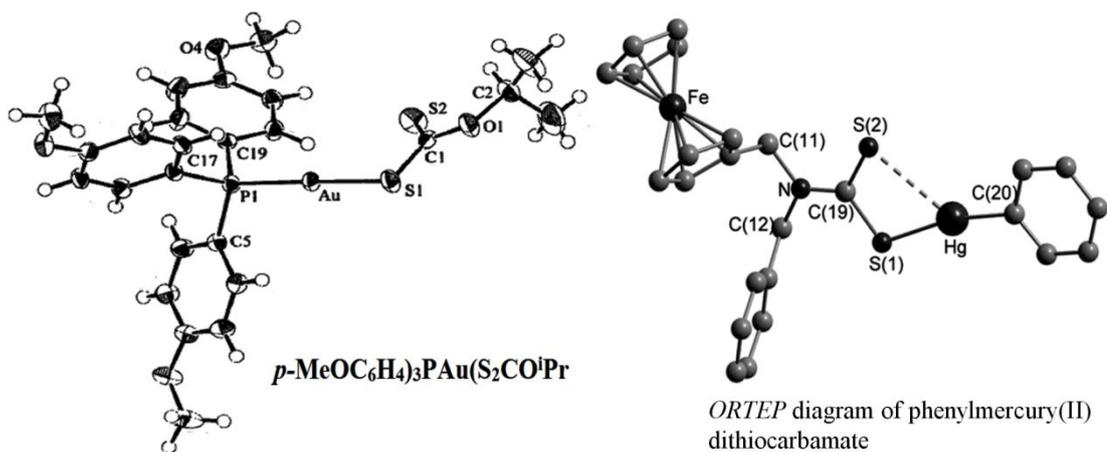


Fig. 6. ORTEP diagrams of monodentate binding mode of dithiocarbamate ligand

1.2.4. Structural features of dithiocarbamate complexes

In the absence of other coordinating ligands, dithiocarbamate complexes can assume four structural geometries: square planar/tetrahedral coordination geometry, octahedral coordination geometry, four and five coordinate dimer (Fig. 7). In fact, as per the stereoelectronic requirements, dithiocarbamate ligands can adopt mono or

bidentate, however, bidentate binding could be isobidentate or anisobidentate binding. Some reported examples of dithiocarbamate metal complexes illustrating diverse binding modes [21-22] in different geometries are summarized (Fig. 8).

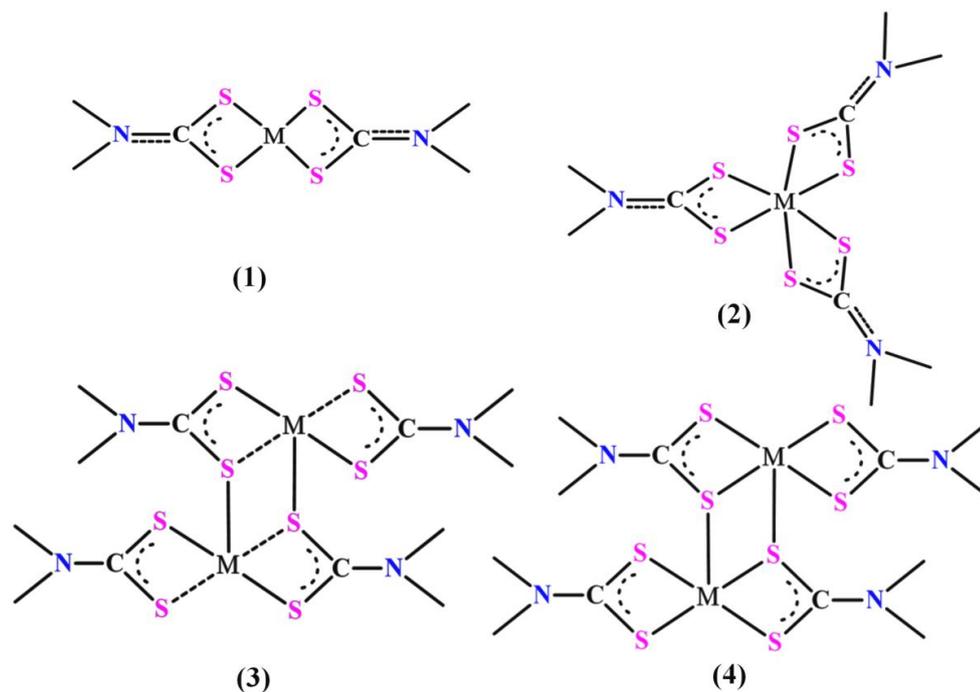
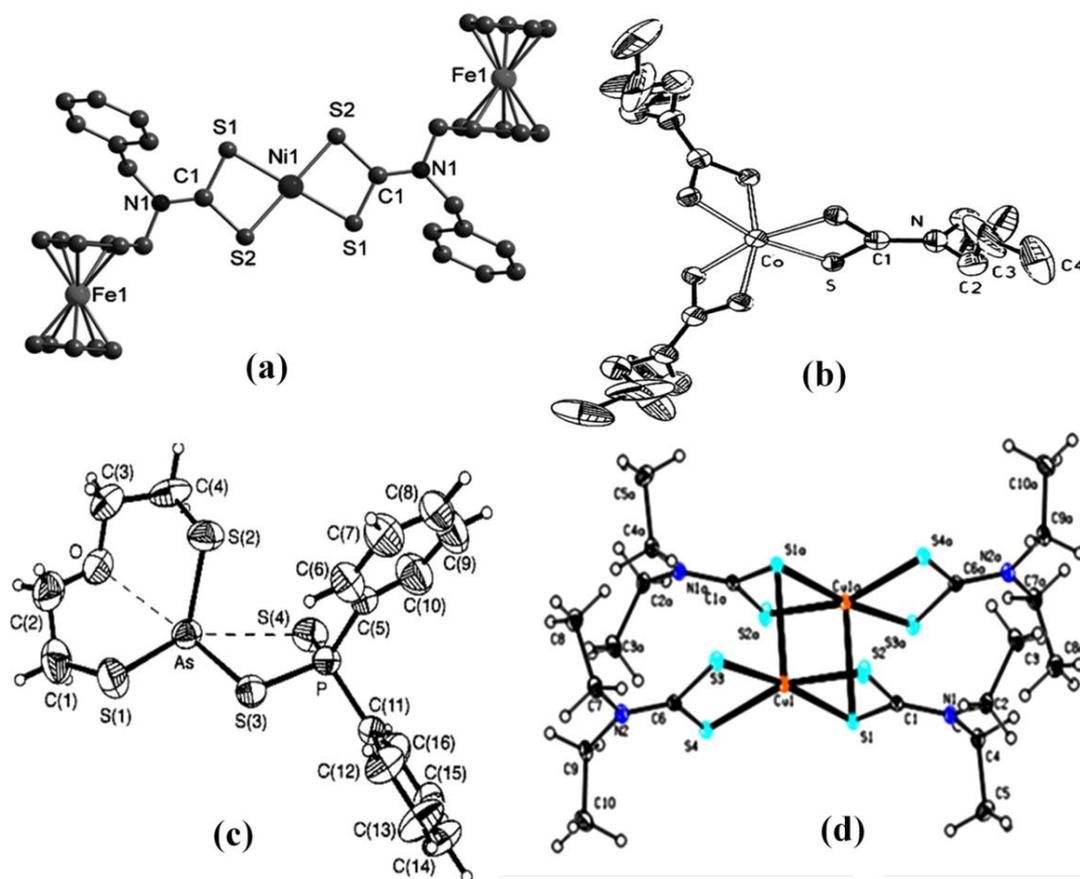


Fig. 7. Structural arrangements of dithiocarbamate complexes



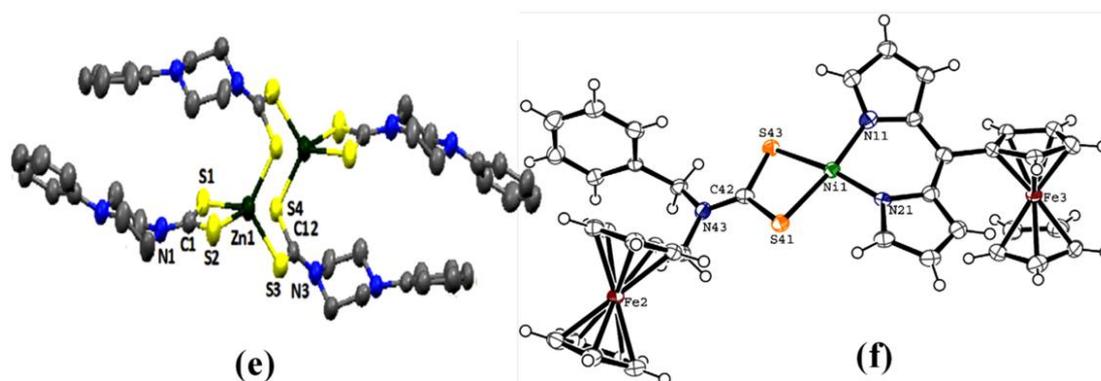


Fig. 8. (a) Ferrocene based Ni(II) dithiocarbamate complex (b) Co($n\text{Pr}_2\text{dtc}$) complex (c) As based (PS_2) complex (d) copper(II) bis(diethyldithiocarbamate) dimer (e) Piperazine Zn(II) dithiocarbamate complex (f) Ferrocene containing Ni(II) complex of mixed ligand.

