COORDINATION CHEMISTRY OF 3d-TRANSITION METALS OF SOME N,S/N,N DONOR SETS: SYNTHESIS, CHARACTERIZATION, STRUCTURE AND REACTIVITY

SYNOPSIS

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The research field dealing with the transition metal complexes of the ligands having N,S/N,S,O donor centers has expanded enormously during recent years. The interest is due to the application of these chelates in modeling of biomolecules, in the field of chemical and biological reactivity and in nuclear medicine. Nowadays it is a challenge for the coordination chemists to design appropriate ligand frames with the purpose to synthesize metal complexes with predetermined properties. The tetradentate/tridentate N₂S₂/N,S,O environment and their 3d metal complexes are of current interest because of their rich physicochemical properties, reactivity patterns, and potential applications in many important chemical processes in the fields of medicine, bioorganic chemistry, catalysis and electrochemical, organic solar cells and electrooptical sensors.

1,3-bis(2-pyridylmethylthio)alkane/toluene and salicylideneamino-dithiaalkane are such type of ligands in which N,S and N,S,O donor centres exist respectively. Here, 1,3-bis(2-pyridylmethylthio)alkane/toluene organic moieties containing two borderline base pyridine-N and two soft thioether-S donor centres act as tetradentate neutral N₂S₂ ligands and 1,8-bis(salicylideneamino)-3,6-dithiaoctane having hard donor imine-N and phenolate-O, soft thioether S donor centres act as a tridentate dibasic/monobasic ligands. In this thesis the synthesis, structure and reactivity of 3d metal ions with these ligands have been explored. The characterization of the complexes have been carried out by elemental analyses, conductance measurement, IR, UV-Vis, CV study and, in most of the cases the detailed structural analysis has been established by single crystal X-ray crystallography in terms of their bond length, bond angles etc.

Chapter I deals with a partial review of coordination chemistry of some 3d metal ions with N,S and N,S,O donor sets. Open chain or macrocyclic ligands having different types of organic backbone have been used to obtain transition metal complexes to explore chemical and biological reactivities in terms of electron exchange properties. The environments of the donor sets have been discussed to point out the donor behaviour. For this purpose to explore the factors which govern the coordination behaviour towards 3d metal ions and pharmacological applications of the resulting complexes, the reactivities of benzothiazole, 2-aminobenzothiazoles, 2-amino-5,7-disubstituted benzothiazoles, 2-pyrrolylthiones, 2-mercaptopbenzothiazole, pyrazole-thioether, mercatoamine, 2-formylpyridine thiosemicarbazone, 2-acetylpyridine
thiosemi-carbazone towards transition metals, particularly 3d metal ions have been discussed in details.

**Chapter II** describes the synthesis, spectral, structural characterization of the [Fe(II)(L1)Cl2] (1), [Co(II)(L1)Cl2] (2) and [Ni(II)(L1)Cl2] (3) [where L1 = 1,3-bis(2-pyridylmethylthio)propane], were synthesized and isolated in their pure form and along with the reactivity of complexes. The solid state structures of complexes [Fe(II)(L1)Cl2] (1) and [Ni(II)(L1)Cl2] (3) have been established by single crystal X-ray crystallography. The structural analysis evidences isomorphous crystals with the metal ion in a distorted octahedral geometry that comprises N2S2 ligand donors with trans located pyridine rings and chlorides in cis positions (Fig.1a and 1b).

![Fig. 1. An ORTEP drawing (ellipsoids at 50% probability) of complex [Fe(L1)Cl2] (1a) and [Ni(L1)Cl2] (1b)](image)

The complexes (1, 2 and 3) were obtained in good yield from the reaction of respective metal(II) chloride with equimolar amounts of the organic moiety (L1) in the methanol medium (viz. **Scheme 1**).

