



Review Paper

## Metal Complexes of Quinoxaline Derivatives: Review (Part-II)

C. Justin Dhanaraj\* and Jijo Johnson

Department of Chemistry, University College of Engineering, Nagercoil, Anna University Constituent College, Nagercoil 629004, Tamil Nadu, INDIA

Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 9<sup>th</sup> March 2015, revised 10<sup>th</sup> April 2015, accepted 17<sup>th</sup> April 2015

### Abstract

Over the past decades, there is increasing information about synthesis, characterization and applications of metal complexes including quinoxaline derivative metal complexes. The focus of the review is emphasized on synthesis, characterization, structural analysis, theoretical calculations and biological studies of quinoxaline derivative metal complexes. These types of review provide unique platform for systematically studying the various quinoxaline derivative metal complexes synthesized so far and their characterizations. We have also highlighted the synthetic strategies developed to synthesize metal complexes. Several characterizations which are not covered in part-I like CD-spectroscopy are also included in this review paper. This review is also a focus of the reports on the structural aspects that the quinoxaline based ligands plays on compounds reported in last seven years. Furthermore in this review the current progress of research in the field of quinoxaline derivative metal complexes from 2007 to end of 2014 is summarized. The structure was confirmed by single crystal x-ray diffraction studies. An overview of application of quinoxaline derivative metal complexes is also presented. Structural elucidation using Density Functional Theory (DFT) and Time Dependent-Density Functional Theory (TD-DFT) are included. In addition to various biological studies included in the previous part, cytotoxicity, photo cytotoxicity studies, anti-tubercular studies, insulin mimetic activity, anti-trypanosome cruzi activity, anti-proliferative activities are included.

**Keywords:** Quinoxaline, mixed metal, mixed ligand, metal complexes.

### Introduction

Studies on the synthesis of new quinoxaline derivative metal complexes have been of considerable importance because of their interesting chemical as well as biological properties. Quinoxaline derivatives are widely distributed in nature and many of them, such as the antibiotics, levomycin and actinomycin possess very useful biological activity. The complexes of quinoxaline with several metal ions have been studied by various workers. Quinoxaline derivatives has been employed as a bridging ligand in both homobimetallic and heterobimetallic complexes.

**Quinoxaline derivative metal complexes:** Rahman et al <sup>1</sup> reported the a new series of Cu(II) ternary complex with N-(benzoyl) leucinate and n-(acetyl)phenylglycinate and some N-heterocyclic ligands such as quinoxaline (11). The metal complexes were characterized by elemental analysis, IR and EPR spectra and thermogravimetric analysis.

A series of luminescent Ru(II) amidodipyridoquinoxaline biotin (dpq-B) complexes [Ru(N-N)<sub>2</sub>(N-N')](PF<sub>6</sub>)<sub>2</sub> {N-N=2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,7-diphenyl-1,10-phenanthroline (Ph<sub>2</sub>-phen); N-N' = 2-((2-biotinamido)ethyl) amidodipyrido [3,2-f:2',3'-h] quinoxaline(dpq-C<sub>2</sub>-B), 2-((6-biotinamido) hexyl) amidodipyrido [3,2-f:2',3'-h] quinoxaline (dpq-C<sub>6</sub>-B)} were designed as new luminescent

probes for avidin. The electrochemical and photophysical properties of these complexes have been investigated. Upon irradiation, all the complexes exhibited <sup>3</sup>MLCT (dπ(Ru) → π\*(diimine)) emission in fluid solutions at 298 K and in low-temperature glass. In aqueous buffer, due to hydrogen-bonding interactions between the amide moiety of the dpq-B ligands and the water molecules the emission was weak. The avidin binding properties of all the complexes have been studied by 4'-hydroxyazobenzene-2-carboxylic acid (HABA) assays, luminescence titrations, kinetics experiments and confocal microscopy using avidin conjugated microspheres<sup>2</sup>.

Ternary Fe(II) complex [Fe(L<sub>1</sub>)B](PF<sub>6</sub>)<sub>2</sub> {L<sub>1</sub> is formed by FeCl<sub>3</sub> mediated cyclization of N,N'-(2-hydroxypropane-1,3-d iyl) bis (pyridine-2-aldimine) and B is dipyrdo [3,2-d:2',3'-f]quinoxaline (dpq)} was synthesized. The diamagnetic Fe(II) complex with L<sub>1</sub> and B showing respective tetradentate and bidentate chelating modes in a FeN<sub>6</sub> coordination geometry exhibit two metal centered visible electronic bands near 520 and 570 nm in MeCN. The complex binds with calf thymus DNA. DNA cleavage experiments using supercoiled (SC) pUC19 DNA and distamycin-A suggest minor groove binding for the complex. The redox active complex cleaves SC DNA to its nicked circular (NC) form with H<sub>2</sub>O<sub>2</sub> involving hydroxyl radical as the cleavage active species. The complex shows photoinduced DNA cleavage activity at UV light of 365 nm in absence of H<sub>2</sub>O<sub>2</sub> via singlet oxygen mechanism. Complex of

d<sub>pq</sub> and shows relatively poor DNA cleavage activity at visible light<sup>3</sup>.

Miao et al<sup>4</sup> reported a structurally diverse supramolecular complex,  $\{[(\text{bpy})_2\text{Os}(\text{dpp})]_2\text{Ru}\}_2(\text{dpq})](\text{PF}_6)_{12}$  {bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine and dpq = 2,3-bis(2-pyridyl) quinoxaline}. The supramolecular assembly contains four light absorbing Os metal centers coupled to two Ru metal centers linked by two different bridging ligands (BL) capped by bpy terminal ligands. This supramolecule possesses LUMO localized on the central  $\mu$ -dpq bridging ligand and a HOMO localized on the terminal Os centers, providing significant spatial separation of these donor and acceptor orbitals. The above hexametallic complex absorbs throughout the visible region due to overlapping<sup>1</sup> MLCT transitions from the Os and Ru chromophores to each  $\pi$ -acceptor ligand.

The interactions between the chiral metal complexes  $\Delta$ - and  $\Lambda$ -[Co(phen)<sub>2</sub>dpq]<sup>3+</sup> {phen=1,10-phenanthroline and dpq=dipyrido[3,2-d:2',3'-f]quinoxaline,  $\Delta$ =D and  $\Lambda$ =L} and sheared DNA d(CCGAATGAGG)<sub>2</sub> were studied with molecular modeling method. The results reveal that the interactions show enantioselectivity, groove-selectivity and site-specificity<sup>5</sup>.

Three novel Cd(II) metal complexes were synthesized hydrothermally and their structures were determined by X-ray analysis. They used dipyrido[3,2-d:2',3'-f]quinoxaline (Dpq) and three structurely related benzene-dicarboxylic acid ligands (benzene-1,3-dicarboxylic acid benzene-1,2-dicarboxylic acid and biphenyl-4,4'dicarboxylic acid). The Dpq ligand takes chelating coordination mode while the other two nitrogen atoms did not coordinate to the Cd(II) ions. The three benzene dicarboxylate were able to link Cd(II) ions in various coordination modes, gives 1,2 and 3-dimensional Cd(II) complexes. In addition the complexes exhibit blue/green emission in the solid state at room temperature<sup>6</sup>.

Plitt et al<sup>7</sup> reported dipyrrolyl quinoxaline based anion receptors for emission based selective detection of dihydrogen phosphate. Here for the synthesis of receptors, dipyrrolyl quinoxaline coordinated to transition metals are used. Kemp et al<sup>8</sup> reported Pt(II)-based metallointercalators of dipyrido [3,2-d:2',3'-f] quinoxaline (dpq) as bridging ligand. They used the chiral ancillary ligands 1S,2S-diaminocyclohexane (S,S-dach) and 1R,2R-diaminocyclohexane (R,R-dach). The cytotoxicity of the complexes in L1210 murine leukaemia cell line was determined using growth inhibition assays. They also studied the DNA binding studies of the synthesized complexes.

The determination of composition and stability constants of Cd(II)-2-aminoquinoxaline complexes in 25, 50 and 75% (by volume) aqueous methanol solution was reported. The complexes formed by 2-aminoquinoxaline are very weak. The low stabilities of the complexes of 2-aminoquinoxaline may be due to the less tendency of the amino-group to donate electrons because of delocalization of electrons in the heterocyclic ring<sup>9</sup>.

Mononuclear Ni(II) and Cu(II) complexes of (E,E)-dioxime, 7,8-bis(hydroxyimino)-1,14-bis(monoaza[8]crown-6)-benzo[f]-4,11-dioxa-1,14-diazadecane[7,8-g]quinoxaline (H<sub>2</sub>L), has been synthesized. The complexes have a M:L ratio of 1:2 and the ligand coordinates through two hydroxyimino nitrogen atoms. Structure of the ligand and its complexes are assigned using elemental analysis, magnetic susceptibility measurements, <sup>1</sup>H, <sup>13</sup>C NMR, IR and MS spectral data<sup>10</sup>.

Ghosh et al<sup>11</sup> reported the chemistry of first row transition metal complexes prepared from the ligand dipyrido[3,2-f:2',3'-h]quinoxaline (dpq). They studied the structural properties of three polymorphic Cu(II) complexes viz. [Cu(dpq)<sub>2</sub>(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, [Cu(dpq)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) and [{Cu(dpq)<sub>2</sub>(H<sub>2</sub>O)}{Cu(dpq)<sub>2</sub>(ClO<sub>4</sub>)}] (ClO<sub>4</sub>)<sub>3</sub>. The compound [Cu(dpq)<sub>2</sub>(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O has a distorted trigonal bipyramidal structure. In [Cu(dpq)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) the Cu(II) centre has a distorted square planar geometry. The structure determination of [{Cu(dpq)<sub>2</sub>(H<sub>2</sub>O)}{Cu(dpq)<sub>2</sub>(ClO<sub>4</sub>)}] (ClO<sub>4</sub>)<sub>3</sub> has established the presence of two different complex cations in the asymmetric unit and they are considered as co-crystals. In the Zn(II) compound [Zn(dpq)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>], the two perchlorates are unidentately coordinated to the metal centre, providing a distorted octahedral geometry. The quinoxaline ring in it is involved in intermolecular  $\pi$ - $\pi$  interactions, leading to the generation of a sinusoidal chain. The <sup>1</sup>H NMR spectra of the paramagnetic complexes [Ni(dpq)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Co(dpq)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> have been studied in detail. The electronic absorption spectra and the redox behaviour of the Co(II), Co(III), Cu (I) and Cu(II) complexes have been studied.

Synthesis of [Pd(pa)(pyq)Cl], [Ag(pa)(pyq)] and trans-[UO<sub>2</sub>(pa)(pyq)](BPh<sub>4</sub>) {Hpa=2-piperidine-carboxylic acid and pyq=2(2'l)quinoxaline} and their elemental analyses, conductance, thermal measurements, Raman, IR, electronic, <sup>1</sup>H NMR and mass spectra have been discussed. 2-Piperidine-carboxylic acid and its Pd complex have been tested as growth inhibitors against Ehrlich ascites tumour cells (EAC) in Swiss albino mice<sup>12</sup>. Therrien et al reported mono and dinuclear arene Ru complexes containing 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline as chelating ligand. The crystal strcture of some complexes were also reported<sup>13</sup>.

Organic ultraviolet (UV) detector based on photovoltaic (PV) diode was established by using a phosphorescent Cu-complex and a diamine derivative as electron acceptor and electron donor respectively. The Cu-complex is Cu(DPEphos) ((phen))BF<sub>4</sub> {DPEphos and phen denote 6,7-dicyanodipyrido[2, 2-d: 2', 3'-f]quinoxaline and 1, 10-phenanthroline} and the diamine derivative, m-MTDA is 4, 4', 4"-tris-(2-meth-ylphenyl phenylamino) triphenylamine. The UV diode is highly sensitive to UV light and has no response to the visible light larger than 400 nm<sup>14</sup>.

Novel [Cu<sub>2</sub>(Dpq)<sub>2</sub>(Ac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and [Cu(Dpq)<sub>2</sub>(H<sub>2</sub>O)] (ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O complexes {where Dpq =

dipyrido [3,2-d:2',3'-f]quinoxaline, Ac=acetate} were prepared by electrostatic layer-by-layer self-assembly technique. The complexes have been synthesized and structurally characterized by elemental analyses, IR spectroscopy and single crystal X-ray diffraction analyses. Single crystal X-ray analyses show that the complexes possess a dinuclear and mononuclear structures respectively and are extended into layered frameworks by  $\pi$ - $\pi$  stacking and hydrogen-bonding interactions. The multilayer films were characterized by UV-Vis. spectroscopy, fluorescence spectroscopy, small angle X-ray reflectivity measurements and atomic force microscopy (AFM) imaging<sup>15</sup>.

Lin et al<sup>16</sup> reported the synthesis, photophysical and anion sensing properties of quinoxaline bis(sulfonamide) functionalized receptors and their metal complexes. The synthesis, resolution and characterization of novel Ru(II) complexes have been reported. Four mononuclear complexes,  $[\text{Ru}(\text{dpq})_2(3\text{-Br-phen})]^{2+}$ ,  $[\text{Ru}(\text{dpq})_2(4\text{-Cl-phen})]^{2+}$ ,  $[\text{Ru}(\text{dpq})_2(5\text{-Cl-phen})]^{2+}$  and  $[\text{Ru}(\text{dpq})_2(\text{phen})]^{2+}$  were synthesised {where dpq=dipyrido[3,2-d: 2',3'-f]quinoxaline, phen=1,10-phenanthroline, 3-Br-phen = 3-bromo-1,10-phenanthroline, 4-Cl-phen=4-chloro-1,10-phenanthroline, 5-Cl-phen=5-chloro-1,10-phenanthroline}. These complexes were resolved using the chiral TRISPHAT anion, [tris(tetrachlorocatecholato)phosphate]. All metal complexes were characterised by  $^1\text{H}$  NMR, ESI-MS, UV-Vis. and luminescence spectroscopy. Resolved metal complexes were further characterized using CD spectroscopy and chiral  $^1\text{H}$  NMR titrations<sup>17</sup>.

Mononuclear Ni(II) and Cu(II) complexes of 13,14-bis(Hydroxyimino)-4,7-bis (ferrocenylmethyl)-2,3,4,5,6,7,8, 9-octahydrobenzo[k]-4,7-diaza-1,10-dithiacyclododecene[13,14-g]-quinoxaline ( $\text{H}_2\text{L}$ ) has been prepared. The complexes of  $\text{H}_2\text{L}$  have a metal ligand ratio of 1:2 and the ligand coordinates through two nitrogen atoms. The homotrinuclear  $[\text{Cu}(\text{L})_2\text{Cu}_2(\text{dipy})_2](\text{NO}_3)_2$  compound coordinates to the other two Cu(II) ions through deprotonated oximate oxygens and two 2,2'-dipyridyl as an end-cap ligand to yield the trinuclear structure. The ligand and its complexes have been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, MS spectroscopy and elemental analyses<sup>18</sup>.

New quinoxaline substituted vicinal dioxime ligand containing bis(12-diazacrown-4) units ( $\text{H}_2\text{L}$ ) and its mononuclear Ni(II) and Cu(II) complexes and a trinuclear Cu(II) complex were also synthesized. The mononuclear Cu(II) species coordinated to two Cu(II) ions through the deprotonated oximate oxygens to yield a trinuclear structure cis-bridged by the oximate groups with 1,10-phenanthroline as an end-cap ligand. The mononuclear Co(III) complex of  $\text{H}_2\text{L}$  was isolated with pyridine and chlorine as axial ligands. In addition, a Co(III) complex containing the  $\text{BF}_2^+$  bridge macrocycle was synthesized using a precursor hydrogen bridged Co(III) complex via a template effect. Structures of the ligands and metal complexes were solved by elemental analyses,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, FT-IR, UV-Vis. and mass spectra<sup>19</sup>.

VO(IV) complexes,  $[\text{VO}(\text{salmet})(\text{B})]$  and  $[\text{VO}(\text{saltrp})(\text{B})]$  {salmet=N-Salicylidene-L-methionate, saltrp=N-salicylidene-L-tryptophanate and B = dipyrido-3,2-d:2'3'f quinoxaline (dpq)} of N-salicylidene  $\alpha$ -amino acids and dpq were prepared, characterized and their DNA binding and photo induced DNA cleavage activities were studied. The complexes show good binding property to calf thymus DNA. The complex exhibits an irreversible oxidative cyclic voltammetric response near 0.8 V, assignable to the V(V)/V(IV) couple and a quasi reversible V(IV)/V(III) reduction. The binding site size, thermal, melting and viscosity data suggest DNA surface and/ or groove nature of the complexes. The complexes show poor chemical nuclease activity in the dark and in the presence of 3-mercaptopropionic acid or hydrogen peroxide. The complexes show efficient DNA cleavage on irradiation and also they show significant DNA cleavage activity on photo excitation in red light<sup>20</sup>.