1.2.5. Potential application of dithiocarbamates and their complexes

Dithiocarbamates (DTCs) are a group of small organic molecules with a strong chelating ability toward inorganic species have widely been used in the agricultural industry [23] for more than 80 years. In recent years their applications have not only become perceptible as pesticides and fungicides, [24, 25] but also widely used as vulcanization accelerators in the rubber industry. Moreover, DTCs are also of biological importance due to their antibacterial, antituberculosis and antifungal properties (Fig. 9). Their anti-oxidant properties [26] make them even more valuable compounds, among them are disodium ethylenebisdithiocarbamate (commercially known as Nabam), its zinc and manganese complexes (Zineb and Maneb) and the zinc and iron complexes of dimethyldithiocarbamic acid (Ziram and Ferbam) are shown to be quite promising. Thiram [27] is a fungicide, ectoparasiticide, and animal repellent. It is used to prevent fungal diseases in seed and crops. It is also used as an animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents and deer. Ziram or Zinc Dimethyldithiocarbamate is a carbamate fungicide [24]. It is used in agriculture either as a spray applied to the leaves to control fungal infections. It may also be used for seed treatment to improve the chances of germination. Mancozeb [29] is a dithiocarbamate non-systemic agricultural fungicide with multi-site, protective action on contact. It is a combination of two other dithiocarbamates: maneb and zineb. The insolubility of metal salts (with the exception of sodium and other alkali and alkaline earth metals) and the capacity of the DTCs to form stable metal-complexes are mainly responsible for the extensive use of this class of compounds as superior ligands.

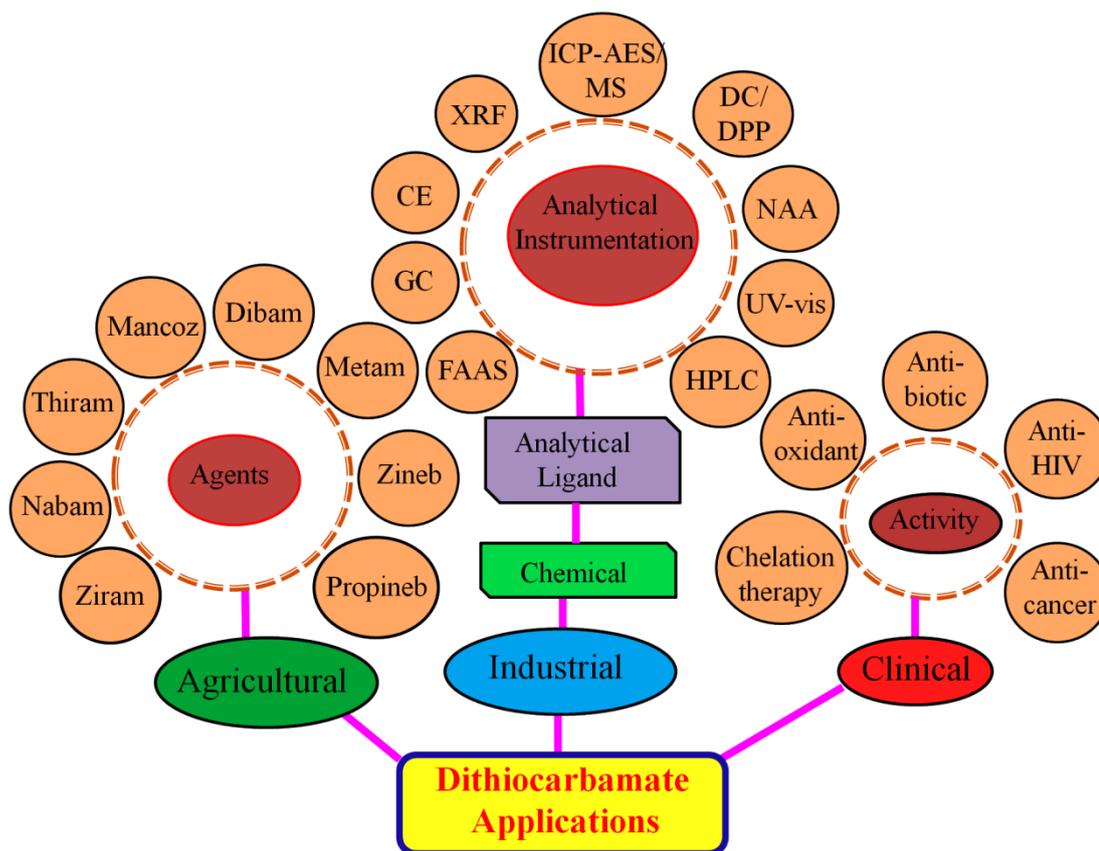


Fig. 9. Flow chart of some dithiocarbamates in various field

Therefore, DTCs exhibit strong binding properties with a number of transition metal ions resulting in stable coloured complexes. The quantitative determination is often carried out by spectroscopy, although other techniques such as gravimetry, fluorimetry, titrimetry, neutron activation analysis (NAA), turbidimetry, voltammetry and chromatography are less widely used [30]. Melanoma is the most serious type of skin cancer and since it is resistant to chemo-therapy, it is also one of the most deadliest types of cancers. Melanocytes are skin cells that make melanin, which gives skin its color (Fig. 10). Dithiocarbamates (DTCs) are potential melanoma drugs. Mainly the metal complexes of pDTC (pyrrolidine dithiocarbamate) have been studied; they are commonly used as antioxidants in cell toxicity studies.

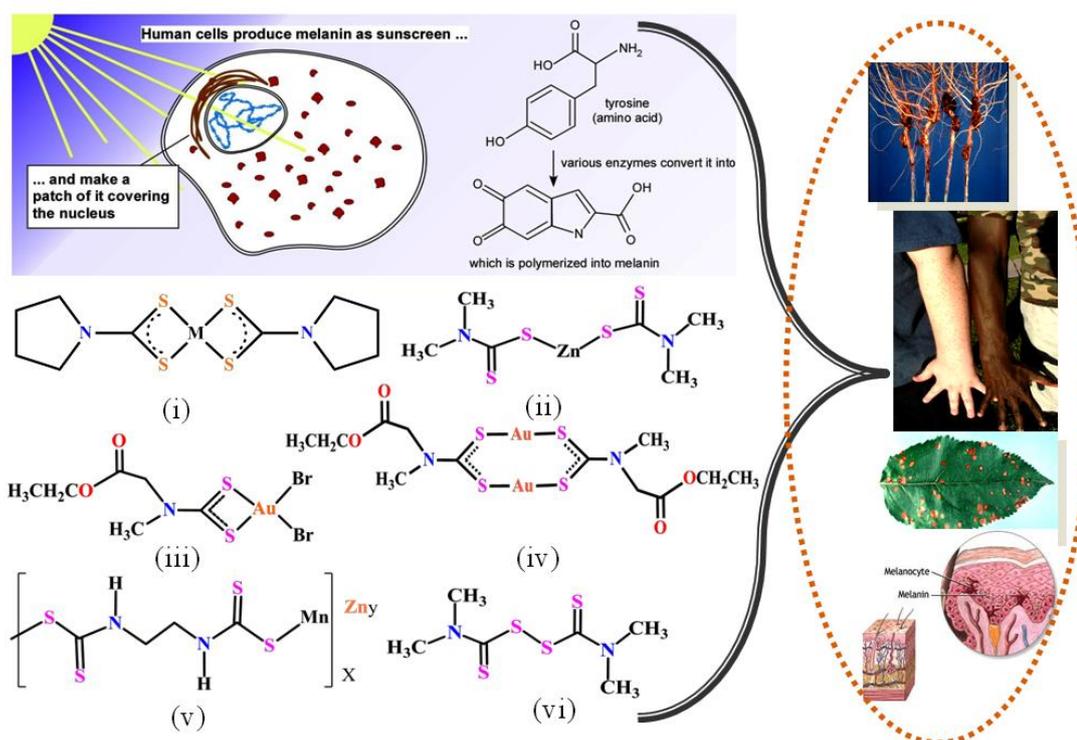


Fig. 10. (i) Metal complex of pyroldine dithiocarbamates ($M = \text{Zn, Cu, Ni}$); (ii) Ziram [N,N -dimethyl dithiocarbamate zinc salt]; (iii) $\text{Au}(\text{ESDT})_2$ $\text{ESDT} =$ Ethylsarcosine dithiocarbamate; (iv) $[\text{AuBr}_2(\text{ESDT})]$ (v) Mancozeb [manganese ethylenebis(dithiocarbamate) (polymeric complex with Zn salt)]; (vi) Thiram [tetramethyl thiuran disulfide].