![Scheme 1. Ligand structure and synthetic route of the complexes.](image)

Monomeric complexes of 1, 2 and 3 are soluble in DMF but sparingly soluble in Methanol and acetonitrile. The conductivity measurement of complexes 1, 2 and 3 in DMF shows conductance of 45, 52 and 42 Ω mol\(^{-1}\) cm\(^{-1}\), respectively, these values suggest that all the complexes exist as 1:2 electrolytes. At room temperature the
magnetic moment (μ) of all the complexes are 5.45, 4.91 and 3.08 B.M. which are equivalent to four, three and one unpaired electron, as expected, in each case. Infrared spectral data of all the complexes 1-3 exhibit an intense band at 1468-1472 cm⁻¹ indicate νC=N band for all the complexes and in addition to the νC=S at 760cm⁻¹. The ν(Fe–Cl), ν(Co–Cl) and ν(Ni–Cl) band is observed at 362, 327 and 285 cm⁻¹ respectively. The electronic absorption spectra of complexes 1–3 were recorded at room temperature using dimethylformamide as the solvent. All the spectra in the high energy region (below 400 nm) exhibit bands corresponding to intramolecular π→π* and n→π* transitions.

In the electronic spectrum of [Fe(L¹)Cl₂], a prominent peak around 475 nm with a shoulder at about 752 nm was observed, corresponding to MLCT and d–d transitions, respectively. The electronic spectrum of 2 shows bands at 425, 560 and 967 nm, assignable to the transitions 4T₁g→4T₁g(P), 4T₁g→4A₂g(F) and 4T₁g→4T₂g(F), respectively. The position of these bands indicates an octahedral geometry about the CoII ion. The spectrum of 3 exhibits bands at 475, 685 and 873 nm, which may be assigned to 3A₂g(F)→3T₁g(P), 3A₂g(F)→3T₁g(F) and 3A₂g(F)→3T₂g(F) transitions, respectively.

In solution all compounds displayed a quasi-reversible voltammogram (Fig. 2a and 2b) having iₚ/iᵣ ≈ 1 in the scan rate interval 50–400 mV s⁻¹. The voltammetric response for [Fe(L¹)Cl₂] (1) exhibits an oxidative couple at the E₁/₂ value of +0.295 V, assigned to the Fe²⁺/Fe³⁺ pair, with a peak potential separation (DEp) of 120 mV and cathodic to anodic current intensity ratio of 0.97. The cyclic voltammogram of [Co(L¹)Cl₂] (2) shows a quasi-reversible peak for the Co²⁺/Co³⁺ redox couple at E₁/₂ of 0.795 V with DEp of 195 mV. The cyclic voltammogram of [Ni(L¹)Cl₂] (3) exhibits a quasi-reversible Ni²⁺/Ni³⁺ redox couple centered at 0.745 V versus Ag/AgCl.

![Fig.2. Cyclic voltammogram of (a) complex [Fe(L¹)Cl₂] (1) (b) [Ni(L¹)Cl₂] (3) in DMF](image-url)
Here, the $E_{1/2}$ value for complex 3 lies at the higher side of the range generally measured, 0.3–0.8 V, for the Ni$^{II}$/Ni$^{III}$ oxidation potential data for thioether containing nickel(II) complexes, indicating that Ni$^{II}$ is fairly stabilised in 3.

The synthesis and characterization of four new mononuclear complexes (4a-d) and a polymeric coordination zinc(II) complex (5) with a pyridylmethylthioether $\text{Ni}_2\text{S}_2$ donor set have been described in the Chapter III. On reaction with chloride ions or pseudohalides (azide, cyanate and thiocyanate ions) in ethanol at refluxing temperature, the reaction mixture of the organic molecule $L^1$ and zinc(II) acetate gave hexacoordinated mononuclear zinc(II) complexes of the general formula $[\text{Zn}(L^1)(X_2)]$ ($X = \text{Cl}$, N$_3^-$, NCO$^-$ and SCN$^-$). On the other hand, the organic ligand $L^1$ with the zinc(II) perchlorate salt, a coordination polymeric complex formulated as $\{[\text{Zn}(L^1)(\text{ClO}_4)(\text{H}_2\text{O})]\text{ClO}_4\}_n$ (5) was separated in the solid state. The synthetic procedure of the complexes is shown in Scheme 2.

