

## Review Paper

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

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## Abstract

The purpose of the present review is to provide an overview about the synthesis, characterization techniques involved and various physico-chemical properties of quinoxaline derivative metal complexes reported upto 2006 by several researchers. The synthesis of variety of metal complexes such as mono, bi and trimetallic complexes, homo bimetallic complexes, polynuclear, mixed metal and mixed ligand complexes of quinoxaline derivatives were reported by various authors. Several techniques like flash photolysis, photochemical irradiation, pulse radiolysis, hydrothermal synthesis were used in addition to the routine methods employed in the synthesis of metal complexes. The structure of the complexes was arrived mainly based on elemental analysis, molar conductance, magnetic, spectral and single crystal XRD data. The spectral studies include IR, Far IR, UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P NMR, Mass, ESR, <sup>57</sup>Fe Mossbauer, resonance Raman spectra, photo electron spectroscopy, etc. Semi empirical computational calculations, stability constant studies, gravimetric determinations of the metal complexes and thermal studies were also involved. Excited state properties like emission, photochemical properties, excited state life time measurements, luminescent studies were also ascertained. Electrochemical studies using Oster young, square wave and cyclic voltammetry, DNA binding (by thermal denaturation, electronic absorption and viscometry method), DNA cleavage, Powder XRD, etc was also done by many authors.

**Keywords:** Quinoxaline, Mixed metal, Mixed ligand, Metal complexes.

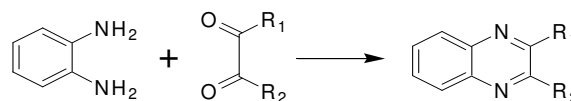
## Introduction

Metal complexes are made up of a metal ion (the acceptor) and one or more ligands containing the donor atoms. A ligand may be attached to a metal ion by more than one donor atom, thus forming a heterocyclic ring called a chelate ring. In such case the ligand may be termed a chelating agent and the resulting complex a metal chelate<sup>1</sup>. The environment around the metal centre plays a vital role in the reactivity of metal complexes. The properties of the model complexes can be changed or controlled by using modified ligands. Synthesis and characterization of complexes provides a clear idea about structure, nature of bonding and other properties. It is now possible to predict accurately the physical properties of new metal-ligand combinations and tune these properties by suitable changes in the ligand structure.

**Importance of quinoxaline derivatives:** Quinoxaline(1)<sup>2</sup> also called 1,4-benzodiazine, benzoparadiazine, phenpiazine and benzopyrazine. It is a heterocyclic compound containing a ring complex made up of benzene ring and a pyrazine ring. Quinoxaline and its derivatives are very important class of nitrogen containing heterocycles. The presence of hetero atoms in their ring ion radical and extended  $\pi$ -conjugation causes decreasing columbic repulsion. Six membered aromatic nitrogen heterocycles (azines) have relatively low  $\pi^*$  orbitals which act as good acceptors of metal d-orbital density<sup>3</sup>. Quinoxaline derivatives serve as rigid sub units in macrocyclic receptors.

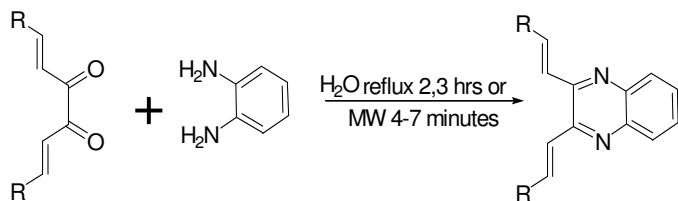
The metal complexes of quinoxaline derivatives are important due to their photochemical, photophysical, catalytic and biological properties. Derivatives of 1 are widely used as bridging ligand in both homobimetallic and heterobimetallic complexes. They have wide variety of biological applications<sup>4-11</sup>. They are also used as optoelectronic devices<sup>12</sup>, self-extinguishing and flame resistant polymer<sup>13</sup>, flourophores<sup>14</sup>, photosensitizer<sup>15</sup>, corrosion inhibitor<sup>16</sup>, and electron-transport material<sup>17</sup> and in photovoltaics<sup>18</sup>.

**Synthesis of Quinoxaline derivatives:** A number of synthetic methods are available for the synthesis of 1 and its derivatives. The most common method is condensation of an aryl 1,2-diamine with 1,2-dicarbonyl compound in suitable solvent<sup>19, 20</sup> (scheme-1). The derivatives of 1 are also prepared from cinnamils in water under conventional method or microwave irradiation method<sup>21</sup> (scheme-2). Thakuria et al.<sup>22</sup> reported one-pot efficient green synthesis for derivatives of 1. They synthesized substituted 1,4-dihydroquinoxaline-2,3-diones in one-pot reaction at room temperature from substituted o-phenylenediamines and oxalic acid (scheme-3).

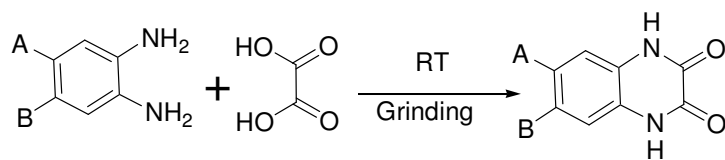


Scheme-1

Synthesis of quinoxaline by the condensation of an aryl 1,2-diamine with 1,2-dicarbonyl compound



**Scheme 2**  
**Derivatives of quinoxaline prepared from cinnamils**



**Scheme 3**  
**One-pot efficient green synthesis for derivatives of quinoxaline**

**Quinoxaline derivative metal complexes:** Spectrophotometric study of Co(II) and Ni(II) complexes with quinoxaline-2,3-dithiol has been reported by Ayres et al<sup>23</sup>. The studies revealed that the absorbing complex have polymeric structure in which the polymer chains consists of alternating metal ion and quinoxalinedithiolates. They also reported the spectrophotometric determination of platinum. It involves the reaction of platinum with 2,3-quinoxalinedithiol and complex formation<sup>24</sup>. Cu(II) halides form complexes of the type  $CuX_2L_2$  (L is 2,3-diphenyl and 2-methylquinoxaline) and  $CuX_2L$  (L is 2,3-dimethyl quinoxaline) with substituted quinoxaline. The 2,3-diphenylquinoxaline complexes appear to be monomeric whereas the others are polymeric. The 2-methylquinoxaline complexes have halide bridges and the 2,3-dimethylquinoxaline complexes are square-planar with organic ligand bridges. The structures are deduced from reflectance, far-infrared spectra and molecular models<sup>25</sup>.

Quinoxaline-2-carboxylic acid, 3-chloro and 3-hydroxy derivatives have been studied as analytical reagents. The solubility products, the optimum pH range for complete precipitation and the thermal behaviours of the metal complexes have been established. Quinoxaline-2-carboxylic acid allows the gravimetric determination of Cu(II), Cd(II), Co(II), Ni(II), Zn(II) and Pd(II) with 3-chloro and 3-hydroxy derivatives. Among these only Pd(II) could be precipitated quantitatively<sup>26</sup>. Series of complexes of Co(II) with quinoxaline (Q), 2-methylquinoxaline (Mq) and 2,3-dimethylquinoxaline (Dmq) were reported. Spectral and magnetic data were used to assign polymeric octahedral structures to the complexes  $QCoCl_2$ ,  $MqCoCl_2$  and  $Mq_3CoCl_4$  and tetrahedral structures to complexes of the type  $Q_2CoX_2$  and  $DmqCoX_2$  (where X= Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>) together with  $QCoBr_2$  and  $MqCoBr_2$ . The absorption bands

were assigned, Dq and B' values were also calculated<sup>27</sup>.

Billig et al reported a number of complexes of Ni(II) with quinoxaline (Q), 2-methylquinoxaline (Mq) and 2,3-dimethylquinoxaline (Dmq). Magnetic and spectral properties indicate that the complexes  $MqNiX_2$  (X=Cl<sup>-</sup> or Br<sup>-</sup>) and  $LNi(NO_3)_2$  (L=Q or Mq) have octahedral stereochemistry, while those of  $MqNiCl_2$  and  $Dmq_2NiCl_2$  have monomeric square planar structures. The octahedral halide complex  $MqNiCl_2$  is considered to involve both bridging halide and bidentate organic ligands<sup>28</sup>. The Co(II), Ni(II) and Cu(II) halide complexes of 2,3-di-(6-methyl-2-pyridyl)quinoxaline (dmpyq) were reported. The structures of the above complexes were assigned on the basis of magnetic and spectral data. For Co(II), the tetrahedral complexes  $CoX_2(dmpyq)$  (x=Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) were isolated and for Ni(II), the complexes  $NiX_2(dmpyq)$  (X=Cl<sup>-</sup>, and Br<sup>-</sup>) were found to be distorted octahedral. Cu(II) complexes of stoichiometry  $CuX_2(dmpyq)$  were obtained<sup>29</sup>.