1.2.6. Ferrocene functionalized transition metal dithiocarbamate complexes

Organometallic chemistry primarily deals with chemical compounds containing at least one bond between a carbon atom of an organic compound and a metal. [31-32] Organometallic chemistry is as combined aspects of inorganic chemistry and organic chemistry.

In 1951, a new compound containing iron and two cyclopentadienide ligands was reported. [33-34] Although even the first reports noted its high and unexpected stability, the correct structure was only soon afterward suggested independently. Ferrocene or $\text{di}(\eta^5\text{-cyclopentadienyl})\text{iron(II)}$ was accidentally discovered by Peter L. Pauson and his graduate student Tom Kealy in 1951 when they attempted the reductive coupling of the Grignard reagent cyclopentadienyl magnesium bromide in the presence of ferric chloride. The unique sandwich structure of ferrocene was first predicted by IR and NMR spectroscopies and later confirmed by X-ray crystallography in 1954. It is well established that the properties of new inorganic materials are highly influenced by the chemical nature of the attached groups as well

as by the electronic nature of the metal ions used. In the recent past, ferrocenyl group has been used as a cornerstone in making a number of diverse structural motifs that exhibit fascinating physicochemical properties. Owing to the resemblance of its reactivity to that of benzene, the name ferrocene was coined for the new compound by Woodward [35]. The term “sandwich compound” for this compound is universally accepted today for a much wider class of compounds. Ferrocene is an organometallic compounds with the formula $\text{Fe}(\text{C}_5\text{H}_5)_2$. It is the prototypical metallocene, a type of organometallic chemical compound consisting of two rings bound on opposite sides of a central metal atom. Such organometallic compounds are also known as sandwich compounds. The rapid growth of organometallic chemistry is often attributed to the excitement arising from the discovery of ferrocene and its many analogues.

Medicinal chemists are also open to the inclusion of ferrocene into their drug design strategies because of the novelty introduced by its presence. Ferrocene is a stable, nontoxic compound and having good redox properties. Now research is going on to design new compounds which are active against a wide range of cancers and have lesser side effects. Ferrocenes are also known to exhibit a wide range of biological activity and also ferrocene has attracted special attention since it is a neutral chemically stable and non-toxic molecule. Many ferrocenyl compounds display interesting, cytotoxic, antitumor, antimalarial, anti-fungal and DNA cleaving activities [36]. On the other hand, significant changes in activity profiles had been recorded when ferrocene was introduced into established drugs like tamoxifen and chloroquine [37] and the antiparasite ferroquine derivatives [38]. A series of antibiotics containing ferrocene moiety such as ferrocenyl penicillin, ferrocenyl cephalosporine and ferrocenyl hybrid of penicillin and cephalosporine have been reported by Edward's research group [39].

Metal complexes with sulfur rich ligands are very interesting from the viewpoint of their electrical conductivity, molecular magnetism, electrochemical properties, biological processes and optoelectronic properties [40]. Ferrocene containing polydentate dithiocarbamate ligands[41-42], have emerged as one of the most active area of research in chemistry in recent years because of their versatile coordination chemistry and material properties [41e]. These type of complexes have also been used in light harvesting and as sensitizers in dye sensitized solar cells. Supramolecular structures of several organic molecules and their properties are clearly shown to be sustained *via* hydrogen bonds and $\pi\cdots\pi$ interactions [43].

Organomercury dithiocarbamate complexes have been found to be an extremely versatile group for supramolecular arrays and exhibited photoluminescence emission.

[44]

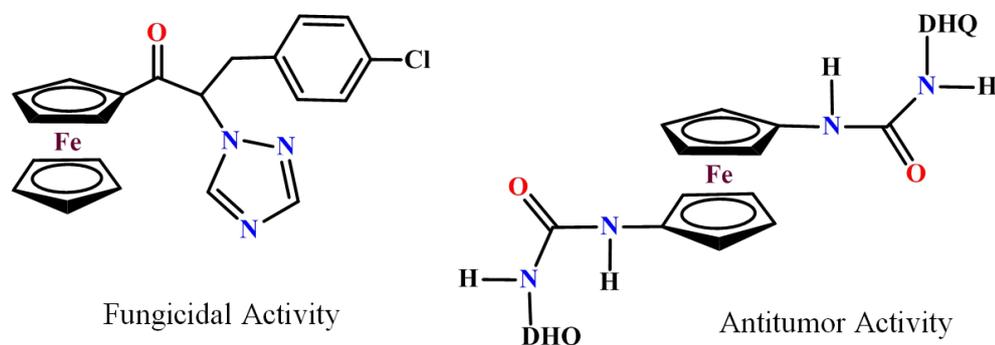


Fig. 11. Ferrocenyl derivatives as fungicidal and antitumor activity

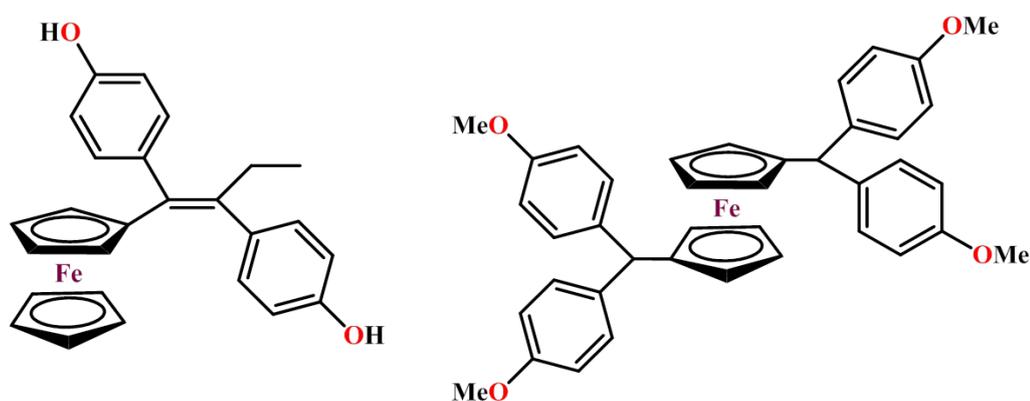


Fig. 12. Water soluble ferrocenyl derivatives as anti-cancer agents

Since the advent of ruthenium (II) diimine sensitizers, there has been remarkable advancement in both inorganic, nanostructures, organometallic and organic sensitizers [45]. Organomercury(II) dithiocarbamates with the ferrocenyl entity also have been documented and their electrochemical properties have been explored. Incorporation of thio functions on the ferrocene backbone in the form of a dithiocarbamate has resulted in the formation of heteropolymetallic compounds with structural diversity as well as interesting electrochemical and material properties. The possibility of switching the redox active state of the ferrocene periphery provides access to potential control of the reactivity at a metal center [46]. The design, synthesis and development of sensitizers to harness sunlight into electrical energy are very important in solar technology. With the other hand, the molecules bearing sulfur atom plays a vital role in biological processes and interacts efficiently with

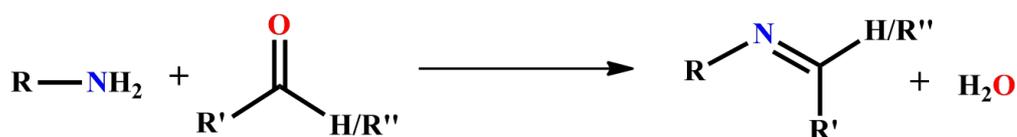
biomolecules [47]. Organic compounds bearing 1,1-dithio moieties exhibit valuable biological effects, including antibacterial, antifungal, antioxidant activity, [48] inhibition of cardiac hypertrophy, [49] etc.