Scheme 2. Ligand structure and synthetic route of the complexes

In the mononuclear complex 4d the organic moiety $L^1$ behaves as a tetradeinate neutral ligand, chelating the metal in such a way as to locate the pyridine rings in trans positions, and the metal ion completes the highly distorted octahedral coordination sphere with two cis located isothiocyanato anions. The Zn–N(py) and Zn–NCS bond lengths are comparable within their e.s.d.’s (mean values 2.142(5) and 2.040(5) Å, respectively), while the Zn–S distances differ by ca. 0.02 Å, being of 2.6500(18) and 2.6990(17) Å. The bond angles subtended at the metal deviate considerably from the ideal octahedral values and the N(1)–Zn–N(2) and N(2)–Zn–S(2) angles of 161.28(17)$^\circ$ and 77.57(13)$^\circ$, respectively show the highest deviation. In fact the crystal packing of
complex 4d shows a 1D polymeric arrangement built by S(4)…p interactions along the a-axis (Fig. 3). The solid state structure of complex 5 (Fig. 4) demonstrates that the organic moiety L behaves as bridging ligand between two zinc ions, chelating N–Zn–S angles (82.08(13)° and 81.52(16)°) being those most deviated. Finally the Zn(1)–O(1)ClO$_4$ bond length of 2.308(5) Å is significantly longer than that of Zn(2)–O(1w) (2.124(5) Å), most likely due to the more bulky perchlorate anion, though packing effects and H-bond formation cannot be ruled out. The polynuclear chains are connected to each other by H-bonds (Fig. 5) occurring between the aquo ligand with the oxygens atoms of the perchlorate anions to form 2D layered arrangement.

![Image](a)

**Fig. 3.** (a) 1D arrangement of 4d formed by S⋯π interaction extended along a-axis; (b) packing view of 4d

![Image](b)

**Fig. 4.** Detail (ORTEP drawing, 35 % probability ellipsoid) of the coordination polymeric chain of complex 5 [ZnL$^1$(ClO$_4$)(H$_2$O)](ClO$_4$).

The Infrared spectra of all the complexes exhibit characteristic strong to medium intensity bands in the region of 1468-1472 and 758-762 cm$^{-1}$–1220, which are assignable to stretching $\nu_{C=N}$ and $\nu_{C=S}$, respectively. In addition, the characteristic intense band at
2035 cm\(^{-1}\) in 4b, intense band at 2167 cm\(^{-1}\) in 4c and the strong band at 2085 cm\(^{-1}\) in 4d confirms the presence of terminal end-on azide, terminal N-bonded NCO, and N-bonded SCN respectively. The spectra exhibit Of complex 5 a very strong and sharp absorption band at ca. 1092 cm\(^{-1}\) along with a weak band at ca. 623 cm\(^{-1}\) due to the symmetric \((\nu_\text{s(ClO}_4\text{)})\) and asymmetric \((\nu_\text{as(ClO}_4\text{)})\) stretching vibration of perchlorate ion respectively.

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![Fig. 5. 2D arrangement of 5 built up by H-bonds involving the aquo ligand with the oxygens of perchlorate anions.](image)

The electronic absorption spectra of the complexes were recorded at room temperature using DMF as the solvent. The spectra of the complexes exhibit transitions lower than 400 nm. The absorption bands at lower than 275 nm correspond to \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions and the weak band at around 300 nm is due to a charge transfer d(Zn)\(\rightarrow\) \(\pi^*\) transition (MLCT).

The binding mode of complex 5 with calf thymus DNA was examined by electronic absorption titration and ethidium bromide (EB) fluorescence displacement experiments. The absorption spectra of the complex 5 in the absence and presence of CT-DNA given in Fig.6. Showed a significant hyperchromism this suggests that there is a strong non-intercalative interaction. The spectral changes of the complex 5 observed in the presence of CT- DNA can be illustrated in terms of groove binding. The apparent association constant \((K_a)\) forthe complex 5 estimated to be \(4.7 \times 10^4\) M\(^{-1}\).