Co(II), Ni(II) and Cu(II) halide complexes of 2,3-di-(2-pyridyl)quinoxaline were reported and the structures were interpreted from magnetic and spectral data. The tetrahedral complexes  $Co(II)$ ,  $CoX_2(DPYQ)$  { X= Cl<sup>-</sup> and Br<sup>-</sup>} and  $Co_2(DPYQ)_2$  { X= Br<sup>-</sup> and I<sup>-</sup>} were isolated. For Cu(II), both the chloro and bromo complexes have the stoichiometry  $CuX_2(DPYQ)$  with different structures. The Ni(II) complexes  $Ni_2Cl_4(DPYQ)(H_2O)_2$  and  $Ni(Br_2)(DPYQ)$  are octahedral<sup>30</sup>. Kidani et al reported the synthesis of indoloquinoxaline derivatives and their metal complexes<sup>31</sup>. They also reported spectrophotometric determination of the stability constants of hydroxyindoloquinoxaline metal complexes<sup>32</sup>. Matsuo et al studied the metal complexes of 1- and 4-hydroxyindoloquinoxaline<sup>33</sup>.

The synthesis of 1-phenyl-5-(2-carboxyphenyl)-3-(3-methyl-2-quinoxalyl)-formazan and its metal complexes with uranyl, Co(II) and Ni(II) ions were reported. The ratio of metal/formazan in uranium and Co(II) complexes is 1:2, in Ni(II) complex 1:1. Besides, Co(II) and Ni(II) complexes of 3-methylquinoxaline-aldehyde-o-hydroxy-anil were synthesized with a metal/azomethine ratio of 1:2<sup>34</sup>. The Co(II), Ni(II) and Cu(II) halide complexes of 6-methyl-2,3-di-(2-dipyridyl)quinoxaline (dpmq) and 6,7-dimethyl-2,3-di-(2-pyridyl)quinoxaline (dpmq) were synthesized and the structure of the complexes were interpreted on the basis of magnetic and spectral data<sup>35</sup>.

Complex,  $MoCl_4L_2$  (L=quinoxaline) was prepared from  $MoCl_4$  and  $MoCl_5$ . The ligand is monodentate in the complexes. The spectroscopic and magnetic properties of the complexes showed octahedral cis- $MoCl_4N_2$  system<sup>36</sup>. The Co(II), Ni(II) and Cu(II) halide complexes of dpq and dmpq were reported. The structures of the complexes were interpreted on the basis of magnetic and spectral data. The solution properties of the synthesized complexes were also reported<sup>37</sup>. They also reported the halide complexes of Co(II), Ni(II) and Cu(II) with 6-nitro-

2,3-di-(2-pyridyl)-quinoxaline (dpnq). The low frequency IR spectra of the synthesized complexes were also reported<sup>38</sup>.

Rignedoli et al.<sup>39</sup> reported the comparative study of the cationic, anionic and neutral crystalline Ni(II) complex of quinoxaline-2,3-dithiol ( $H_2QS_2$ ). The electronic spectra of the complexes are different and characteristic for the three classes of complexes. The very low magnetic moment observed for cationic complexes indicate a much distorted six-coordination. The anionic and the neutral complexes have a square planar coordination. In all the complexes, the ligand is S-S coordinated to the metal and a  $\nu(Ni-S)$  band is observed at around  $420\text{ cm}^{-1}$ .

Cr(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) chloride complexes with quinoxaline-1-oxide (NQxO) were prepared by allowing ligand and salt solutions pretreated with molecular sieve. The complexes were characterized based on spectral and magnetic studies. The results show that the complexes are bi or polynuclear. The Mn(II) complex is pentacoordinated and the rest of the complexes are hexacoordinated. The Fe(III) complex involves spin free-spin paired equilibria. The new metal complexes are magnetically normal high-spin compounds<sup>40</sup>. They also reported the 3d metal perchlorate complexes of NQxO. The subnormal magnetic moment suggests the involvement of two oxygen bonded bridging of NQxO ligands<sup>41</sup>.

3d metal chloride complexes of quinoxaline-1,4-dioxide (L) were prepared and characterized by spectral and magnetic studies. Cr(III) and Fe(III) chlorides formed monomeric complexes involving L, aqua ligands and lattice water. The  $NiCl_2$  yielded the chloride bridged dimer, which also contains unidentate L, coordinated through one of the NO oxygens. The rest of the new complexes contain bridging L of two types i) LO, with one of the NO oxygens acting as a bridge between adjacent metal ions. ii) OLO, with L functioning as a bidentate bridging ligand. The Mn(II) and Zn(II) complexes are polynuclear with chloro and bidentate OLO ligands. The Cr(III), Mn(II) and Ni(II) complexes are magnetically normal high-spin compounds, Fe(III) complex is magnetically subnormal<sup>42</sup>. They also reported metal perchlorate complexes of the same ligand. The synthesized complexes were characterized by IR, electronic and magnetic susceptibility studies<sup>43</sup>.

Rillema and Mark reported the preparation, optical and redox properties of mononuclear and binuclear Ru(II) complexes containing bridging ligands (BL) {2,3-di-2-pyridylquinoxaline [BL(1)] and 2,3,7,8-tetra-2-pyridyl-pyrazino[2,3-g]quinoxaline [BL(2)]}. The  $d\pi \rightarrow \pi^*(BL)$  transitions become well separated from the  $d\pi \rightarrow \pi^*$  (bpy) absorptions<sup>44</sup>. The ion pentacyano(quinoxaline)ferrate(II) was characterized in aqueous solution by Coelho et al. The complex exhibited strong metal to ligand charge transfer absorptions<sup>45</sup>.

Synthesis and chelation properties of hydrazones derived from quinoxaline-2-carboxaldehyde were reported by Case et al<sup>46</sup>.

They also reported the chelation properties of 2-hydrazinoquinoxaline with transition metal ions such as Fe(III), Co(II), Ni(II) and Cu(II). The chelation studies involve the determination of pH ranges over which colour formation occurs, wavelengths and molar absorptivities of maximum absorbance, conformance to Beer's law and ligand metal ratios.

Compounds of the type  $trans\text{-}(\text{quinox})PtCl_2(C_2H_4)$  (2-4) were prepared by the displacement of chloride from  $PtCl_3(C_2H_4)$ . The steric repulsions of the compounds were reduced, because it has one fewer perhydrogen, shows that the quinoxaline is undergoing rapid intermolecular exchange. At down to  $-73\text{ }^\circ\text{C}$ , the compound has the same symmetry as the free ligand and does not exhibit  $^1H\text{-}^{195}Pt$  coupling<sup>47</sup>. Rillema et al<sup>48</sup> reported the structure, redox and photophysical properties of a series of ruthenium heterocycles based on the ligand 2,3-bis(2-pyridyl)quinoxaline (BL),  $[Ru(bpy)_n(BL)_{3-n}]^{2+}$ , where bpy is 2,2'-bipyridine,  $n=0-2$ . The  $[Ru(bpy)_2(BL)](PF_6)_2$  complex recrystallised in the mononuclear space group with cell parameters  $a=14.664\text{ \AA}$ ,  $b=16.345\text{ \AA}$ ,  $c=18.978\text{ \AA}$  and  $Z=4$ . The ruthenium to nitrogen bond distances were  $Ru-N(\text{pyridine})=2.06\text{ \AA}$  and  $Ru-N(\text{pyrazine})=2.096\text{ \AA}$ . Absorption spectra contained bands (250-300 nm) in the ultraviolet region, assigned to ligand  $\pi\text{-}\pi^*$  transitions and visible bands at 517-300 nm, assigned to the  $\pi\text{-}\pi^*$  MLCT transitions. Three reductions observed are assigned to the electron reduction of each bidentate ligands.

The hetero oligonuclear complex,  $[Ru(BL_1)_3(PtCl_2)](PF_6)_2$  [where  $BL_1$  is 2,3-bis(2-pyridyl)quinoxaline] has been synthesized and its properties have been determined by UV-Vis. spectroscopy and electrochemical methods. In the complex Ru(II) acts as the central atom and is bridged to the Pt(II) centres by the  $BL_1$  ligand<sup>49</sup>. Preparation and properties of trimetallic and tetrametallic cluster complexes containing Ru(II) metal centers bridged by 2,3-bis(2-pyridyl)quinoxaline (bpq) were reported. The bimetallic and tetrametallic clusters are symmetrical complexes containing a central Ru(II). In tetrametallic clusters, Ru(II) is coordinated to three (bpq)Ru(bpy)<sub>2</sub><sup>2+</sup> ligands. (bpy-2,2'-bipyridin). The bimetallic clusters symmetric and has the formula  $[(bpy)Ru(bpq)Ru(bpy)_2]^{6+}$ . The complex exhibit low energy MLCT transitions assigned as  $d\pi(Ru(\text{outer})) \rightarrow \pi^*(bpq)$ . The MLCT maxima of the tetrametallic complex appear at slightly higher energies than those of its trimetallic complex. The  $E_{1/2}$  values were determined by cyclic voltammetry<sup>50</sup>.