Visible light induced DNA cleavage activity of dipyridoquinoxaline (dpq) complexes of bivalent 3d-metal ions, viz;  $[\text{Fe}^{II}(\text{dpq})_3](\text{PF}_6)_2$ ,  $[\text{Co}^{II}(\text{dpq})_3](\text{ClO}_4)_2$ ,  $[\text{Ni}^{II}(\text{dpq})_3](\text{ClO}_4)_2$ ,  $[\text{Cu}^{II}(\text{dpq})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$ ,  $[\text{Zn}^{II}(\text{dpq})_3](\text{ClO}_4)_2$  and  $[\text{Zn}^{II}(\text{dpq})_2(\text{DMF})_2](\text{ClO}_4)_2$  (DMF = N,N'-dimethylformamide) have been reported by Roy et al<sup>21</sup>. The X-ray crystal structures of  $[\text{Fe}^{II}(\text{dpq})_3](\text{PF}_6)_2$  and  $[\text{Zn}^{II}(\text{dpq})_2(\text{DMF})_2](\text{ClO}_4)_2$  were also reported. All the complexes show efficient binding property to calf thymus DNA. The diamagnetic Fe(II) and Zn(II) complexes show DNA cleavage only in UV light. DNA cleavage activity at 365 nm involving singlet for the Fe(II), Ni(II), Cu(II) and Zn(II) complexes and hydroxyl radical for the Co(II) species. The ligands are alone inactive in cleaving the SC DNA at 365 nm.

The synthesis and spectroscopic properties of 5,6-didodecyloxyquinoxaline-2-(1H)-one oxime, 2,2'-azobis[5,6-didodecyloxyquinoxaline] and cyclopalladated complex di- $\mu$ -acetato-2,2'-azobis[5,6-didodecyloxyquinoxaline] dipalladium (II) were reported. The novel compounds were characterized by elemental analysis, FT-IR spectroscopy,  $^1\text{H}$  NMR spectroscopy, UV-Vis. spectroscopy and mass spectrometry. 5,6-Didodecyloxyquinoxaline-2-(1H)-one oxime exhibited liquid crystalline properties, as determined using differential scanning calorimetry, optical polarizing microscopy and X-ray investigation. The compound displayed a discotic mesophase over a large temperature interval that included room temperature. X-ray diffraction studies revealed that this compound forms a discotic hexagonal ordered columnar mesophase (Colho) and thus, has potential use as a colored liquid crystal<sup>22</sup>.

The complexes  $\text{Pt}(\text{pq})\text{Cl}_2$  and  $\text{Pt}(\text{pq})(\text{bdt})$  {wpq=2-(2'pyridyl) quinoxaline and bdt=benzene-1,2-dithiolate} have been synthesized and characterized by UV-Vis., FTIR, 1, 2D NMR and cyclic voltammetry. Interactions of the complexes and the free ligands pq and bdt with double stranded CT-DNA were studied by UV-spectrophotometric and circular dichroism (CD) measurements. The results suggest that both complexes are able to form adducts with DNA and to distort the double helix by

changing the base stacking. Pt(pq)(bdt) forms stronger adducts to CT DNA than Pt(pq)Cl<sub>2</sub> and this is due to the substitution of the chlorine atoms of Pt(pq)Cl<sub>2</sub> by the 1,2-dithiolate ligand (bdt) in Pt(pq)(bdt). It also exhibited some cytotoxic effect on the SF-286 cells<sup>23</sup>.

Cu(II) complexes with 3-aminoquinoxaline-2-carbonitrile-N<sub>1</sub>,N<sub>4</sub>-dioxide derivatives as ligands were synthesized and characterized by different spectroscopic methods. The hypoxic selective cytotoxicity towards V79 cells and the superoxide dismutase like activity of the complexes were also determined and related to physicochemical properties of the compounds. The Cu(II) complex with 3-amino-6-chloro-7-fluoroquinoxaline-2-carbonitrile-N<sub>1</sub>,N<sub>4</sub>-dioxide showed cytotoxic selectivity in hypoxia being the most lipophilic compound of the series. The complex with 3-aminoquinoxaline-2-carbonitrile-N<sub>1</sub>,N<sub>4</sub>-dioxide was cytotoxic but not selective and that with 3-amino-7-chloro-6-methoxy-quinoxaline-2-carbonitrile-N<sub>1</sub>,N<sub>4</sub>-dioxide was not cytotoxic towards V79 cells neither in oxia nor in hypoxia in the assayed conditions<sup>24</sup>.

The structure and redox properties of metal complexes of the electron deficient diphosphine chelate ligand 2,2-bis(tert-butylmethylphosphino)-quinoxaline (L) (1) have been reported by Das et al<sup>25</sup>. They synthesized and crystallographically characterized the (L)PtCl<sub>2</sub> (2), (L)PdCl<sub>2</sub> (3) and (L)Re(CO)<sub>3</sub>Cl (4). The crystallographical and NMR studies revealed that the quinoxaline N-donors do not participate in any coordination to the metals. Electron acceptance by the quinoxaline heterocycle is responsible not only for the improved stability of L towards air but also for rather reduction of the complexes to the persistent radical anions 1<sup>·-</sup> and 3<sup>·-</sup>. The reduction to 2<sup>·-</sup> proceeds irreversibly even at 243 K in the absence of excess chloride.

The reaction of 1,4-dihydro-2,3-quinoxalinedione with CuCl<sub>2</sub> in the presence of LiOH in DMF has led to the 3D coordination polymer [Cu<sub>3</sub>L<sub>2</sub>Cl<sub>2</sub>(DMF)<sub>4</sub>]<sub>n</sub>. {L<sup>2-</sup> = 2,3-dioxyquinoxalinate}. It was the first coordination polymer of any transition metal featuring L<sup>2-</sup> and contains the ligand in a novel 3.1111 (Harris notation) coordination mode. IR data are discussed in terms of the chemical composition of the polymer and the coordination mode of L<sup>2-</sup>. Variable-temperature (2-300 K) magnetic susceptibility and variable-field magnetization studies reveal that L<sup>2-</sup> propagates weak antiferromagnetic exchange interactions through its quinoxaline moiety<sup>26</sup>.

A series of complexes based on the flexible ligand 2,3-bis(triazol-1-ylmethyl)quinoxaline were synthesized and characterized by elemental analyses, IR spectroscopy, thermogravimetric analyses and single crystal X-ray diffraction. The results reveal that the coordination geometry of metal ions and the coordinating abilities of the counterions play important roles in defining the overall structure of metal-organic frameworks. In addition, the fluorescent properties of some synthesized complexes and ligand were also investigated<sup>27</sup>. Wang et al<sup>28</sup> reported the hydrothermal synthesis of some new

new Zn(II) metal-organic coordination polymers, [Zn<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>(Dpq)<sub>2</sub>.H<sub>2</sub>O, [Zn(L<sub>2</sub>)(Dpq)(H<sub>2</sub>O)], [Zn(L<sub>3</sub>)(Dpq)(H<sub>2</sub>O)]<sub>2</sub>, [Zn(Dpdq)(L<sub>3</sub>)] and [Zn(Dpdq)(L<sub>4</sub>)].H<sub>2</sub>O {Dpq=dipyrido [3,2-d:2', 3'-f] quinoxaline, Dpdq = 2,3-di-2-pyridylquinoxaline, H<sub>2</sub>L<sub>1</sub>=benzene-1,2-dicarboxylic acid, H<sub>2</sub>L<sub>2</sub>=benzene-1,3-dicarboxylic acid, H<sub>2</sub>L<sub>3</sub>=benzene-1,4-dicarboxylic acid, H<sub>2</sub>L<sub>4</sub>=biphenyl-4,4'-dicarboxylic acid}. The synthesized coordination polymers were structurally characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction analyses.

Kozlov and Goldberg<sup>29</sup> reported the supramolecular interaction pattern in the Zn(II) dichloride and Sn(IV) tetrachloride complexes with dipyrido[f,h]quinoxaline-6,7-dicarbonitrile. The structures of the complexes were studied by X-ray diffraction analysis. Fitchett et al<sup>30</sup> reported the synthesis and X-ray crystal structures of metal complexes of three isomeric bibenzodiazines. In the complexes 2,2'-biquinoxaline shown to offer two modes of coordination; in the first it act as stepped-linear bridging ligand using the two less hindered nitrogen atoms, in the second mode it chelates to Cu(I) centres using its more hindered nitrogen atoms. The presence of the fused heterocyclic ligands leads to a higher priority for π-π stacking of the heterocyclic ligands within the complexes.

A series of mixed ligand Ru(II) complexes [Ru(Hdpa)<sub>2</sub>(diimine)](ClO<sub>4</sub>) {Hdpa is 2,2'-dipyridylamine and diimine is dipyrido[3,2-d:2',3'-f]quinoxaline (dpq) and 5-methyldipyrido[3,2-d:2',3'-f]quinoxaline (mdpq)} have been isolated and characterized by analytical and spectral methods. The interaction of the complexes with CT DNA has been explored by using absorption, emission spectral, viscometry and electrochemical techniques. The DNA binding affinity of the complexes decreases with decrease in number of planar aromatic rings in the co-ligand supporting the intercalation of the diimine co-ligands in between the DNA base pairs. Upon interaction with CT DNA all the complexes show an increase in anodic current in the cyclic voltammograms suggesting that they are involved in electrocatalytic guanine oxidation<sup>31</sup>.

A mononuclear complex Pt(pq)(bdt) {pq=2-(2'pyridyl) quinoxaline and bdt=benzene-1,2-dithiolate} has been prepared and characterized by NMR spectroscopy, ES mass spectroscopy and elemental analysis. The molecular and electronic structure was fully elucidated by means of the density functional theory (DFT) and time-dependent density functional theory (TDDFT). Interactions of complex Pt(pq)(bdt), the free ligands pq and bdt with double stranded CT DNA before and after illumination were studied by UV-spectrophotometric and circular dichroism (CD) measurements. The results indicate that the complex form adducts with DNA and to distort the double helix by changing the base stacking<sup>32</sup>.

A set of three Cu(II) complexes, [Cu<sup>II</sup>(dpq)<sub>2</sub>Cl<sub>2</sub>], [{Cu<sup>II</sup>(dpq)<sub>2</sub>(SCN)}{Cu<sup>II</sup>(dpq)(SCN)<sub>3</sub>}] and [Cu<sup>II</sup>(dpq)<sub>2</sub>(N<sub>3</sub>)](ClO<sub>4</sub>) were derived from the ligand dipyrido [3,2-f: 2',3'-h]-

quinoxaline (dpq) have been reported by Biswas et al<sup>33</sup>. The molecular and the crystal structures of all the complexes have been determined by X-ray crystallography.  $[\text{Cu}^{\text{II}}(\text{dpq})_2\text{Cl}_2]$  has a distorted octahedral geometry with a  $[\text{Cu}_4\text{N}_4\text{Cl}_2]$  core. Compound  $\{[\text{Cu}^{\text{II}}(\text{dpq})_2(\text{SCN})] \cdot [\text{Cu}^{\text{II}}(\text{dpq})(\text{SCN})_3]\}$  consists of a cationic part,  $[\text{Cu}^{\text{II}}(\text{dpq})_2(\text{SCN})]^+$  and an anionic part,  $[\text{Cu}^{\text{II}}(\text{dpq})(\text{SCN})_3]^-$ . In both the cationic and anionic part, the geometry around the Cu(II) ion is distorted square pyramidal. In  $[\text{Cu}^{\text{II}}(\text{dpq})_2(\text{N}_3)] (\text{ClO}_4)_2$ , one azide anion is coordinated to the metal centre and has a distorted square pyramidal geometry. The quinoxaline ring in the first two complexes is involved in intermolecular  $\pi$ - $\pi$  interactions leading to the generation of a sinusoidal chain and a zigzag chain respectively. The electronic absorption spectra and the redox behaviour of all the complexes have been studied.

Co(II), Ni(II), Cu(II) and Zn(II) metal complexes of general formula  $[\text{M}(\text{TpPh})(\text{B})](\text{ClO}_4)$  {where TpPh is anionic tris(3-phenylpyrazolyl)borate, and B is N,N-donor heterocyclic base dipyrido[3,2-d:2',3'-f] quinoxaline (dpq)}, were reported. The complexes were characterized by various physicochemical methods. DNA binding studies were carried out using various spectral techniques and from viscosity measurements. The complexes show moderate binding propensity to CT DNA. The complexes exhibit poor DNA cleavage activity in the dark in the presence of 3-mercaptopropionic acid (MPA) or hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The photoinduced DNA cleavage activity of the complexes was also investigated. The complexes show efficient photoinduced DNA cleavage activity via a metal assisted photo excitation process involving the formation of singlet oxygen as the cleavage active species in a type-II pathway. Steric protection of the photoactive quinoxaline moiety of the dpq ligand inside the hydrophobic  $\{\text{M}(\text{TpPh})\}$  molecular bowl has a positive effect on the photoinduced DNA cleavage activity<sup>34</sup>.

Hydrothermal synthesis of two coordination polymers,  $[\text{Cu}_3(1,3-\text{BDC})_4(\text{Dpq})_2]$  and  $[\text{Cu}_2(\text{BTC})(\text{OH})(\text{Dpq})_2] \cdot \text{H}_2\text{O}$  were reported. {1,3-H<sub>2</sub>BDC=1,3-benzenedicarboxylate, H<sub>5</sub>BTC=1,3,5-benzenetricarboxylate and Dpq = dipyrido[3,2-d:2',3'-f]quinoxaline}. X-ray diffraction analysis reveal that each trinuclear Cu(II) cluster is bridged by two coordination modes of 1,3-BDC ligands to form one-dimensional (1-D) chain structure in complex  $[\text{Cu}_3(1,3-\text{BDC})_4(\text{Dpq})_2]$ . The  $[\text{Cu}_2(\text{BTC})(\text{OH})(\text{Dpq})_2] \cdot \text{H}_2\text{O}$  complex has a two-dimensional (2-D) layer network composed of dinuclear  $[\text{Cu}_2(\text{OH})(\text{Dpq})_2]$  unit and bridging ligand BTC<sup>35</sup>.