Behaviour of the dithiocarbamate complexes of arsenic, antimony, bismuth, mercury, lead, tin and selenium in methanol with a hydride generator has been covered by L. Vuchkova and S. Arpadjan [50]. The crystal structures of a homologous family of alanine-based dithiocarbamates reveal that these chemical systems differ by the steric properties of the pendent alkyl groups (i.e., methyl, ethyl, isopropyl and benzyl) and the structural patterns influenced by intermolecular O–H...O, N–H...O and N–H...S interactions [51]. The literature contains some examples of cyanodithioimido carbonate complexes $[\text{AsPh}_4]_2[\text{Ni}(\text{C}_2\text{N}_2\text{S}_2)]$, [52] $[\text{Au}_2(\text{C}_2\text{N}_2\text{S}_2)_2]$, [53] including organotin compounds of the type $[\text{SnR}_2(\text{C}_2\text{N}_2\text{S}_2)]$, [54] a vanadium complex $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_2\text{N}_2\text{S}_2)]$, [55] an oxytechnetium(V) complex $[\text{TcO}(\text{C}_2\text{N}_2\text{S}_2)_2]$ [56] and a series of salts of the type $[\text{X}]_2[\text{M}(\text{S}_2\text{N}_2\text{C}_2)_2]$ ($\text{X} = (\text{Ph})_4\text{As}$, $(\text{Ph})_4\text{P}$ or $(^n\text{Pr})_4\text{N}$; $\text{M} = \text{Ni}$, Pt , Pd , Zn or Tl) [57]. Colin J. Burchell et. al have extended the coordination chemistry of cyanodithioimidocarbonate ligand based complexes of Pt and Pd and added compounds such as $[\text{PPh}_4]_2[\text{M}(\text{C}_2\text{N}_2\text{S}_2)_2]$ ($\text{M} = \text{Pt}$, Pd), $[\text{Pt}(\text{C}_2\text{N}_2\text{S}_2)(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PPh_3) and $[\text{Pt}(\text{C}_2\text{N}_2\text{S}_2)(\text{PP})]$ ($\text{PP} = \text{dppe}$, dppm , dppf) in the library of literature [58]. Synthesis, crystal structure and photoconductivity of the first [60]fullerene complex with metal diethyldithiocarbamate $\{\text{CuII}(\text{dedtc})_2\} \cdot \text{C}_{60}$ have been reported in recent past [59].

A. R. Hendrickons and R. L. Martin *et. al.* have investigated the electrochemical responses of dithiocarbamates of Cu(I), Cu(II), Cu(III) and Co(III) metal ions [60]. Potassium ion recognition by a facile dithiocarbamate assembly of benzo-15-crown-5-gold nanoparticles has been highlighted only recently [61]. A facile one-pot preparation of cyanamide from dithiocarbamate using molecular iodine has been reported by Jayashree Nath *et al.* [62]. Multiple nitrene insertions into the copper–sulfur bonds of dithiocarbamate ligands and synthesis and molecular structure of the tetraamido complex $[\text{Cu}\{\eta^2\text{-RNSC}(\text{NMe}_2)\text{SNR}\}_2]$ ($\text{R} = \text{SO}_2\text{C}_6\text{H}_4\text{Me-p}$) have been documented by Hogarth and his coworkers [63]. A number of dinuclear dithiocarbamate macrocycles complexes have been synthesized and their utility as ditopic receptors for a variety of guest molecules have been explored by Paul D. Beer and his research group, in recent past [64].

1.3. *N, O*-Schiff Bases

Hugo (Ugo) Schiff (26 April 1834-8 September 1915) was a German scientist, who discovered a class of compounds “Schiff bases” from the condensation of primary amines with aldehydes or ketones (Scheme 7) under specific condition [65]. Schiff bases (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine (N=C) group (RCH=NR', where R, R', R'' are alkyl and (or) aryl substituent).



Scheme 7: General synthetic route for Schiff bases

These ligands are considered privileged ligands, because they are easily prepared by a simple one-pot condensation of aldehydes or ketones and primary amines in variety of solvents [66]. Condensation of amines with aldehydes or ketones has numerous applications which include preparative use, identification, detection and determination of aldehydes or ketones, purification of carbonyl or amino compounds, or protection of these groups during complex or sensitive reactions. *N, O*-Schiff bases of aliphatic aldehydes are relatively unstable and readily undergo polymerization, while those of the aromatic aldehydes having effective conjugation are more stable. *N, O*-Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilisers. *N, O*-Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, [67] (Fig. 13) and antipyretic properties. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities. The presence of azomethine functional group is responsible for antimicrobial activity, which can be altered depending upon the type of substituent present on the aromatic rings [68]. Further, *N, O*-Schiff bases represent an important class of compounds because they are utilized as starting materials in the synthesis of industrial products.

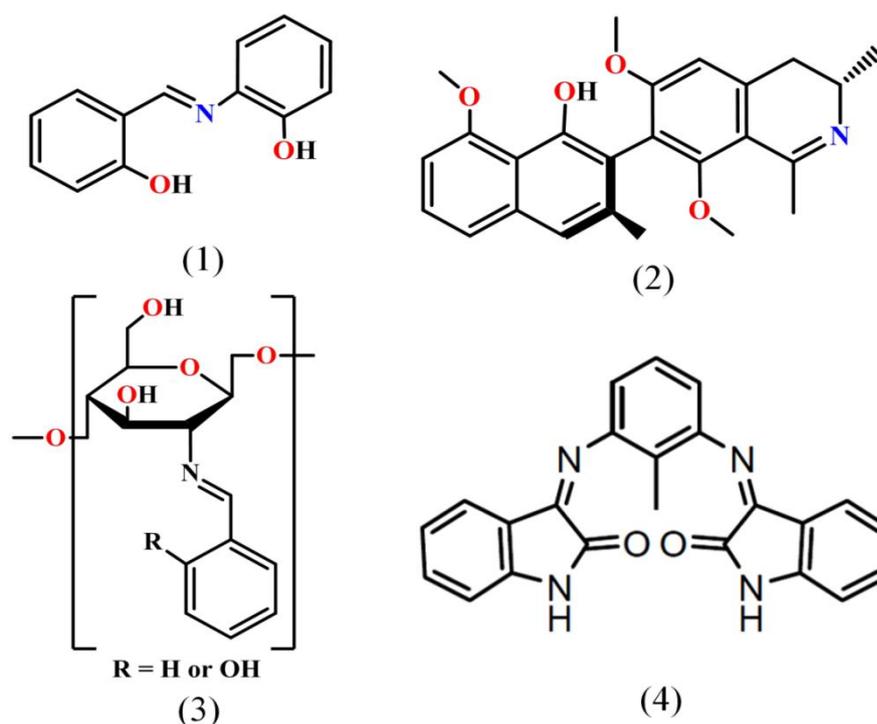


Fig. 13. (1) N-(salicylidine)-2-hydroxyaniline (Antibacterial activity) (2) Ancistocladidine (Antimalarial Natural Product) (3) Chitosan-derived Schiff base (Antifungal activity) (4) Isatin based Schiff base (Antiviral activity)

1.3.1. Metal Complexes of *N, O*-Schiff bases

Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas and thus *N, O*-Schiff bases are among the most widely used ligands due to their facile synthesis, remarkable versatility and good solubility in common solvents. Thus, they have played an important role in the development of coordination chemistry as they readily form stable complexes with most metals in different oxidation states. The high chelation affinity of the *N, O*-Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. The field of *N, O*-Schiff base metal complexes is fast developing because of the wide variety of possible structures for the ligands, depending on the aldehyde and amine used. Many *N, O*-Schiff bases and their complexes have been widely studied because of their industrial and biological applications [66]. Due to their capability to form complexes with different transition metals yielding large number of *N, O*-Schiff base metal complexes with fascinating physico-chemical properties leading to very high potential applicability. A large number of *N, O*-Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their ability to reversibly

bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group [69], photochromic properties [70], and complexing ability towards some toxic metals. The use of salen ligands in monometallic complexes was studied extensively after Kochi and coworkers [71]. They reported their high and chemoselective catalytic activity in epoxidation reactions. Extensive studies were done by Jacobsen and coworkers [72].

Moreover, the metal complexes derived from chiral salen ligands [73] are among the most powerful catalysts of many reactions including alkene epoxidation, epoxide ring opening, selective hydrogenations, carbonyl cyanosilylation, imine additions, and others. Epoxides are very useful and versatile intermediates for the synthesis of plethora of commodity and fine chemicals, The epoxidation of C=C bond by using such Schiff bases complexes [74-76] have received considerable attention. The traditional procedure for epoxidation of alkene is centered on oxidation by stoichiometric amount of peracids. Peracids are very expensive, are hazardous to handle, and are nonselective for the epoxide formation and also lead to formation of undesirable products, creating a lot of waste. Many catalytic epoxidation methods have been developed which include asymmetric epoxidation, but selective epoxidation of alkenes using heterogeneous catalysts and clean oxidants under mild conditions is still a challenge. Catalysts derived by immobilization of transition metal complex in microporous or mesoporous matrixes by various means have been employed in epoxidation reactions. The use of salen ligands in monometallic complexes was studied extensively after Kochi and coworkers reported their high and chemoselective catalytic activity in epoxidation reactions [77]. Extensive studies were done by Jacobsen and coworkers and Katsuki and coworkers, who reported independently the importance of chiral manganese (III) complexes with a large number of salen ligands with various chiralities and bulky alkyl or aryl groups in the enantioselective catalytic oxidation of unfunctionalized olefins (Fig. 14). Despite extensive work on tuning the asymmetric induction of salen ligands, hardly any attention was paid to O-functionalized salen complexes. e. g. hydroxyl or carboxyl substituents, or their activity in catalytic epoxidation [78-80].