Mono and bimetallic complexes of Ru(II) containing 1,10-phenanthroline and bidentate bridging ligand (BL) 2,3-bis(2'-pyridyl)quinoxaline (dpq) were prepared and characterized. All the mono and bimetallic complexes show emission in acetonitrile at room temperature. The lowest energy absorption feature has been assigned as a MLCT band localized on BL<sup>51</sup>. Carlton and Belciug reported the <sup>15</sup>N NMR spectra of a series of complexes  $[RhH_2(pph_3)_2(NArCO_2)]$  ( $NArCO_2$ =quinoxaline-2-carboxylate) and were obtained by the INEPT method with

polarization transfer from the hydride lying trans to nitrogen.  $^{15}\text{N}$  NMR signal moves upfield by 35-50 ppm upon coordination of nitrogen atom to the metal<sup>52</sup>.

The thermal analysis of the chloride and perchlorate complexes of divalent Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) containing one or two quinoxaline molecules and different numbers of  $\text{H}_2\text{O}$  molecules were reported. The perchlorate complexes containing two or three quinoxaline molecules in the case of Mn(II), Fe(II) and Zn(II) did not decompose to pure perchlorate during heating before an explosion occurred. The coordination of the quinoxaline is confirmed from the IR spectral data<sup>53</sup>. Some new compounds of 6,7-dimethyl-2,3-di-(2-pyridyl)quinoxaline with Co(II), Ni(II), Cu(II) and Zn(II) were prepared in toluene. The Co(II) and Zn(II) compounds have tetrahedral structures while the Ni(II) and Cu(II) complexes have octahedral structures. The thermal behavior of these compounds has been studied by thermogravimetry and differential thermal analysis. All the complexes are highly stable and decompose without the formation of any intermediate compounds to the metal oxide<sup>54</sup>.

The mixed ligand complexes of Ru(II) with 5,6-di-(2'-pyridyl)quinoxaline (dbpq) and 2,3-di-(2'-pyridyl)-quinoxaline (dpq) and the excited state properties (emission, lifetimes and redox potentials) were reported<sup>55</sup>. Pulsed laser resonance Raman studies of mono and binuclear complexes of Cu(I) with the bridging ligand dpq and triphenyl phosphine ( $\text{Ph}_3\text{P}$ ) were reported<sup>56</sup>. The solvchromism of few  $\text{W}(\text{CO})_5$  mono nuclear and dinuclear complexes of quinoxaline was reported<sup>57</sup>.

Preparation, competitive hydrogen production and emission through photochemical irradiation of the complexes  $[\text{RhH}_2(\text{PPh}_3)_2\text{L}]^+$ ,  $[\text{RhH}_2(\text{PPh}_3)_2\text{L}]^{2+}$  and  $[(\text{bpy})_2\text{RuLRhH}_2(\text{PPh}_3)_2]^{3+}$  {where  $\text{L}=\text{dpq}$ } were reported. The monometallic Rh complexes and heterobimetallic (RuLRh) complexes undergo emission in fluid solution at room temperature from a state different than the photoactive state. In the case of the heterobimetallic complexes, the photoemissive state is described as a Ru based MLCT state while the photoreaction is assigned as a Rh-based LF state in all the complexes<sup>58</sup>.

Mono and bimetallic complexes of  $\text{Re}(\text{CO})_3\text{Cl}$  containing the bidentate bridging ligands dpq and dpb have been prepared and characterized. The acceptor state in the complexes was localized primarily on the bridging ligand. Unlike the analogous Ru bimetallic complexes of dpq, the bimetallic complexes containing Re are not luminescent<sup>59</sup>. A series of Os(II) compounds of polypyridyl bridging ligands such as dpq and dpb  $\{[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$  and  $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2\}$  have been synthesized and their electrochemical and spectroscopic properties have been reported. The complexes show absorbance throughout the visible region of the spectrum. MLCT excited states are dependent upon the nature of the polypyridyl ligand<sup>60</sup>.

Carlson and Murphy Jr.<sup>61</sup> have reported the synthesis, electrochemical and spectral properties of  $[\text{Ru}(\text{dpb})_3](\text{PF}_6)_2$ . The cyclic voltammetry of  $[\text{Mo}(\text{qdt})_3]^{2-}$  in N,N-dimethylformamide was reported. The non-radiative decay of the low lying emissive MLCT excited states of a series of complexes of the type  $[\text{Re}(\text{dpq})(\text{CO})_3\text{L}]^+$  and  $[\text{Re}(\text{dpb})(\text{CO})_3\text{L}]^+$  {where, dpq = 2,3-di-2-pyridylquinoxaline; dpb = 2,3-di-2-[pyridylbenzoquinoxaline];  $\text{L} = \text{Cl}^-$ , N-methylimidazole, pyridine, 4-phenyl-pyridine, 4-methylpyridine, trimethylphosphine, acetonitrile} were reported<sup>62</sup>.

Synthesis, characterization and crystal structure of mononucleated Ni(II) complex of quinoxaline-2,3-dithiolate have been reported by Ye and co-workers. In bis (quinoxaline-2,3-dithiolato)nickel(II), sulphur atoms are coordinated to Ni(II), but one of the nitrogen atom is protonated and the other is not protonated<sup>63</sup>. The non-radiative decay of the low lying emissive MLCT excited states of a series of complexes of the type  $[\text{Re}(\text{dpq})(\text{CO})_3\text{L}]^+$  and  $[\text{Re}(\text{dpb})(\text{CO})_3\text{L}]^+$  {where, dpq = 2,3-di-2-pyridylquinoxaline; dpb = 2,3-di-2-[pyridylbenzoquinoxaline];  $\text{L} = \text{Cl}^-$ , N-methylimidazole, pyridine, 4-phenyl-pyridine, 4-methylpyridine, trimethylphosphine, acetonitrile} were reported<sup>64</sup>.

The synthesis and properties of Re(I) carbonyl incorporating bidentate ligand 6,7-dimethyl-2,3-bis(2-pyridyl) quinoxaline (ddpq) have been investigated by Yoblinski et al<sup>65</sup>. The complex is emissive in room temperature at fluid solution. The luminescence originates from an MLCT excited state. The ddpq complex did not show any emission, is due to the perturbation of the  $\pi^*$  orbital on the bridging ligand. Life time measurements confirm the existence of a correlation between MLCT energy and the non-radiative decay rate.

The synthesis, electrochemical, spectroscopic and spectroelectrochemical properties of  $[(\text{bpy})_2\text{Os}(\text{BL})\text{Ru}(\text{bpy})_2](\text{PF}_6)_2$  {BL=2,3-bis(2'-pyridyl)quinoxaline (dpq) and 2,3-bis(2,-pyridyl)benzoquinoxaline (dpb), bpy=2,2'-bipyridine} were reported. Addition of  $\text{Ru}(\text{bpy})_2^{2+}$  to the vacant coordination site on the bridging ligand in  $[\text{Os}(\text{bpy})_2\text{BL}]^{2+}$  parent compounds result a shift to lower energies of the metal-to-ligand charge transfer (MLCT) transitions terminating in the bridging ligand based  $\pi^*$  orbitals as well as shift to more positive potential of the bridging ligand based electrochemical reduction<sup>66</sup>.

The  $\text{Ln}(\text{Qdca})\cdot n\text{H}_2\text{O}$  complexes of quinoxaline-2,3-dicarboxylic acid (HQdca) with different Ln(III) metal salts have been prepared and characterized by elemental analysis, IR, UV, molar conductance, TG and DTA. The data show that the ligand coordinates to the metal ion through a nitrogen atom in the amide group and an oxygen atom in the carboxyl group. The complexes are thermally stable than the ligand and are non-electrolytes in methanol and DMF<sup>67</sup>.

The polyazine bridging ligands  $\text{Cl}_2\text{dpq}$  and  $\text{Me}_2\text{dpq}$  have been

synthesized and their electrochemical and spectroscopic properties were studied. They also synthesized monometallic and bimetallic complexes of the above bridging ligands  $\{[(bpy)_2Ru(BL)]^{2+}$  and  $[(bpy)_2Ru]_2(BL)^{4+}$ . The spectroscopic and electrochemical properties of the complexes were also reported<sup>68</sup>. The ligand L=2-(2'-pyridyl)quinoxaline and its Co(II), Ni(II), Cu(II) and Zn(II) complexes were characterized by a variety of physical and spectroscopic techniques. The ligand behaves as a bidentate chelating ligand in the monomeric pseudotetrahedral Zn(II) complex; all three nitrogen atoms of the ligand are involved in coordination in the polymeric Co(II), Ni(II) and Cu(II) complexes giving five-coordinate (Co(II)) or six-coordinate (Ni(II) and Cu(II)) structures<sup>69</sup>.