Fluorescence intensity of EB bound to DNA at 522 nm showed a decreasing trend with the increasing concentration of the complex 5 given in Fig.7. The quenching of EB bound to DNA by the complex 5 is in agreement with the linear Stern–Volmer equation (Eqn. 1):

\[
I_0/I = 1 + K_{sv}[Q] \quad \text{(Eqn. 1)}
\]

where \(I_0\) and \(I\) represent the fluorescence intensities in the absence and presence of quencher, respectively. \(K_{sv}\) is a linear Stern–Volmer quenching constant, \(Q\) is the concentration of quencher. In the quenching plot of \(I_0/I\) versus [complex], \(K_{sv}\) value is given by the ratio of the slope to intercept. The \(K_{sv}\) value calculated from the plot...
(Fig.7) of $I_0/I$ versus [complex] for the complex 5 is $1.3 \times 10^3$ ($R = 0.95648$ for four points), suggesting a strong affinity of the complex 5 to CT-DNA.

**Fig.6.** Electronic spectra titration of (a) complex 5 and (b) Plot of $[\text{DNA}] / (\varepsilon_a - \varepsilon_f)$ vs. $[\text{DNA}]$ for the absorption titration of CT-DNA with the zinc(II) complex (5) in Tris–HCl buffer.

**Fig.7.** Emission spectra of the CT-DNA–EB system in tris–HCl buffer upon the titration of (a) complex 5 and (b) Plot of $I_0/I$ vs [complex] for the titration of zinc(II) complex 5 to CT-DNA–EB system.

Number of binding sites can be calculated from fluorescence titration data using the following equation (*Eqn.2*)

$$\log[(I_0 - I)/I] = \log K + n\log[Q] \quad \ldots \ldots \quad (*Eqn.2*)$$

$K$ and $n$ are the binding constant and binding site of complex 5 to CT-DNA respectively. The number of binding sites ($n$) determined from the intercept of $\log[(I_0 - I)/I]$ versus $\log[Q]$ is 0.92 which indicates less association of the complex 5 to the
number of DNA bases, also suggesting strong affinity of the complex 5 through surface or groove binding.

Chapter IV deals with the reactions of Nickel(II) complexes of 1,3-bis(2-pyridylmethylthio)propane (L1) in different chemical environments (Scheme 4).

Scheme 4. Synthetic strategy of the complexes

The X-ray crystal structure analyses of compounds 6 and 8 confirm the formation of neutral complexes where the nickel(II) ion is coordinated by the tetradeutate donor organic moiety L1 by means of the N2S2 donors. The ligand embraces the metal in such a way that pyridine rings are in trans positions, while the two thioether-S donors are located in the equatorial plane beside two azide anions (in complex 6) and thiocyanates (in 8), which are at mutual cis positions and complete the distorted octahedral coordination sphere around metal ion (Fig.8)

Fig.8. ORTEP view of complex 6 (a) and (b) complex 8 with labeling scheme

The infrared spectra of all the complexes exhibit characteristic strong to medium intensity bands in the region of 1468-1472 and 758-762 cm\(^{-1}\), which are assignable to \(\nu_{C=N}\) and \(\nu_{C=S}\), respectively along with other characteristic bands. In addition, the characteristic intense band at ca. 2027 cm\(^{-1}\) for complex 6; 2182 cm\(^{-1}\) for 7; 2082 cm\(^{-1}\)
for 8 are assignable to $\nu_{N_3}$, $\nu_{NCO}$ and $\nu_{NCS}$ respectively. The electronic absorption spectra of complexes 6-8 were recorded at room temperature using DMF as solvent. In octahedral nickel (II) complexes, three spin allowed transitions are expected from the energy level diagram for d$^8$ ions due to $^3A_{2g} \rightarrow ^3T_{1g}$ (P), $^3A_{2g} \rightarrow ^3T_{1g}$ (F), $^3A_{2g} \rightarrow ^3T_{2g}$ transitions, which are observed from low to high wavelengths, respectively.

The redox properties of the complexes were examined by cyclic voltammetry and the voltammetric parameters were studied in the scan rate interval 50–400 mV s$^{-1}$. The cyclic voltammograms exhibit quasi-reversible Ni$^{II}$/Ni$^{III}$ redox couples in dimethylformamide solution and the $E_{1/2}$ values were found to be +0.732, +0.747, and +0.815 V for 6, 7 and 8, respectively in Fig.9. Here, the $E_{1/2}$ value for complex 8 lies at the relatively higher anodic side of the range generally measured, 0.3-0.8 V, for the Ni$^{II}$/Ni$^{III}$ oxidation potential data for thioether containing nickel(II) complexes, indicating that Ni$^{II}$ is fairly stabilised in 8 and this feature may be due to the presence of the soft isothiocyanate ligand compared to the azide and cyanate ones, and also to the chloride coligand. The ratio between the cathodic peak current and the square root of the scan rate ($I_{pc}/\sqrt{\nu}$) is approximately constant. The ratio $I_{pc}$ to $I_{pa}$ is close to unity. From these data, it can be concluded that the redox couple is related to a quasi-reversible one-electron transfer process controlled by diffusion.