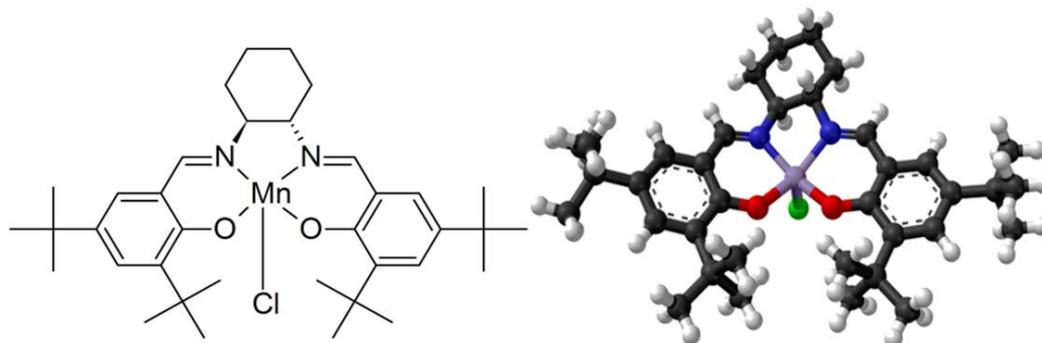


Fig. 14. N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese (III) chloride

Transition metal complexes containing phenoxyimine ligands useful for the polymerization of ethylene or propylene were developed by the group of Fujita [81-84]. Especially alkyl or aryl alkyl substituted phenoxyimine ligands were employed to prepare a wide variety of titanium, zirconium, or vanadium complexes; whereas hetero atom substituted ligand frameworks are quite rare. A few titanium and zirconium complexes containing fluorinated iminophenyl moieties are known to polymerize ethylene and propylene. Olefin polymerization by cationic complexes of d^8 metals (late transition metals) has been studied intensely in the past decade. Due to their functional group tolerance, ethylene and 1-olefins can be copolymerized with polar monomers such as acrylates. These studies prompted renewed interest in neutral Ni(II) ethylene polymerization catalysts. There is a strong interest in the discovery of more active neutral Ni(II) polymerization catalysts that polymerize ethylene to high molecular weight polymer and heterogeneous and homogeneous catalysis for oxidation and polymerization of organic compounds (Fig. 15 (b)) [85-86].

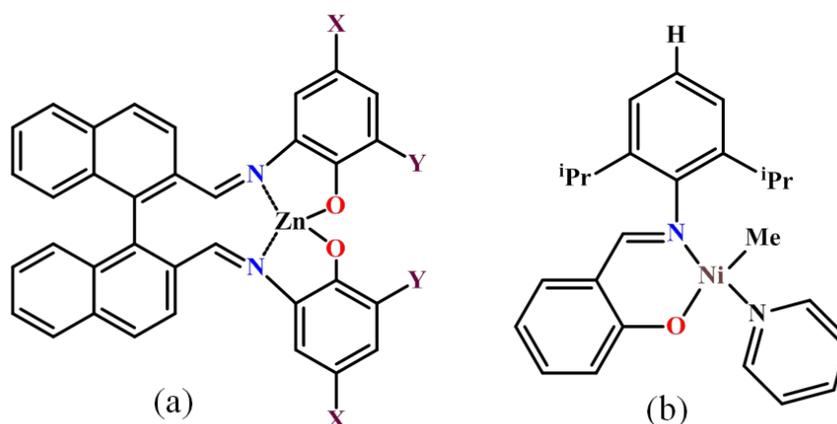


Fig. 15. (a) Zn binaphthyl-derived salen complex catalyzes CO_2 insertion leading to epoxides (b) Nickel(II) catalysts used in high molecular weight polyethylene formation.

Schiff base with metals such as thallium, molybdenum, manganese, zinc, cadmium, copper and silicon form complexes show impaired antimicrobial property when compared with Schiff base [87]. Example- Schiff base of pyrolidone, pyridone with *O*-phenylenediamine and their metal complexes show better antibacterial activity [88]. Schiff base with metals such as Arsenic, antimony and bismuth show considerable antifungal property against *A.niger* and *A.alternata* [89]. Example *N, O*-Schiff bases and their metal complexes formed between furan (or) furylgycoxal with amines show antifungal activity against various organisms [90]. *N, O*-Schiff base metal complexes with silver show considerable antiviral activity [91]. Example silver complexes in oxidation state showed inhibition against cucumber mosaic virus. Apart from this, antimicrobial, antifungal, antiviral activity, anti-inflammatory, allergic inhibitory, antioxidant and analgesic action of *N, O*-Schiff bases and their metal complexes are well documented in the literature. For instance- Furan semicarbazone bearing Schiff base metal complexes exhibit significant antihelminthic and analgesics activities [92]. *N, O*-Schiff base complexes of chromium and cobalt are used in dyes for giving colour to leathers, food package and wool.

A series of transition metal ions, such as Co(II), Mn(II), Fe(II) and Cu(II) form complexes with *N, O*-Schiff bases which have been shown to display a varied theoretical and practical applications. Some of them are capable of reversibly binding molecular oxygen, being consequently employed as models in the study of oxygen's reversible fixation by its natural carriers (hemoglobin, hemocyanin, etc) (Fig. 16). Metal complexes of these bases have numerous applications including antibacterial, antifungal and antiviral activities as well as other biological applications. Several applications have been related for these complexes in chemical analysis, absorption and transport of oxygen, in pesticides.

In the area of bioinorganic chemistry, the interest in the *N, O*-Schiff base metal complexes arises in the way that they provide synthetic models for the metal containing sites in metalloproteins and enzymes [93]. Quinazolinon-4(3H)-ones and its derivatives are versatile nitrogen heterocyclic compounds which have long been known as a promising class of biologically active compounds. Compounds containing 4(3H)-quinazolinone ring system have been reported to possess different biological activities such as antibacterial, antifungal, antitubercular, antiviral, anticancer and anticonvulsant activity depending on the substituent's in the ring system.

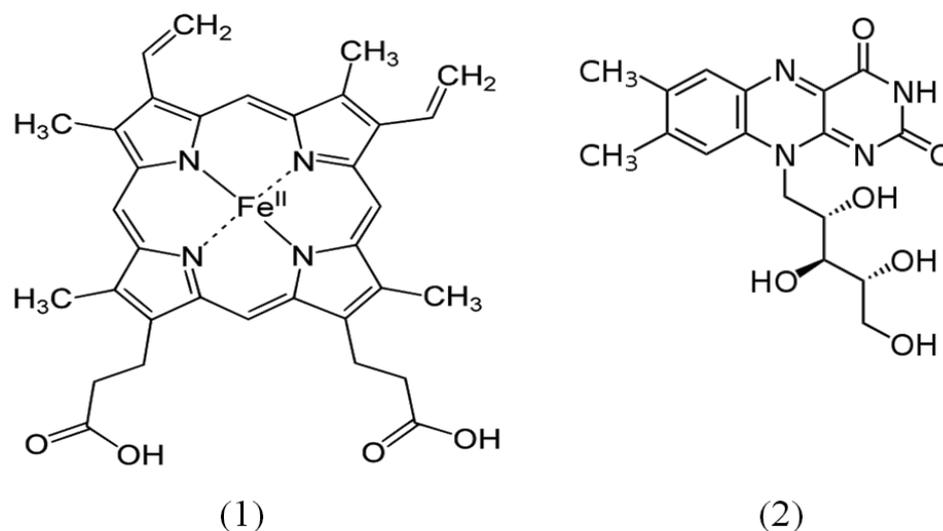


Fig. 16. (1) Haemoglobin b (2) Riboflavin (Vitamin B₂)

Moreover, copper(II)-assisted self-assembly of bis-*N,O*-bidentate Schiff bases and their uses as new building blocks for a double-helical supramolecular motif have been highlighted by Noboru Yoshida and research coworkers in 1999 [94]. Ligating properties of a potentially tetradentate Schiff bases with zinc(II), cadmium(II), cobalt(II), cobalt(III) and manganese(III) ions: synthesis and structural studies [95]. Synthesis, X-ray structure and catalytic efficacy of tetradentate Schiff-base copper(II) complexes towards olefin oxidation have been elaborated by Chandan Adhikary *et al.* [96]. An overview to recoverable and reusable homogeneous and heterogeneous chiral salen complex catalysts has been covered by Carlos Baleizao *et al.* in a review article [97]. The synthesis, electrochemical and spectroscopic characterization of some cobalt(II) complexes with tetradentate Schiff bases derived from bis(salicylaldehyde) ethylenediimine and their catalytic activity in oxidation reactions by molecular oxygen are reported by Aurel Pui *et al.* [98]. Synthesis and characterization of nickel(II) complexes of neutral, tetradentate Schiff base ligands derived from 1, 3-diamines is also documented in the literature [99]. Magnetic and spectral properties of oxovanadium(IV) complexes of ONO donor tridentate, dibasic Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and *o*-hydroxy benzylamine is also reported [100]. Only recently, the influence of Schiff base and lanthanide metals on the synthesis, stability, and reactivity of monoamido lanthanide complexes bearing two Schiff bases have been reported. [101]. Highly active ethylene polymerization and regioselective 1-hexene oligomerization by using

zirconium and titanium catalysts with *O,N,O*-tridentate Schiff base ligands have also been documented only recently [102]. Bivalent transition metal Schiff base complexes of Cu(II), Co(II) and Ni(II) with two coumarin-3-yl thiosemicarbazone derivatives (1E)-1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (OCET) and (1E)-1-(1-(6-bromo-2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide (BOCET) have been synthesized and spectroscopic, antibacterial activity and thermogravimetric studies have been performed by Moamen S. Refat et. al. [103]. A colorimetric and “turn-on” fluorescent chemosensor for Zn(II) based on coumarin Schiff-base derivative is reported [104]. Very recently, Zn(II) and Cu(II) complexes of a new thiophenebased salphen-type Schiff base ligand as solution-processable high-performance field-effect transistor materials have been reported [105].