A series of homobimetallic Os(II) complexes have been prepared with general formula  $[(bpy)_2Os(BL)]^{4+}$  {where BL=2,3-bis(2-pyridyl)quinoxaline (dpq) and 2,3-bis(bis(pyridyl)benzoquinoxaline (dpb)}. The electrochemical, spectroscopic and spectrochemical properties of the compounds have been studied. The lowest energy electronic transitions in these homometallic systems have been assigned as  $Os(d\pi) \rightarrow BL(\pi^*)$  MLCT transitions. The metal centered properties are relatively unaffected by the presence of a metal fragment on the other side of the bridging ligand<sup>70</sup>. They also reported the preparation of mixed metal Os(II)/ Ru(II) trimetallic complexes bridged by polypyridyl ligand of general formula  $\{[(bby)_2Ru(BL)]_2OsCl_s\}$  (where BL = dpq and dpb and bpy = 2,2'-bipyridine). The compounds have been characterized by UV-Vis. absorption, near IR spectroscopy, cyclic, Osteryoung square-wave voltammetry and spectro-electro chemistry. The complexes display absorptions throughout the visible region of the spectrum. The lowest lying excited state of these molecules is  $Os(d\pi) \rightarrow BL(\pi^*)$  MLCT based on the central metal centre. This MLCT occurs in the near-IR region of the spectrum<sup>71</sup>. Ohzeki et al reported a simple and sensitive method for the determination of trace amounts of Ni(II). The method is based on the adsorptive enrichment of Ni(II) as the complex with quinoxaline-2,3-dithiol using a finely divided anion exchange resin<sup>72</sup>.

Anderson and co workers<sup>73</sup> reported the effect of decreasing  $\pi^*$  energies in the series of metal complexes with general formula  $[Ru(Me_2bpy)(Me_4bpy)(BL)]^{2+}$  {Me<sub>4</sub>bpy is 4,4',5,5'-tetramethyl-2,2'-bipyridine, BL=6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (Me<sub>2</sub>dpq), 2,3-bis(2-pyridyl)quinoxaline (dpq)}. Pearson et al<sup>74</sup> reported the absorption spectra of charge transfer excited states and one electron reduced states of a number of mono and binuclear Ru complexes in water obtained using laser flash photolysis and pulse radiolysis techniques. The dpq ligand contains an extended  $\pi$ -conjugated system; it results in the lowering of energies of the  $\pi$ -orbitals of the dpq ligand, hence a red shift in its MLCT transition. A series of mixed-metal trimetallic complexes of dpq and dpb were synthesized and characterized. The synthesized complexes have the general formula  $\{[(bpy)_2Ru(BL)]_2MCl_2\}^{n+}$  {where BL=dpq and dpb, M=Ir(III), Rh(III) or Os(III)}. These systems form the basis of a

molecular device for photoinitiated electron collection<sup>75</sup>.

A series of monometallic Ru(II) complexes of general formula  $[Ru(tpy)(BL)Cl]^+$  and  $[Ru(tpy)(BL)(py)]^{2+}$  were synthesized and characterized using spectroscopic, electrochemical techniques, photochemical properties were also reported<sup>76</sup>. Here the bridging ligands (BL) used are dpq and dpb. The MLCT transitions shift to lower energy when BL is varied from dpq to dpb. Substitution of the chloride ligand with pyridine leads to a blue shift of this transition. The Hg(II) complexes  $[Hg_2X_4L_2]$  (X = Cl, Br) and  $[HgI_2L]$ , where L is 2-(2'-pyridyl)quinoxaline, have been prepared and studied by a combination of conductivity measurements, FT-IR, far-IR, Raman and <sup>1</sup>H NMR spectroscopy. The structures of the free ligand L and  $[Hg_2Cl_4L_2]$  have been determined from three-dimensional X-ray data collected by counter methods. The bromo compound is isostructural with  $[Hg_2Cl_4L_2]$ , while a monomeric pseudotetrahedral structure is assigned for the iodo complex in the solid state<sup>77</sup>.

Spectroscopic and spectroelectrochemical comparison is made among homo and heterobimetallic complexes of  $[(bpy)_2Ru(BL)Os(bpy)_2]^{4+}$ ,  $[(bpy)_2Ru(BL)Ru(bpy)_2]^{4+}$  and  $[(bpy)_2Os(BL)Os(bpy)_2]^{4+}$  {BL=2,3-bis(2'-pyridyl) quinoxaline (dpq) or 2,3-bis(2'-pyridyl) benzoquinoxaline (dpb); bpy = 2,2'-bipyridine}. The visible spectroscopy of mixed-metal systems of this nature can be accurately interpreted by comparison to the homobimetallic analogues<sup>78</sup>. Infrared and Raman spectra of two new metal (II) quinoxaline tetracyanonickelate complexes,  $M(Qx)_2Ni(CN)_4$ , {M = Cd or Ni, Qx = quinoxaline} have been investigated. It is proposed that their structure consists of two dimensional polymeric sheets formed from  $Ni(CN)_4$  ions bridged by  $M(Qx)_2$  cations. They also reported the effective magnetic moments of the complexes<sup>79</sup>. The reactions of  $ZnX_2$  and  $CdX_2$  (X=Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) with the biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline (L) were studied in ethanolic solutions. The new complexes  $[ZnX_2L]$ ,  $[CdI_2L]$  and  $[Cd_2X_4L_2]$  were isolated and characterized by elemental analyses, conductivity measurements, X-ray powder patterns, thermal methods (TG/DTG, DTA) and spectroscopic (IR, far-IR, Raman and <sup>1</sup>H NMR) studies. The data are discussed based on nature of bonding, known and assigned structures<sup>80</sup>.

The photophysical properties of the low lying emissive MLCT excited states of two series of complexes of the type  $[Re(BL)(CO)_3L]^+$  {BL=2,3-di(2-pyridyl)quinoxaline (dpq); L=N-methylimidazole, trimethylphosphine, acetonitrile, and substituted pyridines} have been investigated. These systems have been studied by emission spectroscopy, electronic absorption spectroscopy, IR spectroscopy, excited state lifetime measurements, electrochemistry and resonance Raman spectroscopy. The results show that the rate constant for nonradiative decay is the dominant mode of excited state relaxation and that the energy gap law for radiationless decay in the weak coupling limit is obeyed by these two series of complexes<sup>81</sup>.

The first 1:2 metal complexes of 2-(2'-pyridyl)quinoxaline (L) have been isolated. The physical and spectroscopic characteristics of the compounds  $[MCl_2L_2]$  ( $M=Ni(II)$ ,  $Cu(II)$  and  $Cd(II)$ ) and  $[CuL_2](PF_6)$  are described. The structure of the  $Cu(I)$  complex has been determined by X-ray diffraction methods. The ligand L acts as a bidentate chelate, the ligated atoms being the pyridine nitrogen and the nearest quinoxaline nitrogen. The structure of  $[CuL_2]^+$  consists of a distorted tetrahedral arrangement around the  $Cu(I)$  atom. Monomeric trans pseudo-octahedral stereochemistry is assigned for the  $[MCl_2L_2]$  complexes<sup>82</sup>. Kilpatrick et al<sup>83</sup> reported the resonance Raman Spectra of quinoxaline attached to a  $Cp_2Mo[IV]$  dithiolene chelate [ $Cp=cyclopentadienyl$ ], compared the spectra with Rhodobactersphaeroidesdimethylsulphoxide reductase, an enzyme containing molybdopterin cofactor.

A set of  $Pt(II)$  complexes of 5 have been synthesized and studied in terms of photophysical and electro chemical behaviour.  $dqt$  and  $dmqdt$  has only minor effects on the emissive properties. The report describes the luminescence properties of the complexes  $Pt(phen)(qdt)$ ,  $Pt(COD)(qdt)$  and  $(TBA)_2[Pt(qdt)_2]$ <sup>84</sup>. {phen=1,10-phenanthroline, COD=1,5-cuclooctadiene and TBA=tetra-n-butyl ammonium}. The 2:1 and 1:1 reactions of  $MeHgI$  with 2-(2'-pyridyl)quinoxaline (L) in methanol led to  $Hg-C$  bond cleavage and yielded the dinuclear complex  $[Hg_2L_4]$  as one of the products. The crystal structure of this compound shows a chelating behaviour of L and different (terminal, asymmetric bridging) iodide coordination modes. Spectroscopic characteristics of the dimer and the biological relevance of this reaction are also reported<sup>85</sup>.

Raman spectro-electrochemical and X-ray crystallographic studies have been made for the binuclear  $Cu(I)$  complex,  $[(Ph_3P)_2Cu(dpq)Cu(PPh_3)_2][BF_4]_2$  {where  $dpq$  is the bridging ligand 2,3-di(2-pyridyl)quinoxaline}. The X-ray data show that the pyridine rings are twisted out of plane with respect to the quinoxaline ring which is itself non planar. The UV-Vis. spectra of the MLCT excited state and those of the electrochemically reduced complex are similar. The resonance Raman spectrum of the latter species suggests minimum change in the inter ring C-C bond order in the electrochemically or charge transfer generated radical anion. Semi empirical molecular orbital calculations on both the neutral  $dpq$  and radical anion show two non degenerate lowest unoccupied orbitals in the neutral species. One is strongly bonding across the inter ring C-C bond while the other is almost non-bonding. The Raman data suggest that it is this latter orbital which is populated in the transient and electrochemical experiments<sup>86</sup>.