![Fig.9](image-url) A representative CV of [Ni(L$^1$)(N$_3$)$_2$] (6) showing quasi-reversible Ni$^{II}$/Ni$^{III}$ redox couple in DMF having [n-Bu4N]ClO$_4$ (0.1 M) as a supporting electrolyte at 298 K (scan rate of 100 mVs$^{-1}$).

Due to structural similarity of the complexes, only the behavior of 8 (among the complexes 6-8) with calf thymus DNA was studied by using absorption and emission spectra. Binding of the nickel(II) complex to CT-DNA helix is examined by an increase of the absorption (ca. 265 nm) of nickel(II). Absorption spectra of 8 in the absence and presence of CT-DNA are given in **figure.10**. The spectral changes of the complex 8 observed in the presence of CT-DNA can be illustrated in terms of groove binding. The apparent association constant ($K_b$) for the complex 8 estimated to be $1.07 \times 10^3$ M$^{-1}$. 
Fig. 10. Electronic spectra titration of (a) complex 8 and (b) Plot of [DNA]/(ε_a-ε_f) vs. [DNA] for the absorption titration of CT-DNA with the Nickel(II) complex 8 in Tris–HCl buffer.

Fluorescence intensity of EB bound to DNA at 522 nm shows a decreasing trend with the increasing concentration of complex 8 (Fig.11a). The quenching of EB bound to DNA by the nickel(II) complexes are in agreement with the help of above mentioned Eqn.1. In the quenching plot (Fig.11b) of I_0/I versus [complex], K_{sv} value is calculated to be 0.69 ×10^4 (R = 0.98035 for four points) that also indicates a strong groove binding interaction of the nickel(II) complex with CT-DNA.

Fig.11. Emission spectra of the CT- DNA–EB system in tris–HCl buffer upon the titration of (a) complex 8 and (b) Plot of I_0/I vs [complex] for the titration of Nickel(II) complex 8 to CT-DNA–EB system.

The synthesis and characterization a new NNS ligand named 2-(pyridin-3-ylmethylsulfanyl)-phenylamine (L^2) along with its coordination behavior towards different Ni(II) salts have been described in Chapter V. In these complexes (9-12), the ligand (L^2) acts as a monodentate neutral N donor ligand though it has three donor
centres since only the pyridinic-N atom coordinates with central nickel(II) ion keeping amine and sulphur atom uncoordinated. The synthetic procedure of the complexes is shown in **Scheme 5**.

**Scheme 5.** Synthetic strategy of the complexes

The crystal structure of [Ni(L\(^2\)]\(_4\)Cl\(_2\)] is shown in **Fig.12**. The complex 9 exists as a mononuclear structure and Ni complex located on a fourfold axis with a symmetry plane and exist as a distorted tetragonal environment with ligand L\(^2\) and two trans chloride anions. The ligand L\(^2\) only acts as a monodentate fashion through the pyridine nitrogen atom, while the amine group remains uncoordinated like a tail. In the equatorial plane, each Ni(II) ion is coordinated by four pyridinic nitrogen atoms and two chloride anions in axial of the octahedron in which the bond lengths of Ni(II)–N(1), Ni(II)–Cl(1) and Ni(II)–Cl(2) are (2.13), (2.44) and (2.45) Å, respectively.

**Fig. 12.** An ORTEP diagram of Ni complex 9 located on a fourfold axis.

Crystal packing of the complex 1 shows polynuclear arrangement through the interaction between chloride atom and amino groups (**Fig.13**), down axis showing N(2)–Cl(1) distances are of 3.64 Å.
The binding interaction of the Ni (II) complex with calf thymus DNA (CT-DNA) has been investigated by using absorption and emission spectra. The absorption spectra of the Nickel (II) complex 9 in the absence and presence of CT-DNA are given in (Fig.14). The extent of the hyper-chromism in the charge transfer band is generally consistent with the strength of interaction and the binding constant K_b for the Nickel (II) complex 9 was estimated to be $1.65 \times 10^5$ M$^{-1}$ (R = 0.99135 for four points) indicating in terms of groove binding.