Ternary Cu(II) complexes,  $[\text{Cu}(\text{l-trp})(\text{B})(\text{H}_2\text{O})](\text{NO}_3)_2$  and  $[\text{Cu}(\text{l-phe})(\text{B})(\text{H}_2\text{O})](\text{NO}_3)_2$  of l-tryptophan(l-trp) and l-phenylalanine (l-phe) having phenanthroline bases (B), viz. dipyrido[3,2-d:2',3'-f] quinoxaline (dpq), were prepared and characterized by physico-chemical techniques. All the complexes display good

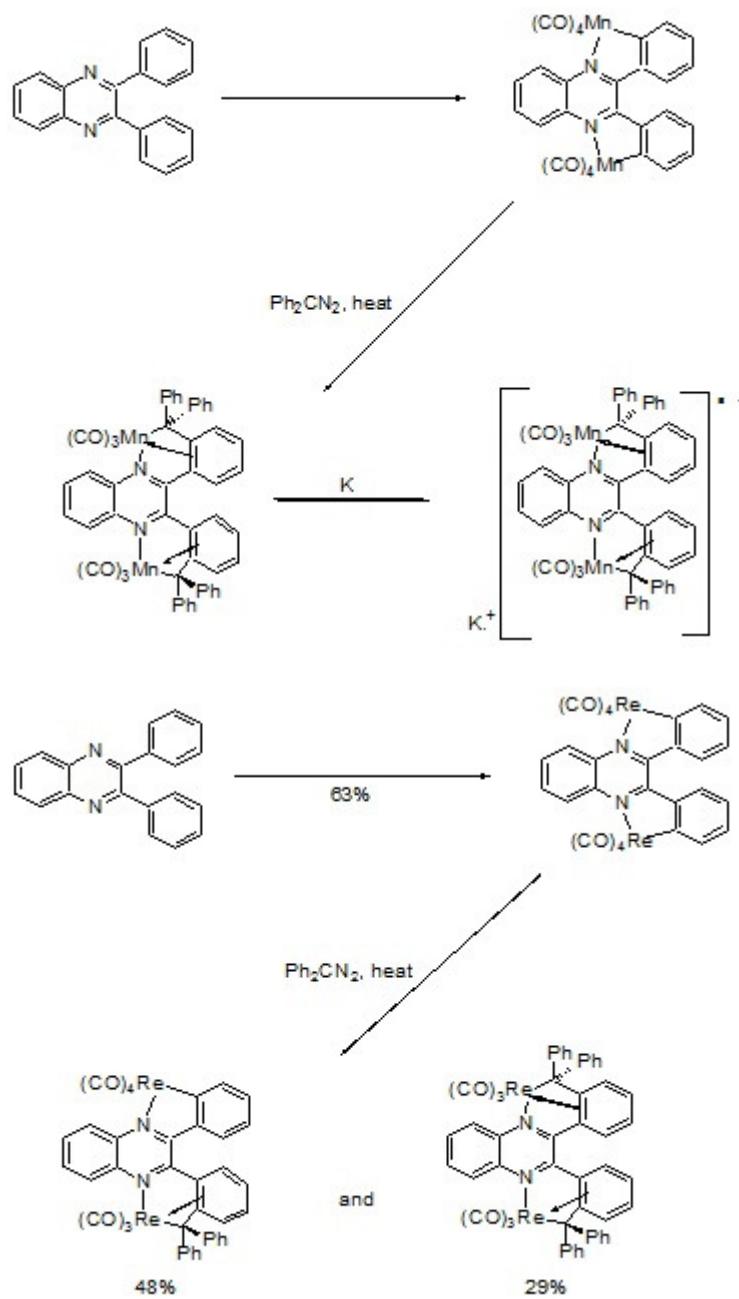
binding propensity to CT DNA. The dpq complexes are minor groove binders. The red light induced DNA cleavage involves metal-assisted photosensitization of l-trp and dpq base resulting in the formation of a reactive singlet oxygen species<sup>36</sup>.

Lahiri et al<sup>37</sup> reported binuclear Cu(II) complexes  $\{(\text{dpq})\text{Cu}^{\text{II}}\}_2(\mu\text{-dtdp})_2$  and  $\{(\text{dpq})\text{Cu}^{\text{II}}\}_2(\mu\text{-az})_2$  {az = azelaic acid (nonanedioic acid) and dipyrido[3,2-d:2',3'-f] quinoxaline (dpq)} were prepared and characterized by physicochemical methods. The complexes show good binding propensity to CT DNA. The photoinduced DNA cleavage activity of the complexes has been studied using 365 nm UV light and 647.1 nm and > 750 nm red light under both aerobic and anaerobic conditions. An enhancement of the DNA cleavage activity under argon has been observed upon increasing the concentration of the DMF solvent in the DMF-Tris buffer medium. The azelate complex of the dpq ligand cleaves DNA in air.

Quinoxaline-pyridine hybrids distributed with long chain alkoxy ethers were synthesized. These compounds self assemble with tetrahedral Cu(I) and Ag(I) to form a double-decker, amphiphilic complexes having a metallocyclophane topology cyclophanes. The di copper(I) metallocyclophanes and its disilver(I) homologues were characterized by inversion symmetry<sup>38</sup>.

Massoud et al<sup>39</sup> reported the synthesis and crystal structure of Cu(II) complex with quinoxaline (qux). In the complex  $[\text{Cu}(\text{qux})(\text{NO}_3)_2]_n$ , quinoxaline acts as a bidentate bridging ligand giving a 1-D chain. Nitro groups undergo chelation with copper and forms square planar complex. The copper as well as both nitrate groups were situated on a crystallographic mirror plane. The Cu(II) is tetra coordinated by two quinoxaline groups and two nitrate groups to form a distorted square planar geometry. The two nitrate groups connect terminally to Cu(II) via oxygen with Cu-O bond. IR and UV-Vis. spectra of the complex also support the crystal structure.

Radical anions derived from tricarbonyl manganese and tricarbonyl rhenium bound quinoxaline chelates were prepared (scheme-1)<sup>40</sup> from neutral substrates by chemical reduction over alkaline metals (K, Rb) and characterized. The electronic structure of the metalloorganic paramagnetic salts was investigated by using structural X-ray diffraction analysis, electrochemistry, solution and crystal EPR spectroscopy. Neutral quinoxaline complexes reveal that, reduction does not have any significant impact over the coordination mode of the metal centers and overall geometry of the triple decker architecture. The DFT studies show that the two metal centers bound to the nitrogen atoms of the quinoxalyl contribute in the HOMO-LUMO gap in the neutral species.



Scheme-1

Bolink et al.<sup>41</sup> reported  $(\text{Ir}(\text{MDQ})_2(\text{acac})$  {Ir(III)bis(2-methyldibenzo-[f,h]quinoxaline (acetylacetone)} as orange dye for the synthesis of white hybrid organic-inorganic light-emitting diode. Four new Pd(II) complexes with the formula  $\text{Pd}(\text{L})_2$  {where L are quinoxaline-2-carbonitrile  $\text{N}_1,\text{N}_4$ -dioxide derivatives} were synthesized and characterized by elemental, conductometric and thermogravimetric analyses, FAB-MS, electronic, FTIR and  $^1\text{H}$  NMR spectroscopies. The complexes were also subjected to cytotoxic evaluation on V79 cells in

hypoxic and aerobic conditions. The synthesized complexes showed different *in-vitro* biological behavior depending on the nature of the substituent on the quinoxaline ring<sup>42</sup>.

A novel metal organic framework  $[\text{Cu}_2(\text{bpdc})_2(\text{Dpq})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$  has been synthesized by hydrothermal reaction. {where,  $\text{H}_2\text{bpdc}$ =biphenyl-4,4'-dicarboxylic acid and  $\text{Dpq}$ =dipyrido[3,2-d:2',3'-f]quinoxaline} and structurally characterized by elemental analysis, IR, TG and

single-crystal X-ray diffraction analysis. Single-crystal X-ray diffraction analysis of  $[\text{Cu}_2(\text{bpdc})_2(\text{Dpq})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$  showed the presence of one-dimensional (1-D) zigzag polymeric chains in the complex. The electrochemical behavior and electrocatalysis of Cu-CPE have been studied. The results indicate that Cu-CPE give one-electron quasi-reversible redox waves in potential range of 400-300 mV due to the metal copper ion Cu(II)/Cu(I). The Cu-CPE showed good electrocatalytic activity toward the reduction of the bromate, nitrite and hydrogen peroxide<sup>43</sup>.

Maity et al<sup>44</sup> reported the photoinduced DNA cleavage activity of ferrocene conjugated ternary Cu(II) complex  $[\text{Cu}(\text{L})(\text{B})(\text{ClO}_4)_2]$  { L=FeCH<sub>2</sub>N(CH<sub>2</sub>Py)<sub>2</sub>, Fc=(η-C<sub>5</sub>Fe<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), B=dipyrido[3,2-d:2',3'-f]quinoxaline(dpq)} . The complex showed good DNA binding and cleaving activities. Ternary Fe(III) complex [FeL(B)] of a trianionic tetradeятate phenolate-based ligand (L) and phenanthroline base (B), dipyridoquinoxaline (dpq) have been prepared and structurally characterized and their DNA binding, cleavage and photocytotoxic properties were studied. The complex with a FeN<sub>3</sub>O<sub>3</sub> core show the Fe(III)/Fe(II) redox couple and a binding propensity to both calf thymus DNA and bovine serum albumin (BSA) protein. It also exhibit red-light-induced DNA cleavage activity.

Synthesis and luminescent study of Iridium complexes containing new dipyridylaquinoxaline derivatives were reported. The main ligand used was 6-methoxy-2,3-bis(4-methoxyphenyl)quinoxaline and the acetylacetone and pyrazolonates were used as ancillary chelating ligands. The photoluminescence of the prepared complexes were observed around 660 nm and electroluminescence maxima were observed around 650 nm<sup>45</sup>. The electrochemical studies of newly synthesized complexes cis-[RuCl<sub>2</sub>(L)(pph<sub>3</sub>)<sub>3</sub>] {L=2-(2'-pyridyl)quinoxaline} was reported. The electrochemical studies include CV, EIS and ESI-MS<sup>46</sup>. Three new mixed chelate copper complexes with 3-aminoquinoxaline-2-carbonitrile-N<sub>1</sub>N<sub>4</sub>-dioxide derivatives and alanine as ligand were reported. The spectroscopic characterization (FT-IR, EPR, UV-Vis.) show that copper coordinated through the amine and the N-oxide groups of quinoxaline derivatives and carboxylate moieties from alanine forming a dimeric species. All the complexes showed *in-vitro* anti tubercular activity but they are inactive against *E. Coli* and *S. aureus*<sup>47</sup>.

Patra et al<sup>48</sup> reported the synthesis, characterization and red light induced DNA cleavage activity of a Cu(II) complex,  $[\text{Cu}(\text{L-arg})(\text{Dpq})\text{Cl}]\text{Cl}$ . The complex showed photocleavage activity in red light due to the presence of two photosensitizers, namely L-arginine and dpq in the complex molecule. Cui et al<sup>49</sup> reported the hydrothermal synthesis of a metal-organic coordination polymer  $[\text{Zn}(\text{Pht})(\text{Medpq})]_n$  { Pht=phthalic acid and Medpq =2-methyldipyrido [3,2-f:2'3'-h] quinoxaline} and it was structurally characterized by elemental analysis, IR spectrum, TG and X-ray single crystal structure analysis. In the crystal

structure, the Zn(II) atom is six-coordinated with four carboxylate oxygen atoms from two different carboxylate groups and two nitrogen atoms from Medpq ligand, showing a slightly distorted octahedral geometry. In addition, it exhibits a one-dimensional structure with Pht-Zn-Medpq as building units.

The synthesis, structural characterization and magnetic studies of a three dimensional Co(II) coordination polymer containing 2,3-dioxyquinoxalinate(-2) ligand has been reported<sup>50</sup>. Variable temperature and variable field magnetic studies reveal that the ligand propagates weak antiferromagnetic exchange interactions through its quinoxaline part. A sensitive, selective and rapid method has been developed for the determination micrograms per liter level of vanadium ion, based on the rapid reaction of V(V) with 2,3-dichloro-6-(2,7-dihydroxy-1-naphthylazo) quinoxaline (DCDHNAQ) and the solid phase extraction of the colored complex. The DCDHNAQ reacts with V(V) in the presence of citric acid-sodium hydroxide buffer solution (pH 3.3) and benzylidimethyl tetradecylammonium chloride (zephiramine) medium to form a violet complex of a molar ratio 1:2. This method was also applied to the determination of V(V) in steel, soil, water and biological samples<sup>51</sup>.

A tris(2-pyridylmethyl)amine (tpa) Ru complexes  $[\text{Ru}(\text{tpa})(\text{N-N})](\text{PF}_6)_2$  with N-N = dpq (dipyrido[3,2-d:2',3'-f]quinoxaline) was prepared and characterized by NMR, UV-Vis. and fluorescence spectroscopy as well as cyclic voltammetry. Structure optimized with DFT methods. DNA binding of the complex was studied with UV-Vis. titrations, the fluorescent ethidium bromide displacement assay and CD spectroscopy<sup>52</sup>.

A series of metal complexes having the general formula  $[\text{Ru}(\text{bpy})_n(\text{mebpq}^+)]_{3-n}^{+}$  {n = 0, 1, 2, 3, bpy=2,2'-bipyridine and mebpq<sup>+</sup>= 2-(N-methylpyridyl)3-pyridyl quinoxaline} were synthesized and characterized by optical, elemental analysis, NMR and electrochemical methods<sup>53</sup>. Pladzyk et al<sup>54</sup> reported the Co(II) tri-tert-butoxysilanethiolate complex with quinoxaline. The complex was characterized by elemental analysis, solid state IR and UV-Vis. spectroscopy and single crystal X-ray analysis.

The bis(pyrazol-1-yl)azine ligand 2,3-bis(pyrazol-1-yl)quinoxaline (bpzqn) was prepared and its Ru(arene) precursors led to the mononuclear complex  $[\text{RuCl}(\text{arene})(\text{L})]\text{BPh}_4$  {arene=p-cymene, L=bpzqn, arene=C<sub>6</sub>H<sub>6</sub>, L=bpzqn} with the N-donor ligand coordinated in a bidentate chelate way. When the reactions between the ruthenium precursors and bpzqn are carried out in MeOH, the complexes  $[\text{RuCl}(\text{arene})(\text{OMepzqn})]\text{BPh}_4$  with partially methanolized ligands are isolated (arene=p-cymene, C<sub>6</sub>H<sub>6</sub>). In this process a methoxy group has replaced one of the pyrazole groups in the ligand. The complexes are active in ketone hydrogenation transfer processes even in the absence of base<sup>55</sup>.

A new series of VO (IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of the 3-hydrazinoquinoxaline-2-one

(HQO) were prepared and characterized. The ligand exhibits biambidenticity. It behaves as a bidentate ON donor in VO(IV), Fe(III) and Cu(II) complexes and as a bis bidentate ONNN donor in Cr(III), Mn(II), Co(II) and Ni(II) complexes. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, thermal, IR, <sup>1</sup>H NMR, electronic spectra, magnetic susceptibility and conductivity measurements. An octahedral geometry was suggested for all the complexes. All the complexes show subnormal magnetic moments. The ligand, HQO and its complexes were tested against one strain Gram positive bacteria (*S. aureus*), Gram negative bacteria (*E. coli*). The prepared metal complexes exhibited higher antimicrobial activities than the parent ligand<sup>56</sup>.

A novel diimine Cu(I) complex [Cu(ABPQ)(DPEphos)]BF<sub>4</sub> {where, ABPQ=acenaphtho [1,2-b]bipyrido [2,3-h;3,2-f]quinoxaline and DPEphos=bis (2-(diphenylphosphanyl)phenyl)ether} was synthesized and its photophysical properties are experimentally and theoretically characterized. The complex also exhibited good luminescent quantum yield<sup>57</sup>. A metal-organic complex [Cu<sub>2</sub>(ipt)(Medpq)<sub>2</sub>]<sub>n</sub> {ipt=isophthalic acid, Medpq=2-methyldipyrido[3, 2-f:2', 3'-h]quinoxaline} has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG and single crystal X-ray diffraction. In the crystal structure, the copper ion is three coordinated with one carboxylate oxygen atom from carboxylate groups and two nitrogen atoms from Medpq ligand, show slightly distorted triangle geometry. Furthermore, it exhibits a zero dimensional structure with ipt-Cu- medpq as building units<sup>58</sup>.

Mono and bimetallic complexes of Re(CO)<sub>3</sub>Cl containing the bidentate binding ligands dpq and dpb (**5**) has been prepared and characterized. The lowest energy electronic absorption band has been assigned as a MLCT process, where the acceptor state is localized primarily on the binding ligand<sup>59</sup>. Zapata et al<sup>60</sup> reported a new chemosensor molecule based on a ferrocene-azaquinoxaline dyad effectively recognizes Hg<sup>2+</sup> in an aqueous environment as well as Pb<sup>2+</sup> and Zn<sup>2+</sup> metal cations in CH<sub>3</sub>CN solution. The spectroscopic and combined <sup>1</sup>H NMR data of the complexes and the theoretical calculation suggest the bridging coordination modes. The binding of ions Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Ba<sup>2+</sup> and paraquat by heterocyclophanes containing quinoxaline fragments connected by 3,6,9-trioxaundecane and 5,8,11,14,17-pentaoxageneicosane spacers, and their acyclic analogues, in the acetonitrile-0.1 M Bu<sub>4</sub>NBF<sub>4</sub> is studied by cyclic voltammetry<sup>61</sup>.

Synthesis and characterization of heteroleptic organic red phosphorescent Ir(III) complexes bearing two-(4-fluorophenyl)-3-methylquinoxaline (fpmqx) cyclometalated ligands combined with three different ancillary ligands [triazolylpyridine(trz), picolinate (pic) and acetylacetone (acac)] have been reported by Schneidenbach et al<sup>62</sup>. They proposed that emission originated predominantly from a <sup>3</sup> MLCT state. The complexes

exhibit strong phosphorescence. The structure of the complexes [(fpmqx)<sub>2</sub>Ir(trz)] and [(fpmqx)<sub>2</sub>Ir(pic)] were studied by X-ray diffraction. In both complexes the coordination geometry at Ir(III) is distorted octahedral.