Spectroscopic and electrochemical properties of a series of mixed metal  $d^6$ ,  $d^8$  bimetallic complexes of the form  $[(bpy)_2M(BL)PtCl_2]^{2+}$  ( $bpy = 2,2'$ -Bipyridine;  $BL = dpq$  (2,3-Bis(2-pyridyl)quinoxaline) or  $dpb$  (2,3-Bis(2-pyridyl)-benzoquinoxaline);  $M = Os(II)$  or  $Ru(II)$ ) were reported<sup>87</sup>. The heteronuclear trimetallic systems,  $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$

{ $bpy$  is 2,2'-bipyridine and  $BL$  are the bridging ligands  $dpq$  or  $dpb$ }, represent a new family of catalysts for the reduction of  $CO_2$ . Two remote  $Ru$  centers serve to tune the redox properties of the central catalytically active  $Ir(III)(BL)_2Cl_2$  core. Controlled potential electrolysis experiments using these new trimetallic catalysts can give current efficiencies as high as 99% for  $CO$  production with high turnover numbers. This is in marked contrast to the lower current efficiency achieved using the monometallic  $[Ir(BL)_2Cl_2]^+$  analogs which produce formate as a reduction product. These catalysts represent a new class of systems in which the redox properties of the catalytic site can be altered through remote metal coordination and variation without a change in the coordination environment of the catalytic iridium site<sup>88</sup>.

$Ru(II)$  complexes with polypyridyl bridging ligand 6,7-dimethyl-2,3-di(2-pyridyl)-quinoxaline ( $dpqm$ ) have been prepared. The electronic and resonance Raman spectra of the parent complexes and their reduced and oxidized products have been measured. These results indicate that for both complexes the first oxidation is metal based and the first reduction is bridging ligand based. The resonance Raman spectra of the reduced species suggest electron localization of the LUMO to be spread across the pyridine and pyrazine/quinoxaline sections of the bridging ligands<sup>89</sup>.

The hydrothermal synthesis of hybrid coordination polymer from  $\beta$ -octamolybdates linked by quinoxaline and its oxidized benzimidazole coordinated to binuclear  $Cu(I)$  fragments has been reported<sup>90</sup>. In this complex organo nitrogen ligand acts as an effective reduction reagent and its product benzimidazole ligand coordinates to  $Cu(I)$  atoms directly under hydrothermal conditions.

The synthesis, characterization and DNA binding properties of a series of mixed metal complexes coupling  $Ru$  light absorbers to  $Pt$  reactive metal sites through polyazine bridging ligands have been prepared<sup>91</sup>. They have the general formula  $[(tpy)RuCl(BL)PtCl_2]PF_6$  { $B=2,3$ -bis(2-pyridyl) quinoxaline ( $dpq$ ), 2,3-bis(2-pyridyl) benzoquinoxaline ( $dpb$ );  $tpy=2,2':6',2''$ -terpyridine)}. These systems possess electron rich  $Ru$  metal centers bound to five polyazine nitrogens and one chloride ligand. This leads to complexes with low energy  $Ru-BL$  charge transfer bands that are tunable with  $BL$ . The chlorides bound to  $Pt(II)$  centre are substantially labile and has the ability to covalently bind to DNA.

A convenient new synthetic route to metallo-1,2-enedithiolates was applied to the synthesis of  $(dppe)M\{S_2C_2-(heterocycle)(H)\}$ ;  $dppe = 1,2$ -bis(diphenyldiphosphino)ethane,  $M = Ni$ ,  $Pd$ , and  $Pt$  and heterocycle = 2-quinoxaline. These complexes were prepared from the corresponding bis(hydrosulfido) complexes  $(dppe)M(SH)_2$  and the  $\alpha$ -bromo ketones, heterocycle- $C(O)CH_2Br$ . The energy of the ILCT transition tracks with the reduction potential of the appended aromatic heterocycle. The  $pK_a$  of the protonated complexes is

1-3 units higher than that of the parent heterocycle, independent of the metal and consistent with resonance stabilization of the protonated heterocycle by the 1,2-enedithiolate ligand<sup>92</sup>.

Series of conjugated polymers functionalized with different Ru polypyridine metal complexes were synthesized by the Pd catalyzed reaction. Two conjugated polymer systems have been studied, poly(phenylenevinylene) with bis(2,2':6',2''-terpyridine) Ru(II) on the main chain and quinoxaline based polymers with tris(2,2'-bipyridine) Ru(II). The Ru polypyridine complexes exhibit a long lived MLCT excited state which can enhance the photosensitivity of the resulting polymers. Different physical properties such as the photoconductivity and charge mobility in these polymers are also studied<sup>93</sup>. A series of novel quinoxaline based conjugated polymers which contain Ru(II) bipyridine complex were synthesized by the Suzuki coupling reaction. Excitation and emission spectroscopy suggest an energy transfer between the backbone and the metal complex. The polymers exhibit hole carrier mobilities of  $\approx 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ , which is comparable to organic photoconductors<sup>94</sup>.

A number of mononuclear Re(I) complexes have been prepared and their physical properties, excited-state and spectro electrochemical resonance Raman spectra were studied. These compounds have the general formula  $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})]$ , {where L can be 2,3-di(2-pyridyl)quinoxaline (dpq), 2-(2-pyridyl)quinoxaline (pq) or 5-methyl-2,3-di(2-pyridyl)quinoxaline (mdpq)}. The structure of  $[\text{Re}(\text{CO})\text{Cl}(\text{dpq})]$  was determined by single-crystal X-ray diffraction. The resonance Raman spectra of the reduced complexes show some polarization of electron density towards the bound pyridyl ring. The excited states have very similar spectral features to those of the reduced complexes. This suggests that electrochemically prepared redox states model the MLCT state for these systems<sup>95</sup>. Four binuclear Re(I) complexes of the form  $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{BL}$ , {where BL is one of the bridging  $\text{N}_4$  donor ligands 2,3-di(2-pyridyl)quinoxaline and 2,3-di(2-pyridyl)-6-methylquinoxaline} have been studied by femto second time-resolved UV-Vis. and IR absorption spectroscopies. The variation in excited state lifetime with bridging ligand structure is attributed to changes in the rate constants for nonradiative decay, which correspond qualitatively with changes in the energy of the excited state in accordance with the energy gap law for nonradiative relaxation<sup>96</sup>.

The 1:1 reactions of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3$  with the biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline (L) were studied in methanol. The new complexes  $[\text{Fe}_2\text{Cl}_4\text{L}_2]$  (a) and  $[\text{Fe}_2\text{Cl}_4\text{L}_2]\text{Cl}_2$  (b) were isolated and characterized by elemental analyses, conductivity measurements, magnetic susceptibilities at room temperature and spectroscopic (IR, far-IR, ligand field and<sup>57</sup> Fe Mössbauer) techniques. The X-ray crystal structure of (a) suggest, Fe(II) is distorted trigonal bipyramidal with the bridging chlorides occupying axial and equatorial sites of each Fe(II) atom. A five-coordinate dinuclear structure is also assigned for the cation of complex (b)<sup>97</sup>.

The Fe(II) compounds of formula  $[\text{Fe}(\text{DPQ})_2(\text{NCS})_2] \cdot \text{CO}(\text{CH}_3)_2$  {DPQ = 2,3-bis-(2'-pyridyl)-quinoxaline} was synthesized and the crystal structure was determined by X-ray diffraction methods. Variable-temperature magnetic susceptibility data in the temperature range 290-4.2 K revealed the complex as high spin. The thermodynamic model of Slichter and Drickamer was applied to account for the magnetic data<sup>98</sup>. The assisted transfer of Cu(II) by interfacial complexation with 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline (DMDPQ) is studied at the polarised water/1,2-dichloroethane junction. Thermodynamic and kinetic aspects were determined by cyclic voltammetry and in situ spectrophotometric measurements. The dependence of the half wave transfer potential on the ligand concentration suggests that the equilibrium is effectively displaced towards a 1:3 (metal:ligand) stoichiometry. Chronoabsorptometric studies in the presence of a ligand suggest that the assisted transfer kinetics are effectively controlled by the diffusion of the metal ion to the interface<sup>99</sup>.