1.4. Objectives of the present work

In the light of all these aspects, efforts have been put into the development of a number of mononuclear/ polynuclear transition metal dithiocarbamate and N, O-Schiff base complexes by using metal-directed self-assembly of corresponding ligands. The objectives of the current study are briefly stated below.

- To design and synthesize novel and functionalized organic secondary amine precursors suitable for the development of mononuclear/ polynuclear transition metal dithiocarbamate complexes.
- To synthesize dithiocarbamate ligands *in situ* from secondary amine precursors, carbon disulphide and the presence of a base.
- To investigate the possible reactivity of 1,1-dithio ie. dithiocarbamate ligands towards transition metal ions.
- To design and synthesize novel and functionalized N,O-Schiff base ligands suitable for the development of mononuclear transition metal N,O-Schiff base complexes.
- To investigate the possible reactivity of *N,O*-Schiff base ligands towards transition metal ions.
- To characterize newly synthesized compounds by micro-, thermogravimetric analysis and relevant spectroscopic techniques such as mass, IR, NMR, UV visible.

- To investigate the electrochemical responses of the newly synthesized compounds.
- To determine the unambiguous structure of compounds by single crystal XRD studies and to evaluate the crystal packing patterns.
- To investigate the impact of structural modifications upon antimicrobial activity against a panel of bacteria *S. aureus*, *B. subtilis* (gram positive), *E. coli*, *P. aeruginosa* (gram negative) and *C. albicans* and *A. niger* (fungi).

1.5. References

1. Ozin, G. A.; Arsenault, A.; Cademartiri L. *Nanochemistry: a chemical approach to nanomaterials*, Royal Society of Chemistry, **2008**.
2. (a) Wikoff, W. R.; Liljas, L.; Duda, R. L.; Tsuruta, H.; Hendrix, R. W.; Johnson, J. E. *Science* **2000**, 289, 2129. (b) Marlovits, T. C.; Kubori, T.; L.-Tejero, M.; Thomas, D.; Unger, V. M.; Galán, J. E. *Nature* **2006**, 441, 637.
3. (a) Zhang, Q.; Ma, J.-P.; Wang, P. Shi, Z.-Q.; Dong, Y.-B.; Huang, R.-Q. *Cryst. Growth Des.* **2008**, 8, 2581. (b) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.*, **1999**, 5, 102.
4. (a) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, 43, 1466. (b) Ferey, C.; M.-Draznieks, C; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, 38, 217. (c) Hosseini, M. W. *Acc. Chem. Res.* **2005**, 38, 313. (d) Nitschke, J. R. *Acc. Chem. Res.* **2007**, 40, 103. (e) Pitt, M. A.; Johnson, D. W. *Chem. Soc. Rev.* **2007**, 36, 1441. (f) Thomas, J. A. *Chem. Soc. Rev.* **2007**, 36, 856. (g) Ariga, K.; Hill, J. P.; Lee, M. V.; Vinu, A.; Charvet, R.; Acharya, S. *Sci. Technol. Adv. Mater.* **2008**, 9, 014109 (96 pp). (h) Fujita, M.; Tominaga, M.; Hori, A. Therrien, B. *Acc. Chem. Res.* **2005**, 38, 369. (i) Zangrando, E.; Casanova, M.; Alessio, E. *Chem. Rev.* **2008**, 108, 4979. (j) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, 111, 6810. (k) T.-Huerta, A.; Höpfl, H.; Tlahuext, H.; H.-Ahuactzi, I. F.; Sánchez, M.; R.; R.-Martínez, M.-Morales, D. *Eur. J. Inorg. Chem.* **2013**, 61.
5. (a) Webber, P. R. A.; Drew, M. G. B.; Hibbert, R.; Beer P. D. *Dalton Trans.*, **2004**, 1127.
6. (a) Lehn, J. -M. *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 9; (b) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int.*

- Ed.*, **2001**, *40*, 2022; (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.*, **2000**, *100*, 853; (d) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.*, **1999**, 1185; (e) Linton, B.; Hamilton, A. D. *Chem. Rev.*, **1997**, *97*, 1669; (f) Fujita, M.; Ogura, K. *Bull. Chem. Soc. Jpn.*, **1996**, *69*, 1471.
7. Lindsey, J. S. *New J. Chem.*, **1991**, *15*, 153.
 8. (a) Halls, D. J. *Mikrochim. Acta*, **1969**, 62; (b) Coucouvanis, D. *Prog. Inorg. Chem.*, **1970**, *11*, 233; (c) Coucouvanis, D. *Prog. Inorg. Chem.*, **1979**, *26*, 301.
 9. (a) Beer, P. D.; Berry, N.; Drew, M. G. B.; Fox, O. D.; Padilla-Tosta, M. E.; Patell, S. *Chem. Commun.*, **2001**, 199; (b) Fox, O. D.; Drew, M. G. B.; Wilkinson, E. J. S.; Beer, P. D. *Chem. Commun.*, **2000**, 391; (c) Fox, O. D.; Drew, M. G. B.; Beer, P. D. *Angew. Chem., Int. Ed.*, **2000**, *39*, 136.
 10. Chant, R.; Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Aust. J. Chem.*, **1973**, *26*, 2533.
 11. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th Ed., John Wiley and Sons, Inc, New York 1996.
 12. Rathore, H. S.; Varshney, G.; Mojumdar S. C.; Saleh, M. T. *J. Therm. Anal. Calorim.* **2007**, *90*, 681.
 13. Karlin, K. D. *Prog. Inorg. Chem.* **53**, John Wiley and Sons, Inc. New Jersey pp 71, (2005).
 14. Sharma, R.; Kaushik, N. K. *J. Therm. Anal. Calorim.* **2004**, *78*, 953.
 15. Karlin, K. D. *Prog. Inorg. Chem.* **53**, John Wiley and Sons, Inc. New Jersey pp 71, (2005).
 16. Kaul, B. B.; Pandeya, A. B. *Transition Met. Chem.* **1979**, *4*, 112.
 17. Sarwar, M.; Ahmad, S.; Ali, S.; Awan, S. A. *Transition Met. Chem.* **2007**, *32*, 199.
 18. Halimehjani, A. Z.; Marjani, K.; Ashouri, A. *Green Chem.*, **2010**, *12*, 1306.
 19. Azizi, N.; Aryanasab, F.; Torkiyan, L.; Ziyaei, A.; Saidi, M. R. *J. Org. Chem.* **2006**, *71*, 3634.
 20. Wong, R.; Dolman, S. J. *J. Org. Chem.* **2007**, *72*, 3969.
 21. Vogel, A. I. *A Text Book of Practical Organic Chemistry*, ELBS Publication, London, 1968, p. 499.
 22. (a) Pastorek, R.; Štarha, P.; Drahoš, B.; Trávníček, Z. *Polyhedron* **2014**, *69* 174. (b) Regulacio, M. D.; Pablico, M. H.; Vasquez, J. A.; Myers, P. N.; Gentry, S.; Prushan, M.; T.-Chang, S.-W.; Stoll, S. L. *Inorg. Chem.* **2008**, *47*, 1512. (c) M.-