A series of luminescent cyclometalated Ir(III) dipyridoquinoxaline complexes [Ir(NC)<sub>2</sub>(NN)](PF<sub>6</sub>) { HNC=1-phenylpyrazole, Hppz, NN = dipyrido[3,2-f:2',3'-h]quinoxaline, dpq (1a), 2-(n-butylamido) dipyrido[3,2-f:2',3'-h]quinoxaline, dpqa (1b); HNC = 7,8-benzoquinoline, Hbzq, NN=dpq (2a), dpqa (2b); HNC=2-phenylquinoline, Hpq, NN=dpq (3a), dpqa (3b)} have been synthesized and characterized. The lipophilicity of all the complexes has been determined by reversed-phase HPLC. The cytotoxicity of these Ir(III) complexes toward the human cervix epithelioid carcinoma (HeLa) and Madin-Darby canine kidney (MDCK) cell lines has been evaluated by the 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide (MTT) assay. The cellular uptake of the complexes by MDCK cells has been examined by laserscanning confocal microscopy. Most importantly, apparent nucleolar staining was observed after the cells were treated by the complexes. The interactions of these complexes with proteins, DNA and RNA have also been studied by emission titrations and SDS-PAGE gel staining. The results revealed that the complexes bound to the hydrophobic pockets of proteins, intercalated into the base-pairs of double-stranded DNA, but did not appear to interact with RNA<sup>63</sup>.

Hussain et al<sup>64</sup> reported the photo cytotoxic La(III) (**6**) and Gd(III) complexes of dpq (**7**). The complexes were prepared, characterized by physicochemical data and using photo induced DNA and protein cleavage activity studies. The dpq complexes in DMF show ligand based reductions. The photo induced DNA and protein cleavage activities of the compounds were also studied. The La(III) complexes are diamagnetic. The complexes do not show any hydrolytic cleavage of plasmid super coiled pUC19 DNA. The dpq complexes efficiently cleave SC DNA to its nicked circular form on exposure to UV-A light of 365 nm at nanomolecular complex concentration. Mechanistic studies reveal the involvement of singlet oxygen (<sup>1</sup>O<sub>2</sub>) and hydroxyl radical (HO<sup>·</sup>) as the cleavage active species.

Photophosphorescent zwitter ionic Ir(III) complexes with dibenzo[f,h]quinoxaline (dbq) and 4-carboxy-2,2'-bipyridine-4'-carboxylate (Hdc bpy) as ancillary ligand has reported. The prepared complexes were characterized and their photophysical properties were studied. Intense luminescence emission was observed based on <sup>3</sup>MLCT, <sup>3</sup>LLCT, ligand centered transitions (<sup>3</sup>LC) or interligand-charge transfer (<sup>3</sup>ILCT) of excited states were confirmed by theoretical calculations<sup>65</sup>. New V(III) mono nuclear complex of maltolato and dpq complex has been synthesized, characterized and reported its DNA cleavage activity. The complex also showed moderate *in-vitro* insulin mimetic activity against insulin responsive R1N 5f cells<sup>66</sup>.

Four luminescent cyclometalated Ir(III) dipyridoquinoxaline complexes appended with an indole moiety [Ir(N<sup>+</sup>C)(2(N<sup>+</sup>N)]

(PF<sub>6</sub>) {HN<sup>+</sup>C=2-phenylpyridine, Hppy; N<sup>+</sup>N=2-(N-(2-(indole-3-acetamido)ethyl) aminocarbonyl) dipyrido [3,2-f:2',3'-h]quinoxaline, dpqC<sub>2</sub>indole (1a), N<sup>+</sup>N=2-(N-(6-(indole-3-acetamido) hexyl) aminocarbonyl) dipyrido [3,2-f:2', 3'-h]quinoxaline, dpq C<sub>6</sub>indole (1b); HN<sup>+</sup>C=7,8-benzoquinoline, Hbzq, N<sup>+</sup>N=dpqC<sub>2</sub>indole (2a), N<sup>+</sup>N=dpqC<sub>6</sub>indole (2b)} have been synthesized and characterized. Upon irradiation, all the complexes displayed moderately intense and long-lived luminescence under ambient conditions and in 77 K glass. The interactions of the complexes with an indole-binding protein, bovine serum albumin (BSA), have been examined by emission titrations<sup>67</sup>.

The coordination behavior of the ligand 3-(2-oxo-2-p-tolylethyl)quinoxaline-2(1H)-one towards some transition metal ions namely Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) (**8**) has been reported<sup>68</sup>. The metal complexes were characterized based on elemental analysis, IR, <sup>1</sup>H NMR, Solid reflectance, magnetic moment, molar conductance and thermal analysis. The chelates have octahedral structure. The synthesized ligands and its metal complexes showed remarkable biological activities.

Cu(II) complex [Cu(dpq)(mal)(H<sub>2</sub>O)]3H<sub>2</sub>O {dpq=dipyrido-[3,2-d:2',3'-f]-quinoxaline, mal= malonato} was synthesized and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis and single-crystal X-ray crystallography. The single-crystal X-ray structure of the complex reveals a square pyramidal structure, with the dipyrido-[3,2-d:2',3'-f]-quinoxaline and malonato at the equatorial positions and water molecule at the axial position. The hydrogen bonding capacity of malonato and the  $\pi$ - $\pi$  stacking interactions of dipyrido-[3,2-d:2',3'-f]-quinoxaline further reinforce the framework. The Cu(II) bound hydroxyl group is demonstrated to mediate hydrolytic cleavage of plasmid pBR322 DNA under dark conditions<sup>69</sup>.

Two novel Fe(III) complexes against tuberculosis, [Fe(L-H)<sub>3</sub>], with 3-aminoquinoxaline-2-carbonitrile-N<sub>1</sub>, N<sub>4</sub>-dioxide derivatives (L) as ligands were synthesized, characterized by a combination of technique. The complexes were also studied by cyclic voltammetry and EPR spectroscopy. Cyclic voltammograms of the Fe(III) compounds showed several cathodic processes which were attributed to the reduction of the metal center (Fe(III)/Fe(II)) and the coordinated ligand. EPR signals were characteristic of magnetically isolated high-spin Fe(III) in a rhombic environment. Mössbauer experiments showed hyperfine parameters that are typical of high-spin Fe(III) ions in a not too distorted environment. The novel complexes showed *in vitro* growth inhibitory activity on *Mycobacterium tuberculosis* H37Rv (ATCC 27294), together with very low unspecific cytotoxicity on eukaryotic cells. Both complexes showed higher inhibitory effects on *M. tuberculosis* than the second-line therapeutic drugs<sup>70</sup>.

The electrochemical studies of newly synthesized complexes cis-[RuCl<sub>2</sub>(L)(pph<sub>3</sub>)<sub>3</sub>] {L = 2-(2'-pyridyl)quinoxaline} has

reported. The electrochemical studies include CV, EIS and ESI-MS<sup>71</sup>. <sup>1</sup>H NMR spectroscopy, electronic absorption and emission spectroscopy and cyclic voltammetry were used for the study of the complexes [M(ppy)ddpq]ClO<sub>4</sub> (M=Pt(II), Pd(II); ddःpq=6,7-dimethyl-2,3-dipyridylquinoxaline)<sup>72</sup>. N,N'-(5,5'-(Quinoxaline-2,3-diyl)bis(1H-pyrrole-5,2-diyl)) bis(methanlylidene) bis (4-methoxy anilne) and N,N'-(5,5'-(quinoxaline-2,3-diyl)-bis(1H-pyrrole-5,2-diyl))bis(methanlylidene)dianiline have been prepared and structurally characterized. These compounds displayed good sensitivity toward transition metal ions with Cd(II), Zn(II) turn on and Cu(II), Hg(II) turn off in fluorescence. It is an elegant example of on/off behavior like a lamp. When Cd(II) or Zn(II) is added into N,N'-(5,5'-(Quinoxaline-2,3-diyl)bis(1H-pyrrole-5,2-diyl)) bis(methanlylidene)bis(4-methoxy anilne) or N,N'-(5,5'-(quinoxaline-2,3-diyl)-bis(1H-pyrrole-5,2-diyl))bis(methanlylidene) dianiline, the lamp will switch on, and then when Cu(II) or Hg(II) is added into the mixture, the lamp will switch off. The fluorescence data and crystal structure indicate that a 1:1 stoichiometry complex is formed between the compound and metal ions and the binding affinity is very high<sup>73</sup>.

Huang et al<sup>74</sup> reported the hydrothermal synthesis of two unusual one-dimensional (1-D) compounds, viz. [Co(Medpq)(QUI)·H<sub>2</sub>O]<sub>2n</sub>·2.4nH<sub>2</sub>O and [Cd(Medpq)(QUI)·H<sub>2</sub>O]<sub>n</sub>·nH<sub>2</sub>O were synthesized by the combination of two different metallic salts and organic ligands, namely 2,3-pyridinedicarboxylic acid (H<sub>2</sub>QUI) and 2-methyldipyrido[3,2-f:2',3'-h]quinoxaline (Medpq) ligand. The compounds were characterized by elemental analyses, TG, fluorescent emission and single-crystal X-ray diffraction analyses.

Two terbium complexes were synthesized with dibenzoylmethane (HDBM) as the first ligand and 1, 10-phenanthroline (phen), dipyrido[3, 2-a:2', 3'-c] quinoxaline as the second ligand. The studies of elemental analysis, rare earth complexometric titration, molar conduction, IR spectra, UV spectra, fluorescence excitation and emission spectra indicate that the complexes have the compositions of Tb(DBM)<sub>3</sub>phen and Tb(DBM)<sub>3</sub>dpq. The results show that the rare earth ion (Tb<sup>3+</sup>) was bonded with the carbonyl oxygen atom of DBM and nitrogen atoms of phen and dpq<sup>75</sup>.

A complex [Ni(Pht)(Medpq)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**) (Pht=phthalic acid, Medpq=2-methyldipyrido [3,2-f:2',3'-h] quinoxaline) was hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG, single crystal X-ray diffraction and theoretical calculations. Natural bond orbital (NBO) analysis was performed by using the NBO method built in Gaussian03 Program. The calculation results show there is the obvious covalent interaction between the coordinated atoms and Ni(II) ion<sup>76</sup>.

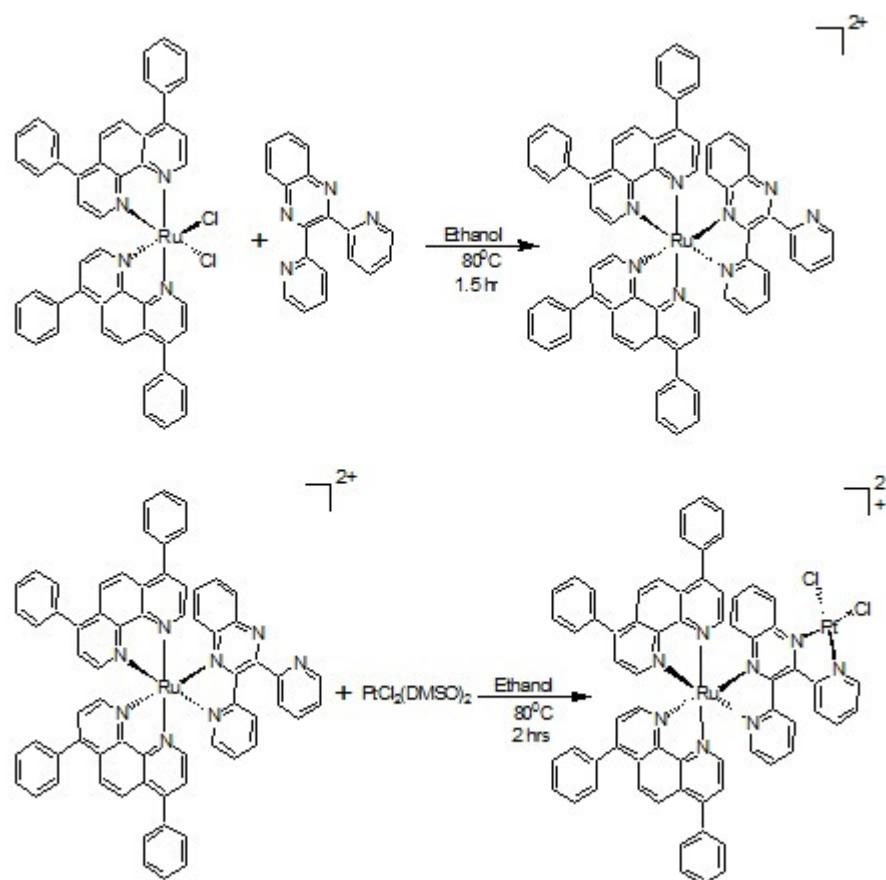
The redox, spectroscopic and photophysical properties as well as DNA interactions of the new bimetallic complex

$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$  was reported (scheme-2)<sup>77</sup> ( $\text{ph}_2\text{phen}=4,7\text{-diphenyl-1,10-phenanthroline}$ ). The electronic absorption spectroscopy is dominated in the UV region, the transition at 600 nm is assigned to  $\pi-\pi^*$  ligand transitions and in the visible region by MLCT transitions for  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$ . The cis Pt(II)Cl<sub>2</sub> bioactive site offers the potential targeting Ambidentate heterocyclic ligand 2,3-bis(1-methylimidazol-2-yl)quinoxaline (bmiq) was obtained from 2,3-bis(1-methylimidazol-2-yl)glyoxal and 1,2-diaminobenzene. Its coordination to PtCl<sub>2</sub> and to the isoelectronic  $[\text{AuCl}_2]^+$  in  $[\text{AuCl}_2(\text{bmiq})](\text{AuCl}_4)$  occurs via the imine N donors of the imidazolyl groups, leading to the formation of seven-membered chelate rings with boat conformation. According to the spectroelectrochemistry (UV-Vis-NIR, EPR), the reversible electron addition to the  $[\text{PtCl}_2(\text{bmiq})]$  and the free ligand takes place in the (non-coordinated) quinoxaline part of the molecule, similarly as for related complexes of dipyrido[3,2-a:2',3'-c] phenazines (dppz), 2,3-bis(2-pyridyl)quinoxalines (bpq) and 2,3-bis(dialkylphosphino) quinoxalines (QuinoxP). DFT calculations confirm the experimental results (structures, spectroscopy) and also point to the coordination potential of the quinoxaline N atoms. The electron addition to  $[\text{AuCl}_2(\text{bmiq})]^+$  takes place not at the ligand but at the metal site, according to experimental and

DFT results<sup>78</sup>.

An oligoquinoxaline derivative with phthalazine core has been prepared by condensation of 1,4-dihydrazinophthalazine with 2,3-dichloroquinoxaline in dry ethanol followed by acid hydrolysis. Classical endogenous bridging of phthalazine core with its diazine fragment was established in the transition metal(II) complexes derived from the ligand system by using various physicochemical and spectral techniques. The organic host acts as a hexadentate chelate with N<sub>4</sub>O<sub>2</sub> donating sites for coordination towards later first-row transition metal ions. Complexes are in good agreement with the octahedral geometry and found to be 1:1 electrolytes. All synthesized compounds were screened for anticonvulsant activity in Wistar rats by using maximal electroshock method. The ligand and Co(II) and Ni(II) complexes show appreciable suppression towards electroshock induced seizures<sup>79</sup>.

Sky blue Tp<sup>\*</sup>WOCl<sub>2</sub> has been synthesized from the high-yielding reaction of Tp<sup>\*</sup>WOCl<sub>2</sub> with boron trichloride in refluxing toluene. Dark red Tp<sup>\*</sup>WOI<sub>2</sub> was prepared via thermal decarbonylation followed by aerial oxidation of Tp<sup>\*</sup>WI(CO)<sub>3</sub> in acetonitrile.