The fluorescence intensity of EB bound to CT-DNA shows a decreasing trend with the increasing concentration of the complex 9 (Fig.15). The quenching of EB bound to DNA by the complex 9 is in agreement with the help of Eqn.1.

The $K_{sv}$ value calculated from the plot (Fig.16) of $I_0/I$ versus [complex] for the complex 9 is $3.12 \times 10^4$ (R = 0.99529 for four points), suggesting a strong affinity of 9 to CT-DNA in terms of groove binding.
Electrochemical investigations is useful technique to analyse metal-DNA interactions over spectroscopic methods. The binding nature of the Nickel(II) complex 9 with DNA, has been shown in (Fig.17). Equilibrium binding constants $K_R/K_0$ can be calculated by using the shift value of the formal potential ($\Delta E^0$) of Ni(II)/Ni(I) according to the following equation:

$$\Delta E^0 = E_b^0 - E_f^0 = 0.0591 \log(K_R/K_0) \quad \ldots \ldots \quad \text{(Eqn.3)}$$

where $E_b^0$ and $E_f^0$ are the formal potentials of the bound and free complex forms, respectively, and $K_R$ and $K_0$ are the corresponding binding constants for the binding of reduction and oxidation species to DNA, respectively. Ratio of equilibrium binding constants, $K_R/K_0$ is calculated to be 2.17 which indicate the strong binding of DNA with reduced form over oxidised form of nickel complex.

**Fig.15.** Emission spectra of the CT-DNA–EB system in tris–HCl buffer upon the titration of the nickel(II) complex 9. $\lambda_{ex} = 522$ nm.

**Fig.16.** plot of $I_0/I$ vs. [complex] for the titration of nickel (II) complex 9 with CT-DNA–EB system in Tris-HCl buffer.

**Fig.17.** Cyclic voltammograms of complex 9 in Tris–HCl buffer in absence (a) and presence (b) of CT-DNA. $v = 1$ V s$^{-1}$. 

The absorption spectra of BSA in the absence and presence of Ni(II) complex 9 were studied at different concentrations. (Fig. 18a) From this study we observed that absorption of BSA increases regularly upon increasing the concentration of the complex. The value of the apparent association constant (K_app) determined from this plot is \(2.37 \times 10^4\) M\(^{-1}\) (R = 0.99459 for four points) (Fig. 18b).

![Fig. 18. Electronic spectra titration of (a) complex 9 and (b) Plot of 1/(A - A_0) vs. 1/[Complex 9] with BSA at 280 nm in tris-HCl buffer.](image)

The fluorescence emission spectrum of BSA were studied with increasing the concentration of the complex and represented in Fig. 19a. With the addition of complex BSA fluorescence emission is quenched. The fluorescence quenching is described by the Eqn. 1 which discussed above. A linear plot [Fig. 19b] between \(I_0/I\) against [complex] was obtained and from the slope we calculated the \(K_{SV}\) as \(4.51 \times 10^4\) (R = 0.99275 for four points).

![Fig. 19. Fluorescence Quenching of BSA in the presence of various concentrations of the complex 9 (a) and (b) a plot of \(I_0/I\) against [Complex 9]](image)