- Hernandez, M.-A.; C.-Olivares, R.; E.-Perez, G.; H.-Ortega, S. *J. Chem. Soc. Dalton Trans.*, **1996**, *21*, 4135.
23. (a) Kanchi, S., Saraswathi, K., Venkatasubba Naidu, N., 2011a. *Environ. Monit. Assess.* **183**, 531; (b) Sharma, S.; Rashid, F.; Banoj, B. *Agric. Food Chem.* **2005**, *53*, 6027.
24. (a) Dhote, S. S., Deshmukh, L.; Paliwal, L. *J. Chromatogr. Sep. Tech.* **2012**, *3*, 1. (b) Milacic, V.; Chen, D.; Ronconi, L.; Landis-Piwowar, K. R.; Fregona, D.; Dou, Q. P. *Cancer Res* **2006**, *66*, 21.
25. Ahamad, M.; Rao, M. R.; Rafi, M. M.; Mohiddin, G. J.; Sreeramulu, J. *Arch. Appl. Sci. Res.*, **2012**, *4*, 858.
26. Al-Amiery, A. A.; Al-Majedy, Y. K.; Ibrahim, H. H.; Al-Tamimi, A. A. *Org. Med. Chem. Lett.*, **2012**, *2*, 4.
27. Blasco, C., Font, G., Pico, Y., *J. Chromatogr. A* **2004**, *1028*, 267.
28. Van Lishaut, H., Schwack, W., *J. AOAC Int.* **2000**, *83*, 720.
29. Van Lishaut, H., Schwack, W., *J. AOAC Int.* **2000**, *83*, 720.
30. Kanchi, P.; Singh, K.; Bisetty. *Arab. J. Chem.* **2014**, *7*, 11.
31. Crabtree, R. H. *The organometallic Chemistry of the Transition Metals*. Wiley p. 560. (2005).
32. Toreki, R. "Organometallics Defined" Interactive Learning Paradigms Incorporated (2003-11-20).
33. Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.
34. Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632.
35. Woodward, R. B.; Rosenblum, M.; Whiting, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 3458.
36. (a) van Stavern, D. R.; Metzler-Nolte, N. *Chem. Rev.* **2004**, *104*, 5931; (b) Gasser, G.; Ott, I.; Metzler-Nolte, N. *J. Med. Chem.* **2011**, *54*, 3; (c) Patra, M.; Gasser, G.; Metzler-Nolte, N. *Dalton Trans.* **2012**, *41*, 6350; (d) Ornelas, C. *New J. Chem.* **2011**, *35*, 1973; (e) Patra, M.; Gasser, G. *ChemBioChem* **2012**, *13*, 1232; (f) Biot, C.; François, N.; Maciejewski, L.; Brocard, J.; Poulain, D. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 839; (g) Chantson, J. T.; Verga, F. M. V.; Crovella, S.; Metzler-Nolte, N. *ChemMedChem* **2006**, *1*, 1268; (h) Tirkey, V.; Mishra, S.; Dash, H. R.; Das, S.; Nayak, B. P.; Mobin, S. M.; Chatterjee, S. *J. Organomet. Chem.*, **2013**, *732*, 122.

37. (a) Hillard, E. A.; Vessières, A.; Thouin, L.; Jaouen, G.; Amatore, C. *Angew. Chem. Int. Ed.* **2006**, *45*, 285; (b) Hamels, D.; Dansette, P.; Hillard, E. A.; Top, S.; Pigeon, P.; Jaouen, G.; Mansuy, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 9124.
38. (a) Dive, D.; Biot, C. *Curr. Top Med. Chem.* **2014**, *14*, 1684; (b) Dubar, F.; Slomianny, C.; Khalife, J.; Dive, D.; Kalamou, H.; Guérardel, Y.; Grellier, P.; Biot, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 7690.
39. (a) Edwards, E. I.; Epton, R.; Marr, G. *J. Organomet. Chem.* **1975**, *85*, C23; (b) Edwards, E. I.; Epton, R.; Marr, G. *J. Organomet. Chem.* **1976**, *122*, C49; (c) Edwards, E. I.; Epton, R.; Marr, G. *J. Organomet. Chem.* **1979**, *168*, 259.
40. (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301; (b) Hogarth, G. *Prog. Inorg. Chem.* **2005**, *53*, 71; (c) Tiekink E. R. T.; Haiduc, I. *Prog. Inorg. Chem.* **2005**, *54*, 127; (d) Haiduc, I. *Coord. Chem. Rev.* **1997**, *158*, 325; (e) Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* **1984**, *54*, 23; (f) Bond, A. M.; Hendrickson, A. R.; Martin, R. L.; Moir, J. E.; Page, D. R. *Inorg. Chem.*, **1983**, *22*, 3440 (g) Kobayashi, A.; Fujiwara, E.; Kobayashi, H.; *Chem. Rev.* **2004**, *104*, 5243.
41. (a) Naeem, S.; Ogilvie, E.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2010**, *39*, 4080; (b) Kumar, A.; Mayer-Figge, H.; Sheldrick, W. S.; Singh, N. *Eur. J. Inorg. Chem.* **2009**, 2720; (c) Wilton-Ely, J. D. E. T.; Solanki, D.; Knight, E. R.; Holt, K. B.; Thompson, A. L.; Hogarth, G. *Inorg. Chem.* **2008**, *47*, 9642; (d) Wilton-Ely, J. D. E. T.; Solanki, D.; Hogarth, G. *Eur. J. Inorg. Chem.* **2005**, 4027; (e) Trindade, T.; O'Brien, P.; Pickett, N. L. *Chem. Mater.* **2001**, *13*, 3843; (f) Wong, W. W. H.; Cookson, J.; Evans, E. A. L.; McInnes, E. J. L.; Wolowska, J.; Maher, J. P.; Bishop, P.; Beer, P. D. *Chem. Commun.* **2005**, 2214.
42. (a) Wong, W. W. H.; Curiel, D.; Lai, S.-W.; Drew, M. G. B.; Beer, P. D. *Dalton Trans.*, **2005**, 774; (b) Lai, S.-W.; Drew, M. G. B.; Beer, P. D. *J. Organomet. Chem.* **2001**, *637*, 89; (c) Cookson J.; Beer, P. D. *Dalton Trans.* **2007**, 1459; (d) Takemoto, S.; Kuwata, S.; Nishibayashi, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 6428; (e) McCulloch, B.; Brubaker, C. H. Jr, *Organometallics* **1984**, *3*, 1707.
43. Sato, M.; Kong, H.; Shiga, M.; Motoyama, I.; Hata, K. *Notes.* **1967**, *41*, 1.
44. (a) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (b) Lai, C. S.; Tiekink, E. R. T. *CrystEngComm.* **2003**, *5*, 253.

45. Singh, V.; Chauhan, R.; Gupta, A. N.; Kumar, V.; Drew, M. G. B.; Bahadur, L.; Singh, N. *Dalton Trans.* **2014**, *43*, 4752.
46. Singh, N.; Kumar, A.; Prasad, R.; Kieran, C.; Molloy,.; Mary, F.; Mahon. *Dalton Trans.* **2010**, *39*, 2667.
47. Alama, A.; Tasso, B.; Novelli, F.; Sparatore, F. *Drug Discovery Today* **2009**, *14*, 500.
48. Schreck, R.; Meier, B.; Mannel, D. N.; Droge, W.; Baeuerle, P. A. *J. Exp. Med.* **1992**, *175*, 1181.
49. Ha, T.; Li, Y.; Gao, X.; McMullen, J. R.; Shioi, T.; Izumo, S.; Kelley, J. L.; Zhao, A.; Haddad, G. E.; Williams, D. L.; Browder, I. W.; Kao, R. L.; Li, C. *Free Radic. Biol. Med.* **2005**, *39*, 1570.
50. Vuchkova, L.; Arpadjan, S. *Talanta.* **1996**, *43*, 479.
51. Wheeler, K.A.; Harrington, B.; Zapp, M.; Casey, E. *CrystEngComm.* **2003**, *5*, 337.
52. Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1968**, *7*, 2140.
53. Assefa, Z.; Staples, R. J.; Fackler, Jr. J. P. *Acta Crystallogr., Sect. C.* **1995**, *51*, 2271.
54. Seltzer, R. *J. Org. Chem.* **1968**, *33*, 3896.
55. Casey, A. T.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2057.
56. Spies, H.; Johannsen, B. *Inorg. Chim. Acta.* **1981**, *48*, 255.
57. Cotton, F. A.; McCleverty, J. A. *Inorg. Chem.* **1967**, *6*, 229.
58. Colin, J.; Burchell, Aucott, S. M.; Milton, H. L.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2004**, 369.
59. Konarev, D. V.; Kovalevsky, A. Y.; Lopatin, D. V.; Umrikhin, A. V.; Yudanov, E. I.; Coppens, P.; Lyubovskaya, R. N.; Saito, G. *Dalton Trans.* **2005**, 1821.
60. (a) Hendrickons, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1976**, *15*, 2116; (b) Bond, A. M.; Hendrickons, A. R.; Martin, R. L.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1983**, *22*, 3440.
61. Patel, G.; Kumar, A.; Pal, U.; Menon, S.; *Chem. Commun.* **2009**, 1849.
62. Nath, J.; Patel, B. K.; Jamir, L.; Bora, U.; Sinha, Satyanarayan, K. V. V. V.; *Green Chem.* **2009**, *11*, 1503.
63. Hogarth, G.; Pateman, A.; Sella, A.; *Chem. Commun.* **1997**, 1029.
64. (a) Wallace, W. H.; Curiel, W. D.; Cowley, A. R.; Beer, P. D. *Dalton Trans.* **2005**, 359; (b) Cookson, J.; Evans, E. A. L.; Maher, J. P.; Serpell, C. J.; Paul,