Scheme-2

Using these precursors, an extensive series of mononuclear tungstenyl complexes,  $Tp^*WOXY$  [ $X=Cl^-$ ,  $Y=OPh^-$ ,  $SPh^-$ ;  $X=Y=OPh^-$ , 2-(n-propyl)phenolate (PP),  $SPh^-$ ,  $SePh^-$ ;  $XY=toluene-3,4$ -dithiolate ( $tdt^{2-}$ ), quinoxaline-2,3-dithiolate ( $qdt^{2-}$ ), benzene-1,2-diselenolate ( $bds^{2-}$ );  $Tp^*=$ hydrotris(3,5-dimethylpyrazol-1-yl)borate], was prepared by metathesis with the respective alkali-metal salt of  $X'/XY^{2-}$  or  $(NHEt_3)_2(qdt)$ . The complexes were characterized by microanalysis, mass spectrometry, electrochemistry, IR, electron paramagnetic resonance (EPR), electronic absorption spectroscopies, and X-ray crystallography (for  $X=Y=OPh^-$ , PP,  $SPh^-$ ;  $XY=bds^{2-}$ ). The six-coordinate, distorted-octahedral tungsten centers are coordinated by terminal oxo [ $W\equiv O=1.689(6)-1.704(3)$  Å], tridentate  $Tp^*$  and monodentate or bidentate O/S/Se-donor ligands. Spin Hamiltonian parameters derived from the simulation of fluid-solution X-band EPR spectra revealed that the soft-donor S/Se ligand complexes had larger g values and smaller  $183$  W hyperfine coupling constants than the less covalent hard-donor O/Cl species. The former showed low energy ligand to metal charge-transfer bands in the near-IR region of their electronic absorption spectra. These  $WQ(V)$  complexes display lower reduction potentials than their molybdenum counterparts, underscoring the preference of tungsten for higher oxidation states. Furthermore, the protonation of the pyrazine nitrogen atoms of the  $qdt^{2-}$  ligand has been examined by spectroelectrochemistry; the product of the one electron reduction of  $[Tp^*WO(qdtH)]^+$  revealed usually intense low-energy bands<sup>80</sup>.

The new nickel bis(dithiolene) complex  $[Bu_4N]_2[Ni(6,7-qdt)_2]$  (1) (6,7-qdt=quinoxaline-6,7-dithiolate) has been synthesized, starting from quinoxaline-6,7-dithiol, nickel chloride and tetrabutylammonium bromide in methanol<sup>81</sup>. Two new metal-organic frameworks,  $\{[CuLi]\cdot CHCl_3\} \infty(1)$  and  $\{[HgL(Br)_2]_4\cdot 2CH_2Cl_2\} \infty(2)$  have been prepared by reacting CuI and HgBr<sub>2</sub> with the new flexible ligand L [L = 2,3-Bis(benzimidazol-1-ylmethyl)quinoxaline]. Both complexes have been characterized by elemental analysis, IR, TGA, XRPD and single crystal X-ray diffraction determination. In 1, the Cu(I) ion takes tetrahedral coordination geometry and the flexible ligands bridge dinuclear units ( $Cu_2I_2$ ) to form a one dimensional (1-D) double chain structure. While in 2, the Hg(II) coordinates to two bromine ions and two nitrogen donors of L to form a 1D coordination polymer. The structure differences in the two complexes mainly depend on the geometry of the metal ions and the influence of anions. The coordination features of the ligand have also been primarily investigated by density functional theory (DFT) calculations. In addition, the fluorescent properties of the complexes and free ligand L have been investigated in the solid state at room temperature<sup>82</sup>.

The dinuclear Cu(II) complex of general formula  $[Cu_2(LH)_2(diimine)_2(ClO_4)_2](ClO_4)_2$  {LH=2-hydroxy-N-[2-(methylamino)ethyl]benzamide and diimine=dipyrido[3,2-d:2',3'-f]quinoxaline (Bpq; 4)} has been isolated and characterized. Absorption, emission spectral studies and viscosity

measurements indicate that complex interacts with calf thymus DNA through strong partial intercalation of the extended planar ring (Bpq) with a DNA base stack. The complex exhibit an ability to cleave DNA (pUC19 DNA) in a 5% DMF/5 mM Tris-HCl/50 mM NaCl buffer at pH 7.1 in the absence of an oxidant at 100 μM complex concentration. It shows an ability to convert supercoiled DNA into nicked coiled DNA even at 6 μM concentration, beyond which complete degradation is observed and the pathway of oxidative DNA cleavage involves hydroxyl radicals<sup>83</sup>.

Five new tetrametallic supramolecules of the motif  $\{[(TL)_2M(dpp)\}_2Ru(BL)PtCl_2\}^{6+}$  and three new trimetallic light absorbers  $\{[(TL)_2M(dpp)\}_2Ru(BL)\}^{6+}$  (TL=bpy=2,2'-bipyridine or phen=1,10-phenanthroline; M=Ru(II) or Os(II); BL=dpp=2,3-bis(2-pyridyl)pyrazine, dpq=2,3-bis(2-pyridyl)quinoxaline, or bpm=2,2'-bipyrimidine) were synthesized and their redox, spectroscopic, and photophysical properties were investigated. The tetrametallic complexes couple a Pt(II) based reactive metal center to Ru and/or Os light absorbers through two different polyazine BL to provide structural diversity and interesting resultant properties<sup>84</sup>.

Synthesis, DNA binding and photo cleavage studies of Ru(II) complexes of an assymmetric ligand (pdpiq) and its ruthenium complex,  $[Ru(L2)pdpiq]^{2+}$  {where pdpiq = 2-(pyridine-2-yl)-6,7-diphenyl-1-H-imidazo[4,5-g]quinoxaline}, L = {2,2'-bipyridine or 1,10-phenanthroline} have been reported by Liu et al (scheme-3)<sup>85</sup>. The complexes were characterized by elemental analysis, ES-MS and <sup>1</sup>H NMR. The DNA binding behavior was also studied by spectroscopic method and viscoicity measurements. The results indicate that the complexes can intercalate into DNA base pairs. On irradiation at 365 nm, the two complexes promote the DNA cleavage.

Pyrolyzed Fe/N/C catalysts were synthesized using a newly designed and synthesized 2,3,7,8-tetra(pyridine-2-yl) pyrazino[2,3-g]quinoxaline (TPPQ) organic compound as the nitrogen containing ligand. Catalysts were prepared by first coordinating TPPQ with Fe, forming Fe-TPPQ complexes, followed by impregnation on with carbon black and pyrolyzed at 900 °C. Catalysts with 0.5%, 1%, 2%, 4% and 8% initial iron content were prepared and their physical characteristics were determined by X-ray diffraction, transmission electron microscopy and X-ray photoelectron microscopy analysis. Electro catalytic activity towards oxygen reduction reaction was evaluated and compared for all catalysts. The catalyst with 2% initial iron content was found to be the best performing catalyst<sup>86</sup>.

Xu et al<sup>87</sup> reported a near-infrared (NIR) phosphorescent probe for F<sup>-</sup> based on a cationic Ir(III) complex  $[Ir(Bpq)_2(Quqo)]PF_6$  with dimesitylboryl (Mes<sub>2</sub>B) groups on the cyclometalated C<sup>N</sup> ligands (Bpq) and 2-(quinolin-2-yl)quinoxaline (Quqo) as N<sup>N</sup> ligand. The excited state properties of the complex have been investigated in detail using molecular orbital calculations and

experimental methods. On excitation, complex shows NIR phosphorescent emission around 680 nm. The complex can be excited with long wavelength around 610 nm. Such long wavelength excitation can reduce the background emission interference and improve the signal to noise ratio. The selective binding between boron atom and  $F^-$  can give rise to the quenching of emission and determined the near-infrared phosphorescent sensing for  $F^-$ .

Sb(III) complexes of 3-aminoquinoxaline-2-carbonitrile 1,4-dioxides were prepared to improve the anti *Trypanosoma cruzi* activity of the ligands. The in vitro evaluations show that upon metal complexation the activity of the 3-aminoquinoxaline ligands increased. Coordination to antimony resulted in 2-12 fold increase of the trypanosomicidal activity. These complexes were more active against *T. cruzi* than other metallic complexes with the same ligands in the same conditions<sup>88</sup>. Luminescence, catalytic activities and structure of metal-organic frame works containing CuCN building blocks and bipodal bridging ligand quinoxaline (qox) has been reported by Etaiw<sup>89</sup>. The crystal structure of the complex exhibits puckered CuCN chains connected by qox molecules forms 2-D sheets. The complex act as room temperature luminescent Cu containing polymer. The qox complex also shows catalytic activity in the oxidative degradation of metanil yellow dye by hydrogen peroxide. They also reported<sup>90</sup> the structure and spectral characters of 3-D supramolecular coordination polymers based on 2,3-dimethylquinoxaline (dmqox) and copper cyanide.

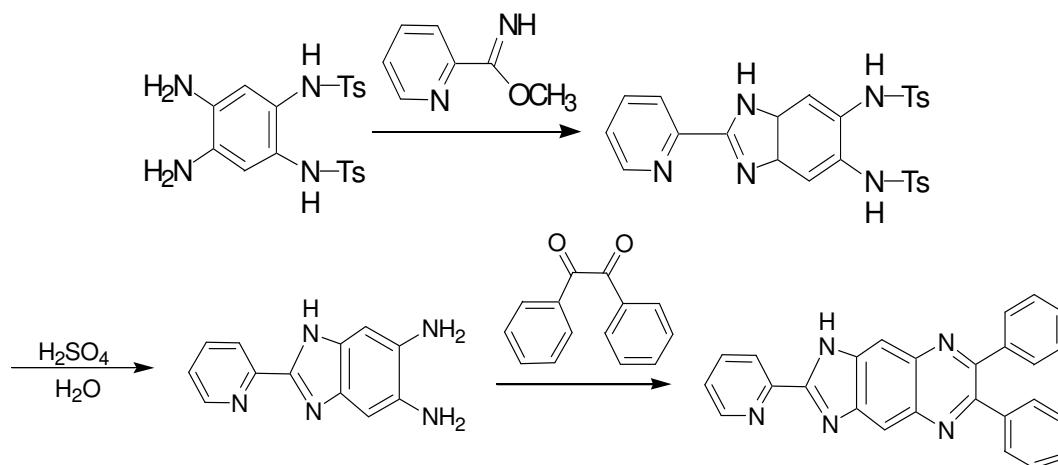
Crystals of the metal-organic framework [Ag(qox)(4-ab)] were obtained at room temperature by the reaction of AgNO<sub>3</sub>, quinoxaline (qox) and 4-amino benzoic acid (4-aba). The cluster molecule containing two silver atoms, two qox and two 4-ab ligands is considered the basic building block of the structure. A 3D-network structure is created via H-bonds and  $\pi-\pi$  stacking. The complex was tested as a corrosion inhibitor for C-steel in 1 M HCl solution using potentiodynamic polarization and electrochemical impedance techniques. [Ag(qox)(4-ab)] is rich with electron donating groups and the  $\pi$ -systems exhibiting high

inhibition efficiency. The results obtained from EIS and potentiodynamic polarization are in good agreement<sup>91</sup>.

Park et al<sup>92</sup> reported the synthesis and photophysical properties of the phosphorescent iridium complexes having symmetric 2,3-dpqx-F<sub>2</sub> ligands and an asymmetric fpmqx ligands and compared their luminescent properties. They also employed two different ancillary ligands and investigated the effect of ancillary ligand on the luminescence of their complexes. The prepared complexes, [Ir(2,3-dpqx-F<sub>2</sub>)(acac)] [Ir(2,3-dpqx-F<sub>2</sub>)(trzL-CH<sub>3</sub>)] exhibited red emission. The complexes with asymmetric fpmqx ligands exhibited hypsochromic shift. This blue shift can be explained by substitution of the conjugated phenyl ring with a non-conjugated methyl fragment. The ancillary ligand also influence the blue shift.

A coordination polymer [Cd (ipt) (Medpq)]<sub>n</sub> {H<sub>2</sub>ipt=isophthalic acid, Medpq=2-methyldi-pyrido[3,2-f;3',2'-h]quinoxaline} has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV-Vis. spectrum, TG and single crystal X-ray diffraction. In the crystal structure, the cadmium is six coordinated with four carboxylate oxygen atoms from three different carboxylate groups and two nitrogen atoms from Medpq ligand, showing a slightly distorted octahedral geometry. Furthermore, it exhibits a one dimensional zigzag structure with ipt-Cd-medpq as building units<sup>93</sup>.

A polypyridyl ligand, 2,3,6,7,10,11-hexakis(2-pyridyl)dipyrazino [2,3-f: 2',3'-h]quinoxaline (HPDQ), was found to have excellent fluorescent selectivity for Cd<sup>2+</sup> over many other metal ions {K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup> and Cr<sup>3+</sup>} based on the intramolecular charge transfer mechanism, which makes HPDQ a potential fluorescence sensor or probe for Cd<sup>2+</sup>. An obvious color change between HPDQ and HPDQ<sup>+</sup> Cd<sup>2+</sup> can be visually observed by the naked eye. The structure of the complex HPDQ-Cd has been characterized by X-ray crystallography. Density functional theory calculation results on the HPDQ and HPDQ-Cd complexes could explain the experimental results<sup>94</sup>.



Scheme-3

The zerovalent metal in  $[\text{Mo}(\text{CO})_4(\text{bmiq})]$  binds the two imidazole-N-imine donors of 2,3-bis(1-methylimidazol-2-yl)quinoxaline (bmiq), resulting in a seven-membered chelate ring coordinated in cis configuration. DFT calculations confirm the preference for a seven membered vs five membered ring chelation alternative as well as the experimental structural parameters. The neutral compound with a weak, broad MLCT absorption band at 500 nm is photolabile in solution. The unusual stability of both the anion and the cation is attributed to the spatial and electronic separation of the sites for electron loss (at the metal) and for electron uptake (at the uncoordinated quinoxaline ring)<sup>95</sup>.

The photophysical properties of a series of complexes  $\text{cis}-[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_2(\text{dppn})(\text{L})]^{2+}$  ( $\text{L} = \text{bpy, phen, dpq, dppz and dppn}$ ) were reported. Except dppn ancillary ligand complex all other complexes photocleave DNA efficiently via a mechanism mediated by reactive oxygen species. The toxicity of the complexes towards Hs-27 human skin fibroblasts significantly enhanced by the irradiation with visible light<sup>96</sup>. The photophysical and photochemical properties of monometallic dihydride complex  $[\text{RhH}_2(\text{pph}_3)(\text{dpq})]^+$  was reported. The complex exhibits an MLCT excited state generation by promoting a  $\pi$ -symmetry electron from Rh(III) into a  $\pi^*$  orbital on dpq.

The synthesis and characterization of Cd(II) complex with N, O-bidentate ligands derived from 3-hydroxy-2-quinoxalinecarboxylic acid  $\text{HL}_1$  has been reported. The compound  $[\text{Cd}(\text{L}_1)_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$  was studied by elemental analyses, IR, Raman spectroscopy and thermogravimetric methods (TG, DTG, DSC). In addition, the molecular structure of  $[\text{Cd}(\text{L}_1)_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$  has been determined by X-ray single crystal diffraction. Thermal analysis reveal that decomposition process of complex occurs in multiple stages. The data obtained from TG and DSC curves not only the presence but also the nature of water (crystallization and coordination) and the stoichiometry of the studied metal complexes. The results of thermal studies are in good agreement with their crystal structures<sup>97</sup>.

Metal complexes containing a new multi sulfur atom containing 1,2-dithiolene ligand, [4',5':5,6] [1,4]dithiino[2,3-b]quinoxaline-1',3'-dithiolate, have been synthesized and characterized by electrochemical measurements, IR, UV-NIR and ESR spectroscopies. X-ray structure analysis reveals that the anions of the Ni-complex derived from the new ligand form a zig-zag chain along the b axis and the anions of Au complex of the ligand stack along the a axis while the cations occupy the holes. The Ni(II) complex exhibits remarkable absorption at 1082 nm and good solubility that render this complex as a promising near-IR dye for Q-switching neodymium lasers. The third order non linear optical properties of the complexes are measured by the Z-scan technique with a 6.5 ns pulsed laser at 532 nm. The Au complexes exhibit non linear optical absorptive abilities, while the non linear absorption of the nickel complex is negligible. All of the complexes show effective self-defocusing performance. The third order non linear optical susceptibilities

for the Au complexes have been determined to be of the order of 10-13 esu<sup>98</sup>.

A series of light rare earth complexes,  $[\text{RE}(\text{acac})_3(\text{dpq})]$  ( $\text{RE}=\text{La, Ce, Pr, Nd, Sm}$ ) {where, acac=acetylacetone, dpq=dipyrido[3,2-d:20,30-f]quinoxaline} have been synthesized and structurally characterized. Binding interactions of these complexes with CT DNA and their photo induced DNA cleavage activity with pBR 322 DNA are also investigated. These complexes have strong DNA binding interaction. DNA photocleavage experiments indicate that these complexes are efficient DNA cleaving agents in UV-A (365 nm) and ambient light in the absence of any external reagents. Hydroxyl radical and singlet oxygen are the major cleavage active species from the mechanistic studies. Moreover, cell cytotoxicity studies of these complexes on HeLa, K562 and MDA-MB-231 cells indicate that they have the potential to act as effective metal-based anti-cancer drugs<sup>99</sup>.