Antibacterial activity of the ligand (L\(^2\)) and corresponding complexes (9-12) were studied with five pathogenic bacteria. From the antibacterial studies it is inferred that, all complexes have higher activity than ligand.
The synthesis and characterization of a new N$_2$S$_2$ ligand named 3,4-bis(2-pyridylmethylothio)toluene (L$^3$) along with its coordination behavior towards different nickel(II) salts have been described in Chapter VI. On reaction of different Ni(II) salts with L$^3$, three mononuclear Ni(II) complexes, respectively formulated as [Ni(L$^3$)Cl$_2$] (13), [Ni(L$^3$)(N$_3$)$_2$] (14a), [Ni(L$^3$)(NCO)$_2$] (14b) and [Ni(L$^3$)(NCS)$_2$] (14c) were isolated in pure form (Scheme 6) and all the complexes were characterized by have been established by single crystal X-ray crystallography. The X-ray crystal structure analyses of compounds 13, 14a and 14b given in Fig.20, confirm the formation of neutral complexes where the nickel(II) ion is coordinated by the tetradentate donor organic moiety L$^3$ by means of the N$_2$S$_2$ donors. The ligand embraces the metal in such a way that pyridine rings are in trans positions, while the two thioether-S donors are located in the equatorial plane beside two chloride anions (in complex 13), azide (in 14a) and cyanate( in 14b) which are at mutual cis positions, and complete the distorted octahedral coordination sphere around metal ion. In these complexes the Ni-N(py) bond distances (range 2.113(5)-2.144(3) Å) are slightly longer than the Ni-N(pseudohalide) ones that vary from 2.097(5) to 2.109(5) Å, while the Ni-S(1) bond lengths in complex 13 is higher than pseudohalides between 2.4174(19)- 2.3951(14)Å but Ni-S(2) bond length in NiCl$_2$ complex is lower than pseudohalides complexes vary from 2.3887(18)-2.415(2).

Scheme 6. Synthetic route of ligand(L$^3$) and complexes (13, 14a, 14b and 14b)
The groove binding behavior of the Ni(II) complex (13) with calf thymus DNA was observed using absorption and emission spectra. The absorption spectra of the copper(II) complex 13 in the absence and presence of CT-DNA are shown in Fig. 21a. The hypochromism nature in the charge transfer band is consistent with the strength of intercalative binding/interaction. The binding constant (K_b) was found to be $1.01 \times 10^6$ M$^{-1}$ (R = 0.97281) from the figure Fig.21b. This value clearly indicates that the complex 13 interacts with DNA strongly and the spectral changes of the complex observed in the presence of CT-DNA can be rationalized in terms of groove binding.

A decreasing trend of fluorescence intensity at 522 nm due to the binding of ethidium bromide to DNA was observed with the increasing concentration of the nickel(II) complex and it has been depicted in Fig.22a. The quenching of EB bound to DNA by the nickel(II) complexes are in agreement with the help of Eqn.1. The $K_{sv}$ value
for the nickel(II) complex was found to be $2.09 \times 10^4$ (R = 0.95661 for four points) (vide Fig. 22b) and it indicates a strong affinity of the complex, 23 to CT-DNA.

**Fig. 22.** (a) Emission spectra of the CT-DNA–EB system in tris–HCl buffer upon the titration of 13 with CT-DNA at 265 nm; (b) Plot of $I_0/I$ vs [complex 13]

Electrochemical investigation is useful technique to analyse metal-DNA interactions over spectroscopic methods. The binding nature of the nickel(II) complex 13 with DNA, has been shown in (Fig. 23). Cyclic voltammograms of the nickel(II) complex 13 in the absence and presence of CT-DNA is exhibited significant shifts in the anodic and cathodic peak potentials followed by decrease in both peak currents, indicating the interaction existing between the nickel(II) complex and CT-DNA. Equilibrium binding constants $K_R/K_0$ can be calculated by using the *Eqn. 3*. Ratio of equilibrium binding constants, $K_R/K_0$ is calculated to be 1.07 which indicates the strong binding of DNA with reduced form over oxidised form of nickel complex.

**Fig. 23.** Cyclic voltammograms of complex 1 in Tris–HCl buffer in the absence (a) and presence (b) of CT-DNA. $v = 1$ V s$^{-1}$

The absorption spectra of BSA in the absence and presence of Ni(II) complex 13 (other complexes give same binding interaction) at different concentrations were studied(Fig. 24a). The enhancement of absorbance at 280 nm was due to absorption of the surface complex, based on the linear relationship between $1/(A_{\text{obs}} - A_0)$ vs reciprocal concentration of the complex (Fig. 24b) with a slope equal to $1/K_{\text{app}}(A_c - A_0)$ and an intercept equal to $1/(A_c - A_0)$. The value of the apparent association constant ($K_{\text{app}}$) determined from this plot $2.73 \times 10^4$ M$^{-1}$ (R = 0.98362 for four points)
**Fig. 24.** Electronic spectral titration of complex 13 (a) and (b) Plot of $1/(A - A_0)$ vs.
$1/[$Complex 13$]$ with BSA at 280 nm in tris-HCl buffer