<sup>1</sup>H NMR spectroscopy was used to study the oligonucleotide binding of the  $\Delta$  enantiomers of  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  {where the bidentate ligand L is dipyrido[3,2-d:2',3'-f]quinoxaline (dpq) or dipyrido[3,2-a:2'3'-c](6,7,8,9-tetrahydro)phenazine (dpqC)}. The data from one and two dimensional NMR experiments of the oligonucleotide metal complex binding suggest that all two Ru(II) polypyridyl complexes bind in the DNA minor groove. Molecular modeling of the metal complex in the intercalation site suggests that  $\Delta$ - $[\text{Ru}(\text{phen})_2\text{dpq}]^{2+}$  binds in a head on fashion with the phenanthroline rings in the minor groove and the dpq ligand inserted into the nucleotide base stack. NOESY experiments of the binding of  $\Delta$ - $[\text{Ru}(\text{phen})_2\text{dpq}]^{2+}$  with  $d(\text{GTCGAC})_2$  and  $d(\text{TCGGGATCCCGA})_2$  suggest that intercalation from the minor groove is favored at purine-purine/pyrimidine-pyrimidine sequences for this complex. The syntheses of  $\Delta$ - $[\text{Ru}(\text{phen})_2\text{dpq}]^{2+}$  and  $\Delta$ - $[\text{Ru}(\text{phen})_2\text{dpqC}]^{2+}$  were reported<sup>100</sup>.

The electrochemistry and spectral properties of a series of mono- and binuclear complexes with bridging ligands based on 2,3-di(2-quinolyl)quinoxaline were reported. The ligands are 2,3-di(2-quinolyl)quinoxaline (dqq), 6,7-dimethyl-2,3-di(2-quinolyl)quinoxaline (dqqMe<sub>2</sub>) and 6,7-dichloro-2,3-di(2-quinolyl)quinoxaline (dqqCl<sub>2</sub>). The mononuclear complexes reduce at the metal and dechelate, as evidenced by UV-Vis. spectroelectrochemistry. The reduction species are identified using resonance Raman spectroscopy<sup>101</sup>. The electrochemical behaviours of 2,3-dihydroxy-quinoxaline (2,3-DH<sub>2</sub>Qx) and the complex species formed with Zn(II) have been studied in non aqueous media. Neither the protonated ligand nor its quinonic form exhibit the formation of stable complexes with Zn(II) whereas the dianionic species produces two coordination compounds having M:L stoichiometric ratios of 1:1 and 1:2. The semiquinone form of the ligand by itself shows the tendency to polymerize on the surface of the electrode and it is not stabilized in the presence of this metal ion<sup>102</sup>. Cr(III),

Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of 3-(3,5-dimethyl pyrazole-1-yl) quinoxaline-2-one have been prepared and characterized on the basis of analytical, electrical conductance, IR, electronic spectral and magnetic susceptibility studies<sup>103</sup>.

The reaction of  $MnCl_2 \cdot 4H_2O$  with the biheteroaromatic ligand (L), formed the dinuclear complex bis[aquachloro-2-(2'-pyridyl)quinoxaline]di- $\mu$ -chloro dimanganese  $\{[Mn_2L_2Cl_4(H_2O)_2]\}$ , which was studied in the solid state by thermal techniques [thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA)], spectroscopy (IR, far-IR and electronic spectra), magnetic susceptibility, X-ray diffraction methods as well as in methanolic solution by electrospray mass spectrometry (ES-MS). The X-ray crystal structure showed two Mn(II) ions bridged by two chloro ligands with a terminal chloride, a water molecule and a chelating molecule of L, completing a six-coordinate octahedral geometry around each metal centre<sup>104</sup>.

The synthesis of the new complex  $Au(qdt)_2$  as the tetraphenylphosphonium salt and the preparation of (bedt-ttf)M(qdt)<sub>2</sub>, (tmtsf)M(qdt)<sub>2</sub> and (ttf)M(qdt)<sub>2</sub> with M=Au, Cu(II) and (ttf)<sub>3</sub>[Ni(qdt)<sub>2</sub>]<sub>2</sub> were reported. Their electrical conductivity and thermoelectric power were measured showing in all cases activated behaviour with room temperature values of  $\sigma$  ranging from  $10^{-7}$  to  $10^{-3}$  S cm<sup>-1</sup>, the highest value being for (bedt-ttf)Au(qdt)<sub>2</sub> which has a gap  $\Delta E=0.32$  eV. Preliminary E.S.R. results for (ttf)Cu(qdt)<sub>2</sub> are also presented<sup>105</sup>.

<sup>1</sup>H NMR spectroscopy and viscosity measurements have been used to study the oligonucleotide binding of the  $\Delta$  and  $\Lambda$  enantiomers of the metal complex  $[Ru(dmphen)_2dpq]^{2+}$  {dmphen = 2,9-dimethyl-1,10-phenanthroline and dpq = dipyrido[3,2-f:2',3'-h]quinoxaline}. The addition of the  $\Delta$  enantiomer increased the relative viscosity of the DNA solution, while a decrease in the relative viscosity of the DNA was observed upon addition of the  $\Lambda$  metal complex. These results confirm that octahedral metalointercalators can intercalate from the minor groove. In addition, the results demonstrate that the left handed enantiomer of  $[Ru(dmphen)_2dpq]^{2+}$  prefers to intercalate from the narrow minor groove despite only being able to partially insert a polycyclic aromatic ligand into the DNA base stack<sup>106</sup>.

Absorption of quinoxaline-2,3-dithiol ( $H_2QS_2$ ) (6) and disodiumbis(quinoxaline-2,3-dithiolato) nickelate(II). ( $Na_2-[Ni(QS_2)_2]$ ) on a silver surface was studied by SERRS as well as FT-SERS techniques.  $H_2QS_2$  was found to decompose on the silver surface to the dithiolate ion, which binds the surface through its sulfur atoms. The absorbed dithiolate ion has a perpendicular orientation on the silver surface<sup>107</sup>. New solid complexes of transition metal Co(II), Ni(II) and Cu(II) with quinoxaline-2,3-dicarboxamide were synthesized and the composition of the complexes was confirmed to be  $M(Qx_2)_2Cl_2$  {M=Co(II), Ni(II), Cu(II)} by elemental analysis

molar conductance and thermal analysis. The coordination pattern and structure were discussed by IR and electronic spectra<sup>108</sup>.

The compounds  $(L-N_3)MoO(qdt)$  and  $(L-N_3)MoO(tdt)$  [ $(L-N_3)$  = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; tdt = toluene-3,4-dithiolate; qdt = quinoxaline-2,3-dithiolate] have been studied by cyclic voltammetry, photoelectron, magnetic circular dichroism and electronic absorption spectroscopy. The experimental data have been interpreted in the context of ab-initio molecular orbital calculations on a variety of dithiolate dianion ligands<sup>109</sup>. Reaction of Co(II) perchlorate hexahydrate and anhydrous Co(II) chloride with the ligand 2-(2'pyridyl)quinoxaline (L) leads to the formation of the novel five- and six-coordinated complexes  $CoCl_2(DMF)$  and  $[CoL_2(H_2O)_2](ClO_4)_2 \cdot H_2O \cdot 2CH_3OH$  correspondingly. The crystal structures of the above complexes show a trigonal bipyramidal geometry around the metal atom for complex  $CoLCl_2(DMF)$  and a distorted octahedral geometry for complex  $[CoL_2(H_2O)_2](ClO_4)_2 \cdot H_2O \cdot 2CH_3OH$ <sup>110</sup>.

The resonance Raman spectra of the ground and lowest excited states for a series of binuclear Cu(I) complexes with bridging ligands based on 2,3-di-(2-pyridyl)quinoxaline have been measured. Analyses of the ground-state resonance Raman spectra show strong enhancement of an inter-ring stretching mode and quinoxaline based modes. The electronic absorption data suggest the initially formed MLCT state is localised towards the quinoxaline ring system. The excited state resonance Raman spectroscopy shows similar spectral features for complexes which have substituent changes at the pyridyl rings of the bridging ligand. They show spectra associated with the radical anion of the bridging ligand<sup>111</sup>.

Platinum and palladium dichlorides react readily with 2,2'-azoquinoxaline to give the di- $\mu$ -chloro-2,2'-azobis-(7,7'-bis-benzoyl-quinoxaline) diplatinum(II) and dipalladium(II) complexes. These crystalline complexes exhibit both metal-carbon binding and coordinate metal-nitrogen binding to azoquinoxaline<sup>112</sup>. Dioximes related to 2,2'-bis[4-(2,3-bis(hydroxyimino)quinoxaline) phenylpropane ( $H_4L_1$ ) and 4,4'-oxy-bis-[2,3-bis(hydroxyimino)quinoxaline] ( $H_4L_2$ ) precursor tetraamine compounds have been prepared. Some polymeric Co(III) complexes have been isolated. In addition, polymeric Cu(II) complex with the ligand ( $H_4L_2$ ) has been prepared. The polymeric complex  $[Cu(H_4L_2)]_n$  obtained gets coordinated through the deprotonated oximate oxygens to afford a new kind of structure bridged by the oximate groups in the cis arrangement with 1,10-phenanthroline as an end cap ligand. These complexes have been characterized by elemental analyses, mass, IR and <sup>1</sup>H NMR spectra and electrical conductivity measurements<sup>113</sup>.