A series of Ru(II) arene complexes with 3-(1H-benzimidazol-2-yl)-1H- quinoxalin-2-one, bearing pharmacophoric groups of known protein kinase inhibitors and related benzoxazole and benzothiazole derivatives have been synthesized. In addition, the corresponding Os complexes of the unsubstituted ligands have also been prepared. The compounds are characterized by NMR, UV-Vis. and IR spectroscopy, ESI mass spectrometry, elemental analysis, and by X-ray crystallography. Antiproliferative activity in three human cancer cell lines (A549, CH1, SW480) was determined by MTT assays, yielding IC 50 values of 6-60  $\mu\text{M}$  for three unsubstituted metal-free ligands, whereas values for the metal complexes vary in a broad range from 0.3 to 140  $\mu\text{M}$ . Complexation with osmium of quinoxalinone derivatives with benzimidazole or benzothiazole results in a more consistent increase in cytotoxicity than complexation with ruthenium. For selected compounds, the capacity to induce apoptosis was confirmed by fluorescence microscopy and flow cytometric analysis, whereas cell cycle effects are only moderate<sup>100</sup>.

A novel metal-organic coordination polymer  $[\text{Co}(\text{m-BDC})(\text{Medpq})\cdot 2\text{H}_2\text{O}]_n$  { m-H<sub>2</sub>BDC=benzene-1,3-dicarboxylic acid, Medpq=2-methyldipyrido[3,2-f:2',3'-h]quinoxaline} has been hydrothermally synthesized and characterized by elemental analysis, IR spectrum and single crystal X-ray diffraction. The compound shows strong fluorescence in the solid state at room temperature. Natural bond orbital (NBO) analysis is performed by using the NBO method built in Gaussian 03 Program. The calculation results show a covalent interaction between the coordinated atoms and Co(III) ions<sup>101</sup>.

Pd(II) and Cu(II) complexes of 3-aminoquinoxaline-2-carbonitrile 1,4-dioxides were synthesized by Benítez et al to improve the anti-Trypanosoma cruzi activity of the ligands. The in vitro evaluations show that the metal complexation modified the activity of the ligands. Complexation with palladium increased the trypanosomicidal activity 20–80-times. Besides, copper also modified the activity<sup>102</sup>. Rani et al reported the synthesis and characterization of VO(II), Fe(II), Co(II), Ni(II)

and Cu(II) complexes of 2, 3-bis (dimethyl -1H-pyrazol-1-yl)quinoxaline (BDMPQ). Octahedral geometries have been proposed for all the complexes. BDMPQ acts as a neutral bis-bidentate NN donor and forms polynuclear complexes<sup>103</sup>.

A complex of the general formula  $\text{Mo}_2(\text{bpy})_2(\text{DCQX})(\text{CO})_3$ , {DCQX and bpy are 6,7-dichloroquinoxaline-2,3-dione and 2,2'-bipyridine} was synthesized in two steps starting with the reaction of  $\text{Mo}(\text{CO})_6$  with bpy then followed by the addition of DCQX ligand. Initial characterization based on the elemental and mass analyses has suggested three possible structures. In the three suggested structures the DCQX ligand bonded to two Mo(0) metal centers; to one Mo metal through its C=O functional groups and the other through the aromatic ring forming  $\eta^6$ -arene type. In structure the DCQX ligands are bonded to  $(\text{bpy})_2\text{Mo}$  and  $\text{Mo}(\text{CO})_3$  moieties, whereas in the other structures the DCQX ligands bonded to  $\text{Mo}(\text{bpy})(\text{CO})$  and cis-(bpy)(CO)<sub>2</sub>Mo or trans-(bpy)(CO)<sub>2</sub>Mo moieties. The thermogravimetric analysis gave the thermal stability of the complex. The structural and vibrational behaviors of the  $\text{Mo}_2(\text{bpy})_2(\text{DCQX})(\text{CO})_3$  complex have been elucidated using semiempirical parameterized PM3 method. Both DCQX ligand and the molybdenum complex showed antimicrobial activities, the complex inhibition to the studied microorganisms was higher<sup>104</sup>.

A new chemosensor, 2,3,15,16-tetrakis (pyridin-2-yl)-7,8,10,11,20,21,23,24-octahydro [1,4,7,10,13,16] hexaoxacyclooctadecino [2,3-g:11,12-g'] diquinoxaline, containing 2,3-bis(pyridin-2-yl)quinoxaline and crown ether moieties has been designed and found to be a ratiometric and selective fluorescent detector of  $\text{Zn}^{2+}$  over a wide range of tested metal ions. The structure of complex  $\text{Zn}^{2+}$  has been characterized by single-crystal X-ray crystallography, mass spectrometry and <sup>1</sup>H NMR titration experiments. Density functional theory calculation results indicate the  $\text{Zn}^{2+}$  complex is well consistent with the experimental results<sup>105</sup>.

Synthesis and characterization of Cd(II) and Ca(II) complexes with N,O-bidentate ligand derived from pyrazinecarboxylic acid (3-hydroxy-2-quinoxalinecarboxylic acid) were reported. Synthesized compounds were studied by elemental analyses, IR, Raman spectroscopy and thermogravimetric methods (TG, DTG, DSC). In addition, the molecular structure of cadmium complex has been determined by X-ray single crystal diffraction. Thermal analysis reveals a decomposition process of Cd(II) complex in multiple stages. The data obtained from TG and DSC curves confirm not only the presence but also the nature of water (crystallization and coordination) and the stoichiometry of the studied metal complex. The results of thermal studies are in good agreement with their crystal structure<sup>106</sup>.

Two new isostructural tetranuclear Ag(I) complexes {where,  $X = \text{I}, \text{Br}$ ; Dpq = dipyrido[3,2-f:2,3-h]-quinoxaline} were synthesized by slow diffusion method for the first time. The central portion of each structure consists of a  $(\text{AgX})_4$  core and is surrounded by four Dpq ligands. The Dpq units in the tetrameric structures are found to stack in almost parallel and display  $\pi-\pi$

stacking interactions. Density functional theory and time-dependent density functional theory calculations at the B3LYP/LanL2DZ\* + 6-31G\* level were performed rationalize their experimental absorption spectra. Both complexes exhibit intense luminescence in ethanol solution at room temperature<sup>107</sup>.

New dinuclear complexes with bridging S—S coupled and dimerized quinoxaline-2,3-dithiolate (dsqdt) ligand,  $[\text{Tp}^{\text{Ph}_2}\text{M}(\text{dsqdt})\text{MTp}^{\text{Ph}_2}]$  { $\text{Tp}^{\text{Ph}_2}$  = hydro-tris(3,5-diphenylpyrazol-1-yl) borate; M = Co(II), Ni(II), Mn(II)}, were prepared. X-ray crystal structure studies for complexes indicate that the dsqdt ligand forms the unique  $\kappa^2$ -coordinated mode through S and N atoms from the same qdt unit. The absorption spectra, redox behavior and magnetic properties of the compounds are reported<sup>108</sup>.

Attia et al<sup>109</sup> reported two new diethoxo-bridged dinuclear Cr(III) complexes derived from 6,7-dichloroquinoxaline-2,3-dione and 6,7-dimethylquinoxaline-2,3-dione. The complexes were characterized using various spectral techniques. The antimicrobial activity studies have indicated a significant inhibitory activity of complexes against the bacteria and fungi. Chetana et al<sup>110</sup> synthesized and characterized a binuclear Cu(II) complex  $[\text{Cu}(\text{oxpn})\text{Cu}(\text{dpq})]^{2+}$  bridged by N, N'-bis[3-(methylamino) propyl] oxamide (oxpn). DNA binding, oxidative cleavage and antibacterial activities of the complex were also studied. The complex was avid binder to the Calf thymus DNA (CT-DNA) and show efficient oxidative cleavage of supercoiled DNA (SC DNA) through hydroxyl radical (OH) pathway in the presence of Mercaptopropionic acid (MPA).

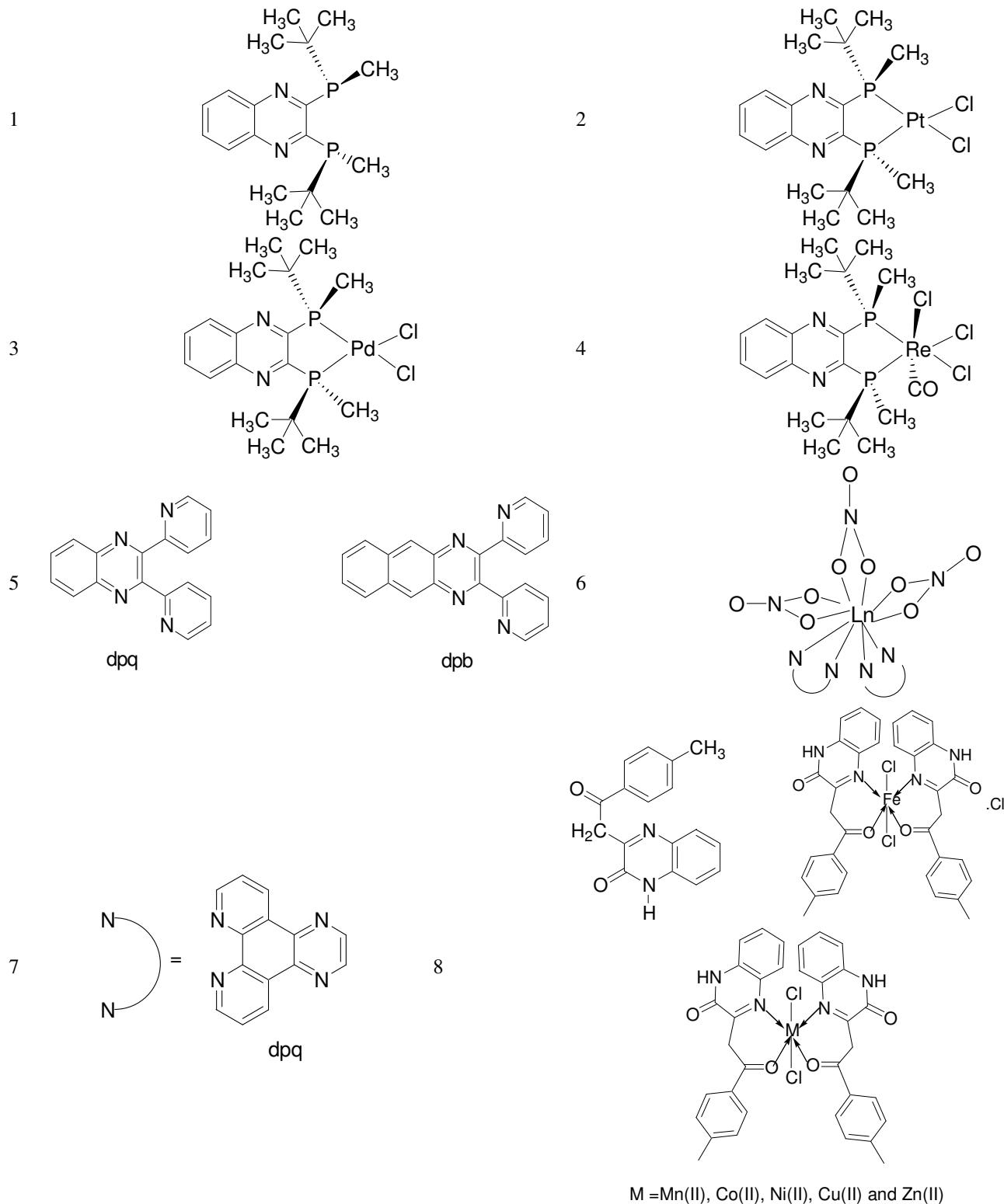
Canaj et al<sup>111</sup> reported the syntheses, structures and magnetic properties of seven new Co complexes of an indeno-quinoxaline based oxime ligand. They found that, the ligand can lead to the synthesis of cobalt clusters and also the ligand adopts eight different coordination modes leading to clusters with various nuclearities.

Three new dicyanamide (dca) mediated isostructural polymeric complexes of quinoxaline of  $d^{10}$  metal ions having the formula  $[\text{M}(\text{quin})_2(\text{dca})_2]_n$  {where M = Zn(II), Cd(II) and Hg(II)} have been synthesized and characterized by Chakraborty et al<sup>112</sup>. All the species exhibit interesting luminescence properties in solution, as well as in the solid state. Thermal study shows the formation of metallic oxide as a thermally stable end product in each case. Novel trivalent antimony complexes with the nitrogen donor heterocyclic ligand dipyrido[3,2-d:2',3'-f]quinoxaline have been synthesized by the reaction with  $\text{SbCl}_3$  or  $\text{PhSbCl}_2$ . All the complexes showed very high antileishmanial activities<sup>113</sup>.

Nehru et al<sup>114</sup> reported a new series of pendant-type polymer-cobalt(III) complexes,  $[\text{Co}(\text{LL})_2(\text{BPEI})\text{Cl}]^{2+}$  {where BPEI = branched polyethyleneimine, LL = dipyrido[3,2-d:2',3'-f]quinoxaline} have been synthesized and characterized. UV-Visible absorption and emission techniques have been accomplished to know the mode and strength of interaction between the polymer-metal complexes and calf thymus DNA. Among the polymer metal complexes, the complexes which

have higher binding strength with DNA has been selected to test against human cancer/normal cell lines. On the basis of spectral studies, they proposed that polymer–metal complexes bind with

DNA mainly through intercalation along with some electrostatic binding.



M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

## Conclusion

Quinoxaline is a structural moiety can be found in broad range of natural and pharmacologically active compounds. We hope this review will make some of the unexplored areas of quinoxaline derivatives more apparent and will encourage further development of the unexplored areas. These studies can contribute to a better understanding of the behavior of these complexes in biological systems to improve their activity. Further the new and established researchers in the quinoxaline area can get clear perspective of this field and this review will provide motivation for new attempts in this promising field.

## Acknowledgment

We thank Council of Scientific and Industrial Research (CSIR), New Delhi for the financial support in the form of a research project (Scheme No: 01(2453)/11/EMR-II).