The effect of increasing the concentration of the complex, the fluorescence emission spectrum of BSA were studied and represented in **Fig. 25a.** The fluorescence quenching is described by the *Eqn. I.* A linear plot [**Fig. 25b**] between $I_0/I$ against [complex] was obtained and from the slope we calculated the $K_{sv}$ as $1.15 \times 10^3$ (R = 0.9908 for four points).

**Fig. 25.** Fluorescence quenching of BSA (a) in the presence of various concentrations of the complex 13 and (b) Plot of $I_0/I$ against [complex 1] in case of fluorescence quenching of BSA.

Antibacterial activity of the lignd(L$^3$) and corresponding complexes were studied with five pathogenic bacteria. From the antibacterial studies it is indicate that, all complexes have higher activity than ligand. The increased activity of the metal chelates due to lipophilic character of the metal complexes.

A new two series of zinc(II) complexes of two Schiff bases (H$_2$L$_4^4$ and H$_2$L$_5^5$) formulated as [Zn(HL$_4^4$/HL$_5^5$)]ClO$_4$ (15a and 15b) and [Zn(L$_4^4$/L$_5^5$)] (16a and 16b) where H$_2$L$_4^4$ = 1,8-bis(salicylideneamino)-3,6-dithiaoctane and H$_2$L$_5^5$ = 1,9-bis(salicylidene-
amino)-3,7-dithianonane have been prepared and elemental, spectral and other physicochemical results characterize the complexes in Chapter VII. Synthetic procedures of the ligands have been schematically represented in the Scheme 7.

Scheme 7. Synthetic procedure of the ligands and complexes

The hexadentate Schiff bases having N₂S₂O₂ donor centers are hexadentate monoanionic and hexadentate dianionic ligands. On the reaction of H₂L with zinc(II) perchlorate in alcohol, complexes of the type [Zn(HL)]ClO₄ (15) were formed and [Zn(L)] complexes (16) were formed in the presence of Et₃N. Complex 16 was obtained following the similar type of reactions of H₂L with acetate or nitrate salts of zinc(II) even in the absence of a base and we could not isolate complex 15 having the hydrogen bonded counter anion what we observed for zinc(II) perchlorate. The metal ion is bonded to two thioether sulfurs, S(18) and S(21), two imine nitrogens, N(15) and N(45), and two phenolate oxygens, O(11) and O(41). An equatorial plane can be defined by the two oxygens and two sulfurs with the two nitrogens in axial positions (Fig.26).

Fig.26. ORTEP diagram of [Zn(HL₄)]ClO₄ (15a) with labeling scheme
The crystal lattice of 15a consists of discrete [Zn(HL₄)]⁺ cations and perchlorate anions. Thus one phenolate oxygen must be protonated in Fig.27. However, the proton is disordered between the two positions, being 50% bonded to O(11) and 50% bonded to O(41). Thus, two hydrogens cannot coexist so dimers must contain either both O(11) atoms protonated or both O(41) atoms protonated.

**Fig.27.** The structure of 15a showing formation of a hydrogen bonded dimer across a two-fold axis. Phenolate hydrogen atoms are disordered over two sites, being bonded either to O(11) as shown or to O(41)

The spectra exhibit a very strong and sharp absorption band at ca. 1088 cm⁻¹ along with a weak band at ca. 623 cm⁻¹ due to the symmetric (ν₆(ClO₄)) and asymmetric (ν₃(ClO₄)) stretching vibration of perchlorate ion respectively along with a weak band around 3340 cm⁻¹ attributable to νOH. The band around 1595-1615 cm⁻¹ due to νC=N stretching frequency of the Schiff base in addition to the band appeared at ca. 762 cm⁻¹ corresponding to νC=S frequency were observed in the IR spectra of all the complexes. In addition to those the weak bands in the range 2980-2900 cm⁻¹ are assignable to the aliphatic C-H stretching frequency.