The reactions of 2,3-bis(2-pyridyl)quinoxaline (bpq) with  $CoCl_2 \cdot 6H_2O$ ,  $Ag(CH_3CN)_4BF_4$ , and  $PdCl_2(C_6H_5CN)_2$  produce  $[CoCl_2(bpq)]_2 \cdot 2CHCl_3$ ,  $[Ag(bpq)CH_3CN]_2(BF_4)_2 \cdot 2CH_3CN$ , and



[PdCl<sub>2</sub>(bpq)], respectively. All the products are distinct 1:1 (metal:bpq) adducts, where the chelation mode of the bpq is dependent upon the metal atoms. The structure of [CoCl<sub>2</sub>(bpq)]<sub>2</sub>·2CHCl<sub>3</sub> is a centrosymmetric Cl<sup>-</sup> bridged four membered dimer. [Co<sub>2</sub>Cl<sub>2</sub>], in which the bpq is bonded to the Co(II) atom in an anisobidentate mode with the nitrogen donors of pyridine and pyrazine rings. For [Ag(bpq)CH<sub>3</sub>CN]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN, each bpq ligand connects two tetrahedral Ag(I) ions in a tridentate mode, resulting in a cationic cyclic dimer. The structure of [PdCl<sub>2</sub>(bpq)] approximates to a molecular rocking chair with an isobidentate bpq through the nitrogen donors of 2-pyridyl rings. The compounds exhibit significant and characteristic relationships between the structures and their thermal properties. For [CoCl<sub>2</sub>(bpq)]<sub>2</sub>·2CHCl<sub>3</sub>, the solvate chloroform molecules are safely contained up to 144 °C but drastically evaporate above this temperature. The striking feature of [Ag(bpq)CH<sub>3</sub>CN]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN is that the skeletal cyclic dimer is basically retained after dissociation of the coordinated acetonitriles in the solid state<sup>114</sup>.

Novel Ru(II) polypyridine complexes [(bpy)<sub>2</sub>Ru(L)]<sup>2+</sup>, {where bpy=2,2'-bipyridine and L=dipyrido[3,2-f:2',3'-h]quinoxaline-2,3-dicarboxylic acid (dpq(COOH)<sub>2</sub>), 3-hydroxydipyrido[3,2-f:2',3'-h]quinoxaline-2-carboxylic acid (dpq(OHCOOH)) and 2,3-dihydroxydipyrido[3,2-f:2',3'-h]quinoxaline (dpq(OH)<sub>2</sub>)} have been synthesized, characterized and anchored to nanocrystalline TiO<sub>2</sub> electrodes for light to electrical energy conversion in regenerative photoelectrochemical cells with I<sup>-</sup>/I<sub>2</sub> acetonitrile electrolyte. The effect of pH on the absorption and emission spectra of these complexes consisting of protonatable ligands has been investigated in water by spectrophotometric titration<sup>115</sup>.

New metal complexes of the type [Mn<sub>2</sub>(dmbq)L<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>, [Fe<sub>2</sub>(dmbq)L<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> (NO<sub>3</sub>)<sub>4</sub>·6H<sub>2</sub>O, [Co<sub>2</sub>(dmbq)Cl<sub>2</sub>L<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [Ni<sub>2</sub>(dmbq)Cl<sub>2</sub>L<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [Cu<sub>2</sub>(dmbq)Cl<sub>2</sub>L<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [Ru<sub>2</sub>(dmbq)L<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Rh<sub>2</sub>(dmbq)Cl<sub>2</sub>L<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](Cl<sub>2</sub>·2H<sub>2</sub>O), [Pd<sub>2</sub>(dmbq)L<sub>2</sub>Cl<sub>2</sub>·5H<sub>2</sub>O and [Ag<sub>2</sub>(dmbq)L<sub>2</sub>] (where dmbq<sup>2-</sup> is the dianion of 2,5-dihydroxy-1,4-benzoquinone and L is the biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline) were synthesized. The new complexes were characterized by elemental analyses and by a variety of physical and spectroscopic techniques. Dinuclear structures are assigned for the complexes in the solid state. The metal ion coordination geometries are octahedral, tetrahedral or square planar<sup>116</sup>.

The molecular recognition of oligonucleotides by chiral Ru complexes has been probed by NMR spectroscopy using the template  $\Delta$ -cis- $\alpha$ - and  $\Delta$ -cis- $\beta$ -[Ru(RR-picchxnMe<sub>2</sub>)(bidentate)]<sup>2+</sup> {bidentate ligand is dpq (dipyrido[3,2-f:2',3'-h]quinoxaline, picchxnMe<sub>2</sub> is N,N'-dimethyl-N,N'-di(2-picolyl)-1,2-diaminocyclohexane}. The interaction of  $\Delta$ -cis- $\alpha$ -[Ru(RR-picchxnMe<sub>2</sub>)-(dpq)]<sup>2+</sup> with [d(CGCGATCGCG)]<sub>2</sub> showed intermediate exchange kinetics

and evidence of minor groove intercalation at the GA base step. The groove binding preferences exhibited by the different bidentate ligands is explained with the aid of molecular modeling experiments<sup>117</sup>.

Unsymmetrical porphyrazines (tetraazaporphyrins) bearing a single bidentate phenanthroline chelating group M[pz(t-butylphenyl)6phen] have been prepared by the base catalyzed cross condensation of 3,4-bis(4-tertbutylphenyl)pyrroline-2,5-diimine (in excess) with 6,7-dicyanodipyridoquinoxaline. Treatment of these centrally metalated (M=Mg(II), Zn(II)) ligands with various Ru(II) salts has yielded several bimetallic complexes including the first coordinatively linked porphyrazine trimer. The optical properties of these complexes are shown to be a function of the additional ligands surrounding the asymmetric Ru center<sup>118</sup>.

New method is proposed by Amin et al<sup>119</sup> for the microdetermination of Hg(II). Hg(II) forms insoluble complexes with 2,3-dichloro-6-(2-hydroxy-3,5-dinitrophenylazo)-quinoxaline, 2,3-dichloro-6-(5-amino-3-carboxy-2-hydroxyphenylazo)-quinoxaline, 2,3-dichloro-6-(2,7-dihydroxynaphth-1-ylazo)-quinoxaline and 2,3-dichloro-6-(3-carboxy-2-hydroxynaphth-1-ylazo)-quinoxaline in aqueous acidic medium; the complexes can be made soluble by the action of an anionic surfactant. The molar absorptivity, sandell sensitivity and relative standard deviations were also calculated. A slight interference from Pd(II) and Cd(II) is exhibited by the first three ligands, whereas the last one is only negligibly affected by these metal ions. The method was applied to the determination of methyl and ethylmercury chloride and the analysis of environmental water samples.

The syntheses, characterization, crystal structures, photophysical and electrochemical properties of two dinuclear and two polymeric Ag(I) complexes with three polypyridyl ligands, 2,3-di-2-pyridylquinoxaline (L<sub>1</sub>), 2,3-di-2-pyridyl-5,8-dimethoxyquinoxaline (L<sub>2</sub>) and 2,3,7,8-tetrakis(2-pyridyl)pyrazino[2,3-g] quinoxaline (L<sub>3</sub>) were reported. The structures of the two box like dinuclear complexes with L<sub>1</sub> and L<sub>2</sub> are chemically the same. Differently crystallized one dimensional zigzag chain coordination polymers also have of boxlike dinuclear subunits have been elucidated by X-ray analysis<sup>120</sup>.

A new series of Ru(II) polypyridyl sensitizers with strongly electron donating dithiolate ligands Ru(dcbpy)<sub>2</sub>(L) and Ru(dcphe)<sub>2</sub>(L) {where L is quinoxaline-2,3-dithiolate (qdt), dcbpy is 4,4'-dicarboxy-2,2'-bipyridine and dcphe is 4,7-dicarboxy-1,10-phenanthroline} have been prepared for sensitization of nanocrystalline TiO<sub>2</sub> electrodes<sup>121</sup>. Spectroelectrochemical investigations of two dinuclear complexes [Ru(III)(bpy)<sub>2</sub>( $\mu$ -BL)Ru(II)(bpy)<sub>2</sub>]<sup>5+</sup> {BL = 2,3-bis(2-pyridyl)-1,4-benzoquinoxaline (dpb)} revealed that the intervalence charge transfer (IT) characteristics are sensitive to the stereochemistry. Thermochromism, redox and semiempirical

computational studies suggest differential ion pairing between the diastereoisomeric forms<sup>122</sup>.