- R. L.; Cowley, A. R.; Drew, M. G. B.; Beer, P. D. *Inorganica Chimica Acta*. **2010**, 363, 1195. *and the references cited in.*
65. Schiff, H. *Annalen.*, **1864**, 131, 118.
66. Shebl, M.; Khalil, S. M. E.; Ahmed, S.A.; Medien, H. A. A. *J. Mol. Struct.* **2010**, 980, 39.
67. Jarrahpour, A.; Khalili, D.; Clercq, E. D.; Salmi C.; Brunel J. M. *Molecules* **2007**, 12, 1720.
68. Silva, C. M. da.; Silva, D. L. da.; Modolo, L. V.; Alves, R. B.; Resende, M. A, de.; Martins, C. V. B.; Fatima, A. de. *Journal of Advanced research.* **2011**, 2, 1.
69. Dugas, H.; Penney, C. "Bioorganic Chemistry", p. 435, Springer, New York, 1981.
70. Margerum, J. D.; Miller, L. J. "Photochromism", p. 569, Wiley Interscience, New York, 1971.
71. Srinivasan, K; Michaud, P; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, 108, 2309.
72. (a) Finnley, N.; Pospil, P. J.; Chang, S.; Palucki, M.; Konsler, R.; Hansen, K.; Jacobsen, E. *Angew. Chem., Int. Ed. Engl.*, **1997**, 36, 1720; (b) Jacobsen, E. N. in *Comprehensive Organometallic Chemistry II*, Eds. Abel, Stone, E. W. F. G. A.; Willinson, E.; Pergamon, New York, vol. 12, p. 1097, 1995.(c) Nishikori, H.; Ohta, C.; Katsuki. T.; *Synlett*, **2000**, 1557; (e) Takeda, T.; Irie, R.; Katsuki. T. *Synlett*, **1999**, 7, 1166; (f) Katsuki, T. *Chem. Soc. Rev.*, **2004**, 33, 437; (g) Wu, M. H.; Jacobsen, E. N. *Tetrahedron Lett.*, 1997, 38, 1693; (h) Brandes, B. D.; Jacobsen, E. N.; *Tetrahedron: Asymmetry* **1997**, 8, 3927.
73. (a) Borisova, N. E.; Reshetova, M. D.; Ustynyuk, Y. A. *Chem. Rev.*, **2007**, 107, 46; (b) Tang, C. W.; VanSlyke, S. A.; *Appl. Phys. Lett.*, **1987**, 51, 913; (c) Yu, T.; Su, W.; Li, W.; Hong, Z.; Hua, R.; Li, B. *Thin solid Films*, **2007**, 515, 4080.
74. Fernández, I.; Pedro, J. R.; Salud. R. *Tetrahedron*, **1996**, 52, 12031.
75. de Souza, V. R.; Nunes, G. S.; Rocha, R. C.; Toma, H. E. *Inorg. Chim. Acta*, **2003**, 348, 50.
76. Kureshy, R. I.; Khan, N. H.; Abdi, S. H. R.; Patel, S. T.; Iyer, P. K.; Jasra, R. V. *J. Catal.*, **2002**, 209, 99.
77. (a) Samel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.*, **1985**, 107, 7606; (b) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.*, **1985**, 24, 4671.
78. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen. *J. Am. Chem. Soc.* **1990**, 112, 2801.

79. Jacobsen, E. N.; Zhang, Wei; Muci, Alexander R.; Ecker, James R.; Deng, Li. *J. Am. Chem. Soc.* **1991** *113*, 7063.
80. Che, C. -M.; Huang, J. -S.; *Coord. Chem. Rev.*, 2003, 242, 97.
81. Nakajima, K.; Kojima, K.; Aoyama, T.; Fujita, J. *Chem. Lett.*, **1986**, 1483.
82. Nakajima, K.; Kojima, M.; Toriumi, K.; Saito, K.; Fujita, J. *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 760.
83. Matsui, S.; Fujita, T. *Catal. Today*, **2001**, *66*, 63.
84. Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *J. Mol. Catal. A: Chem.*, **2004**, *213*, 141.
85. da Silva, C. M. et al. *Journal of Advanced research*. **2011**, *2*, 1.
86. (a) Shen, Y.-M. et al. *J. Org. Chem.* **2003**, *68*, 1559. (b) Wehrmann, P.; Mecking, S.; *Organometallics* **2008**, *27*, 1399.
87. da Silva, C. M.; da Silva, D. L.; Modolo, L. V.; Alves, R. B.; de Resende, M. A.; Martins, C. V. B.; de Fatima, A. J. *Adv. res.* **2011**, *2*, 1.
88. Mamedov, V. A.; Kalinin, A. A.; Gubaidullin, A. T.; Isaikina, O. G.; Litvinov, I. A.; *Russ. J. Org. Chem.*, **2005**, *41*, 599.
89. Zhu, H. -L.; Tan, R. -X. *Eur. J. Med. Chem.* **2007**, *42*, 558.
90. Prasada, K. S.; Kumara, L. S.; Chandanb, S.; Jayalakshmic, B.; Revanasiddappa, H. D. *Spectrochim. Acta, Part A* **2011**, *81*, 276.
91. Patil, M.; Hunoor, R.; Gudasi, K. *Eur. J. Med. Chem.*, **2010**, *45*, 2981.
92. (a) Catarzi, D.; Colotta, V.; Varano, F.; Lenzi, O.; Filacchioni, G.; Trincavelli, L.; Martini, C.; Montopoli, C.; Moro, S. *J. Med. Chem.*, **2005**, *48*, 7932; (b) Jaso, A.; Zarranz, B.; Aldana, I.; Monge, A. *J. Med. Chem.*, **2005**, *48*, 2019; (c) Zarranz, B.; Jaso, A.; Aldana, I.; Monge, A. *Bioinorg. Med. Chem.*, **2004**, *12*, 3711; (c) Tandon, V. K.; Yadav, D. B.; Maurya, H. K.; Chaturvedi, A. K.; Shukla, P. K. *Bioinorg. Med. Chem.*, **2006**, *14*, 6120; (d) Kushida, M.; Wanibuchi, H.; Morimura, K.; Kinoshita, A.; Kang, J. S.; Puatanachokckai, R.; Wei, M.; Funae, Y.; Fukushima, S. *Cancer Sci.*, **2005**, *96*, 747.
93. Molina, R. H.; Mederos, A. T. J. Meyer Mc. Cleverty (Ed.), *Comprehensive Coordination Chemistry*, vol. 1, 2nd ed., Elsevier, 2005, Chapter 19.
94. Yoshida, N.; Oshio, H.; Ito, T. *J. Chem. Soc. Perkin Trans.* **1999**, *2*, 975.
95. Sen, S.; Talukder, P.; Dey, S. K.; Mitra, S.; Rosair, G.; Hughes, D. L.; Yap, G. P. A.; Pilet, G.; Gramlich, V.; Matsushita, T.; *Dalton Trans.* **2006**, 1758.

96. Adhikary, C.; Bera, R.; Dutta, B.; Jana, S.; Bocelli, G.; Cantoni, A.; Chaudhuri, S.; Koner, S. *Polyhedron*. **2008**, *27*, 1556.
97. Baleizao, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987.
98. Pui, A.; Berdan, I.; Morgenstern-Badarau, I.; Gref, A.; Perree-Fauvet, M.; *Inorg. Chim. Acta*, **2001**, *320*, 167.
99. Campbell, T. G.; Urbach, F. L. *Inorg. Chem.* **1973**, *12*, 1836.
100. Syamal A.; Kale, K. S. *Inorg. Chem.* **1979**, *18*, 992.
101. Han, F.; Teng, Q.; Zhang, Y.; Wang, Y.; Shen, Q. *Inorg. Chem.* **2011**, *50*, 2634.
102. Xu, T.; Liu, J.; Wu, Guang-Peng.; Lu, Xiao-Bing. *Inorg. Chem.* **2011**, *50*, 10884.
103. Moamen, S.; Ibrahim, M. El-Deen, R.; Anwer, Z. M.; El-Ghol, S. *J. Mol. Struct.* **2009**, *920*, 149.
104. Li, He-yang.; Gao, S.; Xi, Z. *Inorg. Chem. Commun.* **2009**, *12*, 300.
105. Asatkar, A. K.; Senanayak, S. P.; Panda, B. A. S.; Narayan, K. S.; Zade. S. S. *Chem. Commun.* **2014**, *50*, 7036.