## References

1. Rahman L.H.A. and Ramadan R.M., Synthesis and characterization of some new mono- and binuclear copper(II) ternary complexes; X-ray crystal structure of copper(II)- *N*-(acetyl)phenylglycinate-imidazole ternary complex, *J Coord Chem*, **60**, 1891 (2007)
2. Lo K.K. W. and Lee T.K.M., Luminescent ruthenium(II) amidodipyridoquinoxaline biotin complexes that display higher avidin-induced emission enhancement, *Inorg Chim Acta*, **360**, 293 (2007)
3. Roy M., Patra A.K., Mukherjee A., Nethaji M. and Chakravarty A.R., *Indian J Chem Section A Inorganic, Physical, Theoretical and Analytical Chem*, Ternary iron(II) complexes of phenanthroline bases showing DNA binding and cleavage activity, **46**, 227 (2007)
4. Miao R. and Brewer K.J., A structurally diverse mixed-metal complex with mixed bridging ligands  $\{[(\text{bpy})_2\text{Os}(\text{dpp})]_2\text{Ru}\}_2(\text{dpq})\}(\text{PF}_6)_2$ : Modulating orbital energetics within a supramolecular architecture, *Inorg Chem. Comm*, **10**, 307 (2007)
5. Wu Y.B., Xiong Z.H., Chen H.L. and Yang P.,  $[\text{Co}(\text{phen})_2\text{dpq}]^{3+}$ -sheared DNA interactions: Investigation into the basis for major groove recognition and repair, *J Mol Struct Theochem*, **806**, 247 (2007)
6. Wang X., Bi Y., Lin H. and Liu G., Three Novel Cd(II) Metal–Organic Frameworks Constructed from Mixed Ligands of Dipyrido[3,2-*d*:2',3'-*f*]quinoxaline and Benzene-dicarboxylate: From a 1-D Ribbon, 2-D Layered Network, to a 3-D Architecture, *Crystal Growth and Design*, **7**, 1086 (2007)
7. Plitt P., Gross D.E., Lynch V.M. and Sessler J.L., Dipyrrolyl-Functionalized Bipyridine-Based Anion Receptors for Emission-Based Selective Detection of Dihydrogen Phosphate, *Chemistry - A European Journal*, **13**, 1374 (2007)
8. Kemp S., Wheate N.J., Buck D.P., Nikac M., Collins J.G. and Aldrich-Wright J.R., The effect of ancillary ligand chirality and phenanthroline functional group substitution on the cytotoxicity of platinum(II)-based metallointercalators, *J Inorg Biochem*, **101**, 1049 (2007)
9. Lo K.K., Sze K.S., Tsang K.H. and Zhu N., Luminescent Tricarbonylrhenium(I) Dipyridoquinoxaline Indole Complexes as Sensitive Probes for Indole-Binding Proteins, *Organometallics*, **26**, 3440 (2007)
10. Biyiklioğlu Z., Ertem B., Karsliolu S. and Gök Y., *Trans Met Chem*, Synthesis and characterization of novel (*E,E*)-dioxime and its mono- and polynuclear metal complexes containing azacrown moieties, **32**, 591 (2007)
11. Ghosh M., Biswas P. and Flörke U., Structural, spectroscopic and redox properties of transition metal complexes of dipyrido[3,2-*f*:2',3'-*h*]quinoxaline (dpq), *Polyhedron*, **26**, 3750 (2007)
12. Mostafa S. I., Mixed ligand complexes with 2-piperidine-carboxylic acid as primary ligand and ethylene diamine, 2,2'-bipyridyl, 1,10-phenanthroline and 2(2'-pyridyl)quinoxaline as secondary ligands: preparation, characterization and biological activity, *Trans Met Chem*, **32**, 769 (2007)
13. Therrien B., Süss-Fink G., Govindaswamy P. and Saïd-Mohamed C., Mono and dinuclear arene ruthenium complexes containing 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline as chelating ligand: Synthesis and molecular structure, *Polyhedron*, **26**, 4065 (2007)
14. Kong Z.-G., Li W.-L., Wang D., Chen L.-L. and Zhang G., *J Functional Mat*, **38**, 1575 (2007)
15. Wang X., Fang J., Bi Y., Zhao H., Chen B., Lin H. and Liu G., Self-assembled multilayer films of poor water-soluble copper(II) complexes constructed from dipyrido[3,2-*d*:2',3'-*f*]quinoxaline (Dpq) ligand as well as their fluorescent properties, *J Solid State Chem.*, **180**, 2950 (2007)
16. Lin T.-P., Chen C.-Y., Wen Y.-S. and Sun S.-S., Hydroxide-Promoted Core Conversions of Molybdenum–Iron–Sulfur Edge-Bridged Double Cubanes: Oxygen-Ligated Topological  $\text{P}^{\text{N}}$  Clusters, *Inorg Chem*, **46**, 9201 (2007)
17. Brodie C. R. and Aldrich-Wright J. R., Synthesis of Flexible Bis-Intercalating Ruthenium(II) Complexes, *Eur J Inorg Chem*, 4781 (2007)
18. Ertaş I., Gök Y., Kantekin H. and Ocak Ü., The synthesis and characterization of (*E,E*)-dioxime and its transition metal complexes containing 12-membered macrocycles linked to ferrocenyl-methyl groups, *J Coord Chem*, **60**, 2509 (2007)
19. Bilgin A., Ertem B. and Gök Y., Synthesis and Characterization of a Novel Quinoxaline-Substituted *vic*-Dioxime and Its Complexes Containing Bis(12-

- Diazacrown-4) Derivatives, *Bull Chem Soc Jpn*, **80**, 1549 (2007)
20. Sasmal P.K., Patra A.K., Nethaji M. and Chakravarty A.R., DNA Cleavage by New Oxovanadium(IV) Complexes of *N*-Salicylidene  $\alpha$ -Amino Acids and Phenanthroline Bases in the Photodynamic Therapy Window, *Inorg Chem*, **46**, 11112 (2007)
21. Roy M., Pathak B., Patra A.K., Jemmis E.D., Nethaji M. and Chakravarty A.R., New Insights into the Visible-Light-Induced DNA Cleavage Activity of Dipyridoquinoxaline Complexes of Bivalent 3d-Metal Ions, *Inorg Chem*, **46**, 11122 (2007)
22. Durmus M., Dioncer F. and Ahsen V., The synthesis and spectroscopic characterization of alkoxy substituted 2,2'-azquoquinoxaline and its palladium complex, *Dyes Pigments*, **77**, 402 (2008)
23. Mitsopoulou C.A., Dagas C. E. and Makedonas C., Synthesis, characterization, DFT studies and DNA binding of mixed platinum (II) complexes containing quinoxaline and 1,2-dithiolate ligands, *J Inorg Biochem*, **102**, 77 (2008)
24. Urquiola C., Gambino D., Cabrera M., Lavaggi M. L., Cerecetto H., González M., de Cerain A. L., Monge A., Costa-Filho A. J. and Torre M. H., New copper-based complexes with quinoxaline  $N^1,N^4$ -dioxide derivatives, potential antitumoral agents, *J Inorg Biochem*, **102**, 119 (2008)
25. Das A. K., Balak E., Sarkar B., Lissner F., Scheild T., Neimeyer M., Fielder J. and Kaim W., Structures and Redox Properties of Metal Complexes of the Electron-Deficient Diphosphine Chelate Ligand *R,R*-QuinoxP, *Organometallics*, **27**, 218 (2008)
26. Konidaris K. F., Perlepes S. P., Aromi G., Teat S. J., Escuer A. and Manessi-Zoupa E., First use of 1,4-dihydro-2,3-quinoxalinedione in the chemistry of coordination polymers: A 3D copper(II) complex containing the 2,3-dioxyquinoxalinate(-2) ligand in a novel coordination mode, *Inorg Chem Comm*, **11**, 186 (2008)
27. Du J. -L., Hu T. -L., Li J. -R., Zhang S. -M. and Bu X. -H., Metal Coordination Architectures of 2,3-Bis(triazol-1-ylmethyl)quinoxaline: Effect of Metal Ion and Counterion on Complex Structures, *Eur J Inorg Chem*, 1059 (2008)
28. Wang X. -L., Bi Y. -F., Liu G. -C., Lin H. -Y., Hu T. -L. and Bu X. -H., n(II) coordination architectures with mixed ligands of dipyrido[3,2-d:2',3'-f]quinoxaline/2,3-di-2-pyridylquinoxaline and benzenedicarboxylate: syntheses, crystal structures, and photoluminescence properties, *Cryst Eng Comm*, **10**, 349 (2008)
29. Kozlov L. and Goldberg I., Supramolecular interaction patterns in the zinc(II) dichloride and tin(IV) tetrachloride complexes with dipyrido[f,h]quinoxaline-6,7-dicarbonitrile, *Acta Crystallographica Section C: Crystal Structure Communications*, **64**, m123 (2008)
30. Fitchett C. M. and Steel P. J., Synthesis and X-ray crystal structures of metal complexes of three isomeric bibenzodiazines: Discrete and polymeric assemblies, *Polyhedron*, **27**, 1527 (2008)
31. Rajendiran V., Murali M., Suresh E., Palaniandavar M., Periasamy V. S. and Akbarsha M. A., Non-covalent DNA binding and cytotoxicity of certain mixed-ligandruthenium(II) complexes of 2,2'-dipyridylamine and diimines, *Dalton Trans*, 2157 (2008)
32. Mitsopoulou C. A., Dagas C. E. and Makedonas C., Characterization and DNA interaction of the Pt(II)(pq)(bdt) complex: A theoretical and experimental research, *Inorg Chim Acta*, **361**, 1973 (2008)
33. Biswas P., Dutta S. and Ghosh M., Influence of counter anions on structural, spectroscopic and electrochemical behaviours of copper(II) complexes of dipyrido[3,2-f:2',3'-h]quinoxaline (dpq), *Polyhedron*, **27**, 2105 (2008)
34. Roy S., Patra A. K., Dhar S. and Chakravarty A. R., Photosensitizer in a Molecular Bowl and its Effect on the DNA-Binding and -Cleavage Activity of 3d-Metal Scorpionates, *Inorg. Chem*, **47**, 5625 (2008)
35. Wang X. -L., Lin H. -Y., Liu G. -C., Zhao H. -Y. and Chen B. -K., Synthesis, structures, electrochemistry and electrocatalysis of two novel copper(II) complexes constructed with aromatic polycarboxylates and dipyrido[3,2-d:2',3'-f]quinoxaline, *J Organometallic Chem*, **693**, 2767 (2008)
36. Patra A. K., Bhowmick T., Ramakumar S., Nethaji M. and Chakravarty A. R., DNA cleavage in red light promoted by copper(II) complexes of  $\alpha$ -amino acids and photoactive phenanthroline bases, *Dalton Trans*, 6966 (2008)
37. Lahiri D., Bhowmick T., Pathak B., Shameema O., Patra A. K., Ramakumar S. and Chakravarty A. R., Anaerobic Photocleavage of DNA in Red Light by Dicopper(II) Complexes of 3,3'-Dithiodipropionic Acid, *Inorg Chem*, **48**, 339 (2009)
38. Howard M., Heirtzler F. and Dias S., Synthesis and Stereochemistry of Long-Chain Quinoxaline Metallocyclophanes, *J Org Chem*, **73**, 2548 (2008)
39. Massoud A. A., Langer V., Ohrstrom L. and Abu-Yusuff M. A. M., Two 2-D copper(II) azido compounds:*catena*-poly[*di*- $\mu_{1,1}$ -azido, *di*- $\mu_{N,O}$ -(quinolinecarboxylato) (aqua)copper(II)] and 1-D *catena*-poly [*di*- $\mu_{N,N}$ -(quinoxaline) copper(II)nitrate], *J Coord Chem*, **62**, 519 (2009)
40. Choua S., Djukic P. J., Dallery J., Bieber AWeler., R., Gisselbrecht J. P., Turek P. and Ricard L., Stable and Highly Persistent Quinoxaline-Centered Metalloorganic Radical Anions: Preparation, Structural, Spectroscopic,

- and Computational Investigations, *Inorg Chem*, **48**, 149 (2009)
41. Bolink H. J., Coronado E. and Sessolo M., White Hybrid Organic-Inorganic Light-Emitting Diode Using ZnO as the Air-Stable Cathode, *Chem Mat*, **21**, 439 (2009).
42. Urquiola C., Vieites M., Torre M. H., Cabrera M., Lavaggi M. L., Cerecetto H., González M., Cerain A. L., Monge A., Smircich P., Garat B. and Gambino D., Cytotoxic palladium complexes of bioreductive quinoxaline N<sup>1</sup>,N<sup>4</sup>-dioxide prodrugs, *Bioorg Med Chem*, **17**, 1623 (2009)
43. Lin H., Wang X., Hu H., Chen B. and Liu G., A novel copper(II) complex constructed with mixed ligands of biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>bpdC) and dipyrido[3,2-d:2',3'-f]quinoxaline (Dpq): Synthesis, structure, electrochemistry and electrocatalysis, *Solid State Sciences*, **11**, 643 (2009)
44. Maity B., Roy M., Saha S. and Chakravarty A. R., Photoinduced DNA and Protein Cleavage Activity of Ferrocene-Conjugated Ternary Copper(II) Complexes *Organometallics*, **28**, 1495 (2009)
45. Saha S., Majumdar R., Roy M., Dighe R. R. and Chakravarty A. R., An Iron Complex of Dipyridophenazine as a Potent Photocytotoxic Agent in Visible Light, *Inorg Chem*, **48**, 2652 (2009)
46. Lee H.S., Ahn S. A. and Ha Y., Synthesis and the Luminescent Study of the Iridium Complexes Containing 2,3-Diphenylquinoline Derivatives and the New Ancillary Ligand for OLED, *Mol Cryst Liq Cryst*, **514**, 344 (2009)
47. Tarallo M. B., Costa-Filho A. J., Viera E. D., Monge M., Leite C.Q. Pavan, F. R., Borthagaray G., Gambino D. and Torre M. H., Research of new mixed-chelate copper complexes with quinoxaline N1,N4-dioxide derivatives and alanine as ligands, potential antimycobacterial agents. *The J Arg Chem Soc*, **97**, 80 (2009)
48. Patra A. K., Bhowmick T., Roy S., Ramakumar S. and Chakravarty A. R., Copper(II) complexes of L-arginine as netropsin mimics showing DNA cleavage activity in red light, *Inorg Chem*, **48**, 2932 (2009)
49. Cui Y. -C., Huang Y. -J. and Du G., *Chinese J Inorg Chem*, **25**, 734 (2009)
50. Konidaris K. F., Papaefstathiou G. S., Aromi G., Teat S. J., Manessi-Zoupa E., Escuer A. and Perlepes S. P., A three-dimensional copper(II) coordination polymer featuring the 2,3-dioxyquinoxalinate(-2) ligand: Preparation, structural characterization and magnetic study, *Polyhedron*, **28**, 1646 (2009)
51. Amin A. S., Saber A. L. and Mohammed T. Y., Study on solid phase extraction and spectrophotometric determination of vanadium with 2,3-dichloro-6-(2,7-dihydroxy-1-naphthylazo)quinoxaline, *Spectrochim Acta A*, **73**, 195 (2009)
52. Kraft S. S., Bischof C., Loos A., Braun S., Jafarova N. and Schatzschneider U., *J Inorg Biochem*, A [4+2] mixed ligand approach to ruthenium DNA metallointercalators [Ru(tpa)(N-N)](PF<sub>6</sub>)<sub>2</sub> using a tris(2-pyridylmethyl)amine (tpa) capping ligand, **103**, 1126 (2009)
53. Kulkarni M.S., Kumbhar A.S., Mohan H. and Rao B.S.M., Synthesis, characterization and redox chemistry of Ru(II) complexes of N-methyl pyridyl quinoxaline, *Dalton Trans*, 6185 (2009)
54. Pladzyk A. and Baranowska K., Cobalt(II) Tri-tert-butoxysilanethiolates with Bidentate Spacer Ligands, *Zeitschrift fur Anorganische und Allgemeine Chemie*, **635**, 1638 (2009)
55. Soriano M.L., Jalón F.A., Manzano B.R. and Maestro M., Synthesis and characterization of Ru(arene) complexes of bispyrazolylazines: Catalytic hydrogen transfer of ketones, *Inorg Chim Acta*, **362**, 4486 (2009)
56. Lakshmi P.V.A., Reddy P.S. and Raju V.J., Synthesis, characterization and antimicrobial activity of 3d transition metal complexes of a biambidentate ligand containing quinoxaline moiety, *Spectrochim Acta A*, **74**, 52 (2009)
57. Si Z., Li X., Li X., Pan C. and Zhang H., Synthesis, photoluminescence, and theoretical studies of novel Cu(I) complex, *Inorg Chem Comm*, **12**, 1016 (2009)
58. Huangyan -J., Cui Y. -C. and Du G., Hydrothermal Synthesis and Crystal Structure of a Zero-Dimensional Copper (I ) Complex with Isophthalic Acid and Medpq Ligands, *Chinese J Inorg Chem*, **25**, 1882 (2009)
59. Choua S., Djukic J., Jerome, Bieber A., Welter R., Gisselbrecht J., Turek P. and Ricard L., Stable and Highly Persistent Quinoxaline-Centered Metalloorganic Radical Anions: Preparation, Structural, Spectroscopic, and Computational Investigations, *Inorg Chem*, **48**, 149 (2009)
60. Zapata F., Caballero A., Espinosa A., Tárraga A. and Molina P., A Selective Redox and Chromogenic Probe for Hg(II) in Aqueous Environment Based on a Ferrocene-Azaquinoxaline Dyad, *Inorg Chem*, **48**, 11566 (2009)
61. Yanilkin V. V., Nastapova N. V., Stepanov A. S., Kalinin A. A. and Mamedov V. A., Voltammetric study of metal ions binding by biindolizine heterocyclophanes and their acyclic analogues, *Russian J Electrochem*, **46**, 49 (2010)
62. Sceidenbach D., Ammermann S., Bebeaux M., Freund A., Zollner M., Daniliuc C., Jones P. G., Kowalsky W. and Johannes H., Efficient and Long-Time Stable Red Iridium(III) Complexes for Organic Light-Emitting Diodes Based on Quinoxaline Ligands, *Inorg Chem*, **49**, 397 (2010)

63. Zhang K. Y., Li S. P. -Y., Zhu N., Or L. W. -S., Cheung M. S. -H., Lam Y. -W. and Lo K. K. -W., Efficient and Long-Time Stable Red Iridium(III) Complexes for Organic Light-Emitting Diodes Based on Quinoxaline Ligands, *Inorg Chem*, **49**, 2530 (2010)
64. Hussain A., Lahiri D., Begum M. S. A., Sabu S., Majumdar R., Dighe R.R. and Chakravarty A. R., Photocytotoxic Lanthanum(III) and Gadolinium(III) Complexes of Phenanthroline Bases Showing Light-Induced DNA Cleavage Activity, *Inorg Chem*, **49**, 4036 (2010)
65. Jiang W., Gao Y., Sun Y., Ding F., Xu Y., Bian Z., Li F., Bian J. and Huang C., Zwitterionic Iridium Complexes: Synthesis, Luminescent Properties, and Their Application in Cell Imaging, *Inorg Chem*, **49**, 3252 (2010)
66. Islam M.N., Kumbhar A.A., Kumbhar A.S., Zeller M., Butcher R.J., Dusane M.B. and Joshi B.N., Bis(maltolato) vanadium (III)-Polypyridyl Complexes: Synthesis, Characterization, DNA Cleavage, and Insulin Mimetic Activity, *Inorg Chem*, **49**, 8237 (2010)
67. Lo K.K.W. and H. Leung A.H., Luminescent cyclometalated iridium(III) dipyridoquinoxaline indole complexes as biological probes, *Science China Chemistry*, **53**, 2091 (2010)
68. Badawy M. A., Mohamed G. G. and Omer M. M., Synthesis, spectroscopic and thermal characterization of quinoxaline metal complexes, *Eur J Chem*, **1**, 282 (2010)
69. Deshpande M. S., Kumbhar A. S. and Näther C., Stabilization of acyclic water tetramer in a copper(II) malonate framework structure, *Dalton Trans*, **39**, 9146 (2010)
70. Tarallo M. B., Urquiola C., Monge A., Costa B. P., Ribeiro R. R., Costa-Filho A. J., Mercader R. C., Pavan F. R., Leite C. Q. F., Torre M. H. and Gambino D., Design of novel iron compounds as potential therapeutic agents against tuberculosis, *J. Inorg. Biochem*, **104**, 1164 (2010)
71. Tsierkezos N., Athanassios R., Poulos I. P. and Schroders D., Electrochemical studies of the *bis* (triphenyl phosphine) ruthenium(II) complex, *cis* - [RuCl<sub>2</sub>(L)(PPh<sub>3</sub>)<sub>2</sub>], with L = 2-(2'-pyridyl)quinoxaline, *J Coord Chem*, **63**, 3517 (2010)
72. Finagenova G. O., Nikiforova A. A., Puzyk M. V. and Balashev K. P., Mixed-ligand Pt(II) and Pd(II) complexes on the basis of cyclometalated 2-phenylpyridine and polypyridyl ligands, *Russian J Gen Chem*, **78**, 1780 (2008)
73. Hu Y., Li Q. -Q., Li H., Guo Q. -N., Lu Y.-GLi. and Z. -Y., A novel class of Cd(II), Hg(II) turn-on and Cu(II), Zn(II) turn-off Schiff base fluorescent probes, *Dalton Trans*, **39**, 11344 (2010)
74. Huang Y. -J., Ni L., Du G. and Wang L., *Jiegou Huaxue*, **29**, 1857 (2010)
75. Du Y., Zhao Y. -L., Fu X. -T Sun., H. -J. and Li X., Synthesis and fluorescence properties of complexes of terbium with red fluorescence, *Spectroscopy and Spectral Analysis*, **31**, 158 (2011)
76. Huangyan. -J., Ni L., Wang L. and ZhuC., Hydrothermal Synthesis, Characterization and Natural Bond Orbital(NBO) Analysis of [Ni(Pht)(Medpq)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> Complex, *Chinese J Inorg Chem*, **27**, 157 (2011)
77. SHiggins. L. H., White T. A., Winkel B. S. J. and Brewer K. J., Redox, spectroscopic, and photophysical properties of Ru-Pt mixed-metal complexes incorporating 4,7-diphenyl-1,10-phenanthroline as efficient DNA binding and photocleaving agents, *Inorg Chem*, **50**, 463 (2011)
78. Bulak E., Varnali T., Schwederski B., Sarkar B., Hartenbach I., Fiedler J. and Kaim W., 2,3-Bis(1-methylimidazol-2-yl)quinoxaline (bmiq), a new ligand with decoupled electron transfer and metal coordination sites: the very different redox behaviour of isoelectronic complexes with [PtCl<sub>2</sub>] and [AuCl<sub>2</sub>]<sup>+</sup>, *Dalton Trans*, **40**, 2757 (2011)
79. Budagumpi S., Kulkarni N. V., Sathisha M. P., Netalkar S. P., Revankar V. K. and Suresh D. K., Exploration on structure and anticonvulsant activity of transition metal complexes derived from an 'end-off' compartmental oligoquinoxaline derivative with phthalazyl-diazine as endogenous bridge, *Monatshefte fur Chemie*, **142**, 487 (2011)
80. Sproules S., Eagle A. A., Taylor M. K., Gable R. W., White J. M. and Young C. G., Paramagnetic oxotungsten(V) complexes containing the hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand, *Inorg Chem*, **50**, 4503 (2011)
81. Bolligarla R., Durgaprasad G. and Das S. K., Synthesis, molecular structure and supramolecular chemistry of a new nickel-quinoxaline dithiolate system [Bu<sub>4</sub>N]<sub>2</sub>[Ni(6,7-qdt)2] (6,7-qdt=quinoxaline-6,7-dithiolate) and comparison of its electronic and electrochemical properties with those of [Bu<sub>4</sub>N]<sub>2</sub>[Ni(qdt)2] (qdt=quinoxaline-2,3-dithiolate), *Inorg Chem Comm*, **14**, 809 (2011)
82. Du J. -L., Wei Z. -Z. and Hu T. -L., Metal coordination polymers of 2,3-bis (benzimidazol-1-ylmethyl) quinoxaline: Syntheses, crystal structures and luminescent properties, *Solid State Sciences*, **13**, 1256 (2011)
83. Ramakrishnan S., Shakthipriya D., Suresh E., Periasamy V. S., Akbarsha M. A. and Palaniandavar M., Ternary dinuclear copper(II) complexes of a hydroxybenzamide ligand with diimine coligands: the 5,6-dmp ligand enhances DNA binding and cleavage and induces apoptosis, *Inorg Chem*, **50**, 6458 (2011)

84. Knoll J. D., Arachchige S. M., Wang G., Rangan K., Miao R., Higgins S. L. H., Okyere B., Zhao M., Croasdale P., Magruder K., Sinclair B., Wall C. and Brewer K. J., Electrochemical, spectroscopic, and photophysical properties of structurally diverse polyazine-bridged Ru(II),Pt(II) and Os(II),Ru(II),Pt(II) supramolecular motifs, *Inorg Chem*, **50**, 8850 (2011)
85. Liu X., Li L., Lu J., Chen Y. and Zhang S., Synthesis, DNA-binding, and photocleavage studies of ruthenium(II) complexes with an asymmetric ligand, *J Coord Chem*, **64**, 4344 (2011)
86. Wu J., Li W., Higgins D. and Chen Z., Heat-Treated Nonprecious Catalyst Using Fe and Nitrogen-Rich 2,3,7,8-Tetra(pyridin-2-yl)pyrazino[2,3-g]quinoxaline Coordinated Complex for Oxygen Reduction Reaction in PEM Fuel Cells, *J Phys Chem C*, **115**, 18856 (2011)
87. Xu W. J., Liu S. J., Q. Zhao, Ma T. and Sun S., A near-infrared phosphorescent probe for F<sup>-</sup> based on a cationic iridium(III) complex with triarylboron moieties, *Science China Chemistry*, **54**, 1750 (2011)
88. Varela J., Lessa J. A., Lavaggi M. L., Beraldo H. and Cerecetto H., Coordination of 3-aminoquinoxaline-2-carbonitrile 1,4-dioxides to antimony(III) as a strategy for anti-Trypanosoma cruzi activity improvement, *Med Chem Res Online First*, 30 December (2011)
89. Etiaw S. E. H., Eltaria E., Fayed T. A. and Abdou S. N., Catalytic, Luminescence Activities and Structure of Metal-Organic Frameworks Containing CuCN Building Blocks and Bipodal Bridging Ligands, *J Inorg Organometallic Polymers and materials*, **21**, 465 (2011)
90. Etiaw S. E. H., Eltaria E., Fayed T. A. and Abdou S. N., Structure and Spectral Characteristics of 3D-Supramolecular Coordination Polymers Based on Copper Cyanide and Dimethylquinoxaline, *J. Organometallic Polymers and materials*, **21**, 480 (2011)
91. Etiaw S. E. H., El-Aziz A., Fouad S., Amar S. A. and El-bendary., Structure, Characterization and Anti-Corrosion Activity of the New Metal-Organic Framework [Ag(qox)(4-ab)], *J Inorg Organometallic Polymers and materials*, **21**, 327 (2011)
92. Park H. R. and Ha Y., Luminescence Comparison of Iridium(III) Complexes Containing Symmetric vs. Asymmetric Quinolinate Ligands, *Mol Cryst Liq Cryst*, **538**, 67 (2011)
93. Lei W., Liang N., Chong Z. and Yan-Ju H., Hydrothermal Syntheses and Crystal Structures of Cobalt(II) and Cadmium(II) Complexes with 1,2,4-Benzenetricarboxylic Acid and Pyrazino[2,3-f][1,10]-phenanthroline Ligands, *Chinese J Inorg. Chem*, **27**, 2076 (2011)
94. 49. Zhao Q., Li R. -F., Xing S. -K., Liu X. -M., Hu T. -L. and Bu X. -H., A highly selective on/off fluorescence sensor for cadmium(II), *Inorg Chem*, **50**, 10041 (2011)
95. Bulak E., Varnali T., Schwederski B., Bubrin D., Fiedler J. and Kaim W., Separation of Metal Binding and Electron Transfer Sites as a Strategy To Stabilize the Ligand-Reduced and Metal-Oxidized Form of [Mo(CO)<sub>4</sub>L], *Organometallics*, **30**, 6441 (2011)
96. Xu W., Liu S., Zhao Q., Ma T., Sun S., Zhao X. and Huang W., A near-infrared phosphorescent probe for F<sup>-</sup> based on a cationic iridium(III) complex with triarylboron moieties, *Material Science China Chemistry*, **54**, 1750 (2011)
97. Barszcz B., Masternak J., Hodorowicz M. and Jabłońska-Wawrzyczka A., Cadmium(II) and calcium(II) complexes with N,O-bidentate ligands derived from pyrazinecarboxylic acid, *J Thermal Anal Calorim.* **108**, 971
98. Hu L., Qin J., Zhou N., Meng Y. -F., Xu Y., Zuo J. -L. and You X. -Z., Synthesis, characterization, and optical properties of new metal complexes with the multi-sulfur 1,2-dithiolene ligand, *Dyes Pigments*, **92**, 1223 (2012)
99. Chen G. -J., Qiao X., Gao C. -Y., Xu G. -J., Wang Z. -L., Tian J. -L., Xu J. -Y., Gu W., Liu X. and Yan S.-P., Synthesis, DNA binding, photo-induced DNA cleavage and cell cytotoxicity studies of a family of light rare earth complexes, *J Inorg Biochem*, **109**, 90 (2012)
100. Ginzinger W., Mühlgassner G., Arion V. B., Jakupec M. A., Roller A., Galanski M., Reithofer M., Berger W. and Keppler B. K., A SAR study of novel antiproliferative ruthenium and osmium complexes with quinoxalinone ligands in human cancer cell lines, *J Med Chem*, **55**, 3398 (2012)
101. Wang L., Ni L. and Huangyan. -J., *J Yao Jiegou Huaxue*, **3**, 733 (2012)
102. Benítez D., Lavaggi M. L., Gambino D., Torre M. H. and Cerecetto H., Effect of complexation of 3-aminoquinoxaline-2-carbonitrile 1,4-dioxides with palladium and copper on their anti-*T. cruzi* activity, *Med Chem Res*, **21**, 1439 (2012)
103. Rani D. S., Lakshmi P.V.A., Prasad V.K. and Raju V.J., Synthesis and Characterization of VO(II), Fe(II), Co(II), Ni(II) and Cu(II) Complexes of 2,3-bis(3,5-dimethyl-1H-pyrazol-1-yl) Quinoxaline, *Chin J Inorg Chem*, **28**, 1245 (2012)
104. Attia A.S., Aziz A.A.A., Alfallous K.A. and El-Shahat M.F., A novel bonding of 6,7-dichloroquinoxaline-2,3-dione, DCQX, to two molybdenum (0) metal centers: Synthesis, characterization, biological activity studies and semiempirical calculations of [(bpy)<sub>2</sub>Mo( $\mu_2$ - $\kappa^2$ : $\eta^6$ -DCQX)Mo(CO)<sub>3</sub>] complex, *Polyhedron*, **44**, 238 (2012)
105. Li Y.P., Yang H.R., Zhao Q., Song W.C., Han J. and Bu X.H., Ratiometric and Selective Fluorescent Sensor for Zn<sup>2+</sup> as an "Off-On-Off" Switch and Logic Gate, *Inorg*

- Chem, **51**, 9642 (2012)
- 106.** Barszcz B., Masternak J., Hodorowicz M. and Wawrzycka A. J., Cadmium(II) and calcium(II) complexes with *N,O*-bidentate ligands derived from pyrazinecarboxylic acid, *J Therm Anal Calorim*, **108**, 971 (2012)
- 107.** 107. Chen A., S. Meng, Zhang J. and Zhang C., Two interesting tetranuclear Ag(I) complexes based on dipyrido[3,2-f:2,3-h]-quinoxaline: Synthesis, structural, luminescence and theoretical studies, *Inorg Chem Comm*, **35**, 276 (2013)
- 108.** Zhu R., Hu L., Li Y., Song Y. and Zuo J., Syntheses, crystal structures and properties of dinuclear hydrido-tris(3,5-diphenylpyrazol-1-yl)borate complexes with the S—S coupled and dimerized quinoxaline-2,3-dithiolate ligand, *Inorg Chem Comm*, **35**, 79 (2013)
- 109.** Attia A. S., Aziz A. A., Alfallow K. A. and El-Shahat M. F., New diethoxo-bridged dinuclear Cr(III) complexes with derivatives of the quinoxaline-2,3-dione ligand and 2,2'-bipyridine as a co-ligand: Syntheses, spectral characterizations, magnetic properties, antimicrobial inhibitory activities and interpretation of the electronic absorption spectra using the ZINDO/S-CI semi-empirical method, *Polyhedron*, **51**, 243 (2013)
- 110.** Chetana P.R., Rao R., Lahiri D., Policegoudra R.S., Sankolli R. and Aradhya M.S.,  $\mu$ -Oxamido binuclear copper (II) complexes: Synthesis, crystal structure, DNA interaction and antibacterial studies, *Polyhedron*, **68**, 172 (2014)
- 111.** Canaj A.B., Nodaraki L.E., Slepokura K., Siczek M., Tzimopoulos D.I., Lis T. and Milius C.J., A family of polynuclear cobalt complexes upon employment of an indeno-quinoxaline based oxime ligand, *RSC Adv*, **4**, 23068 (2014)
- 112.** Chakraborty P., Mondal S., Das S., Jana A. D. and Das D., Dicyanamide mediated construction of 1D polymeric networks of quinoxaline with d10 metal ions: Synthesis, thermogravimetric analysis, photoluminescence and a theoretical investigation on the  $\pi$ — $\pi$  interactions, *Polyhedron*, **70**, 11 (2014)
- 113.** Lizarazo-Jaimes E., Reis P. G., Bezerra F. M., Rodrigues B. L., Monte-Neto R. L., Melo M. N., Frézard F. and Demicheli C., Complexes of different nitrogen donor heterocyclic ligands with SbCl3 and PhSbCl2 as potential antileishmanial agents against SbIII-sensitive and -resistant parasites, *J Inorg Biochem*, **132**, 30 (2014)
- 114.** Nehru S., Arunachalam S., Arun R. and Premkumar K., Polymer–cobalt(III) complexes: structural analysis of metal chelates on DNA interaction and comparative cytotoxic activity, *J Biomol Struct Dyn*, **32**, 1876 (2014)