Series of Ru(II) complexes with hexafluorophosphate and chloride salts incorporating a new dipyrido phenazine based ligand, dicnq (6,7-dicyanodipyrido [2,2-d:2',3'-f]quinoxaline) were synthesized (7-9)<sup>123</sup>. These mono ([Ru(phen)<sub>2</sub>(dicnq)]<sup>2+</sup>, bis ([Ru(phen)(dicnq)<sub>2</sub>]<sup>2+</sup>) and tris ([Rdicnq]<sub>3</sub>)<sup>2+</sup>) complexes were characterized by elemental analysis, IR, FAB-MS, <sup>1</sup>H NMR and cyclic voltammetric methods. Thermal denaturation and absorption study revealed that the complexes were moderately strong binders of calf thymus (CT) DNA. Luminescence studies reveal that [Rdicnq]<sub>3</sub>)<sup>2+</sup> is non luminescent and [Ru(phen)<sub>2</sub>(dicnq)]<sup>2+</sup> and [Ru(phen)(dicnq)<sub>2</sub>]<sup>2+</sup> are moderately efficient molecular light switches for DNA.

The trimetallic complexes [{(bpy)<sub>2</sub>M(dpp)}<sub>2</sub>Ru(dpq)]<sup>6+</sup> (M=Ru(II) or Os(II), bpy=2,2'-bipyridine, dpp=2,3-bis(2-pyridyl)pyrazine, and dpq = 2,3-bis(2-pyridyl)quinoxaline) have been prepared and their spectroscopic, electrochemical and spectro-electrochemical properties were investigated. The details of the electrochemical, spectroscopic and spectroelectrochemical studies of these supramolecular light absorbers and the dichloro synthons, [{(bpy)<sub>2</sub>M(dpp)}<sub>2</sub>RuCl<sub>2</sub>]<sup>4+</sup> were reported<sup>124</sup>.

Ru<sub>3</sub>(CO)<sub>12</sub> reacts with 2,3-bis(2'-pyridyl)quinoxaline (dpq) in benzene in the presence of either 2,2'-dipyridine (dpy) or pyridine (py) to give the mononuclear complexes Ru(CO)<sub>3</sub>(dpq) and Ru(CO)<sub>2</sub>(dpq)(py) respectively. Reactions of Os<sub>3</sub>(CO)<sub>12</sub> with dpq alone or in the presence of dipyridine, yield only Os(CO)<sub>3</sub>(dpq). Reactions of RuCl<sub>3</sub> with dpq under reduced pressure in PhH/EtOH gave bis-[Ru(dpq)<sub>2</sub>Cl<sub>2</sub>]Cl. Magnetic measurements showed Ru(III) with low spin electronic configuration. Three complexes, Rh<sub>2</sub>(dpq)<sub>2</sub>Cl<sub>6</sub>, [Rh(dpq)<sub>2</sub>Cl<sub>2</sub>]Cl and Rh(dpq)(py)Cl<sub>3</sub> were isolated from reactions of RhCl<sub>3</sub> with dpq. The type of product was dependent on the reactants and conditions. The complexes exhibit either irreversible or quasi reversible ligand based reductions. In addition, the zerovalent complexes displayed one metal based oxidation in their cyclic voltammograms, due to the formation of M<sup>+</sup> species<sup>125</sup>.

One dimensional polymeric Cu(I) complexes of the type {[CuL(H<sub>2</sub>O)]BF<sub>4</sub>·H<sub>2</sub>O}<sub>n</sub>, L=2,3-diphenylquinoxaline and {[CuL'(H<sub>2</sub>O)]X}<sub>n</sub>, L'=2,3-dimethylquinoxaline and X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>, containing a rare Cu(I)-water bond were synthesised. From the X-ray crystal structures, the Cu(I) centres in these complexes are found to have a planar T shaped N<sub>2</sub>O coordination sphere<sup>126</sup>. Novel anion recognition host molecules, tris-1,10-phenanthroline Co(III) and bis-2,2-bipyridine mono-1,10-phenanthroline Ru(II) complexes bearing fused dipyrrolylquinoxaline moieties have been reported. UV-Vis. The observed binding constants are ascribed to two factors, (i) the presence of a phenanthroline coordinated cationic charge that decreases the electron density on the pyrrole NH protons and (ii) pure electrostatic effects<sup>127</sup>.

A absorption, emission and IR spectra, metal (Ru) and ligand (PP) half wave potentials and ab-initio calculations on the ligands (PP) are compared for several [LnRu(PP)]<sup>2+</sup> and {[LnRu]dpp{RuL'n}}<sup>4+</sup> complexes, Ln and L'n=(bpy)<sub>2</sub> or (NH<sub>3</sub>)<sub>4</sub> and PP= 2,3-bis(2-pyridyl)quinoxaline (dpq) or 2,3-bis(2pyridyl)benzoquinoxaline (dqb). The energy of the MLCT absorption maximum (hv max) varies in nearly direct proportion to the difference between Ru(III)/Ru(II) and (PP)/(PP) half wave potentials, ΔE<sub>1/2</sub>, for the monometallic complexes but not for the bimetallic complexes. The ab-initio calculations indicate that the two lowest energy π\* orbitals are not much different in energy in the PP ligands (they correlate with the degenerate π\* orbitals of benzene) and that both contribute to the observed MLCT transitions<sup>128</sup>. A new spectrophotometric method for the micro determination of zinc is proposed by Amin<sup>129</sup>. The method is based on complexation reaction of Zn(II) with the chromogenic reagent 2,3-dichloro-6-(2-hydroxynaphthylazo)quinoxaline in the presence of cetyltrimethylammonium bromide (CTAB) and nonyl phenoxy polyethoxyethanol (OP)bin slightly basic medium.

The complexes of Co(II), Ni(II), Cu(I), Cu(II) and Zn(II) with a new polypyridyl ligand, 2,3-bis(2-pyridyl)-5,8-dimethoxyquinoxaline (L) have been synthesized and characterized. The crystal structures of the complexes have been determined by X-ray diffraction analyses and three types of coordination modes for L were found to exist in the complexes. The solution behaviors of these complexes have been studied by UV-Vis. and ESR techniques<sup>130</sup>.

Binuclear Re(I) and Re(I)Os(II) complexes with polypyridyl bridging ligands, 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline (dpqMe<sub>2</sub>) were synthesized and resonance Raman spectra were also recorded<sup>131</sup>. Ni(II), Co(II) and Fe(II) complexes of 2-(2-pyridyl)quinoxaline were synthesized and used in the ethylene oligomerization with methyl-aluminoxane (MAO) as cocatalyst. The Ni(II) complex system mainly produced α-olefins with good activity, while the Co(II) and Fe(II) complexes showed only marginal activity<sup>132</sup>.

The resonance Raman spectra of Mo(CO)<sub>4</sub>(dpq) {dpq is 2,3-di(2-pyridyl)-quinoxaline} and Mo(CO)<sub>4</sub>(5mdpq) {5mdpq is 5-methyl-2,3-(2-pyridyl)-quinoxaline} were reported. The spectra of these complexes differ from the corresponding Re(I) complexes. This is due to the less mixing between the metal dπ and ligand π\* MOs in the Mo case. The resonance Raman spectra of the reduced species for Mo(CO)<sub>4</sub>(dpq<sup>-</sup>) show dpq<sup>-</sup> bands close to those observed for [Ru(phen)<sub>2</sub>(dpq<sup>-</sup>)]<sup>+</sup> and significantly different from the corresponding Re(CO)<sub>3</sub>Cl(dpq<sup>-</sup>)<sup>133</sup>.

Novel Mn(II) complex with the planar ligand 6,7-dicyanodipyrido[2,2-d:2',3'-f]quinoxaline (L) [Mn(L(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]NO<sub>3</sub>·CH<sub>3</sub>OH has been synthesized and characterized by elemental analysis, IR, TG-DTA and molar conductance. Its crystal structure was determined by X-ray

diffraction, crystal data. The Mn atom was hexa coordinated to form a distorted octahedral geometry by two nitrogen atoms of L and four oxygen atoms of three H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> in the complex. The binding mode of the complex with calf thymus DNA has also been investigated with spectrophotometric methods, viscosity and thermal denaturation measurements. The results show that the complex intercalated into DNA base pairs via the ligand. Biological tests against four different cell lines (HL-60, KB, HeLa and BGC-823) *in-vitro* showed that the complex had significant antitumor properties<sup>134</sup>.

The synthesis and enantiomeric resolution of metal complex of the type [Ru(bpyMe<sub>2</sub>)<sub>2</sub>L]<sup>2+</sup> { bpyMe<sub>2</sub>=4,4'-dimethyl-2,2'-bipyridine and L = dipyrido[3,2-a:2'3'-c]-quinoxaline (dpq)}. DNA-paper chromatography, absorption spectroscopy, gel electrophoresis and viscometry of linear DNA were used to assess the association and affinity for DNA of the complexes. Optical resolution of the complexes was done by solvent recycled chromatography using Sephadex cation exchange resin and disodium (-)-O,O'-dibenzoyl-L-tartrate. Absorption spectroscopy experiments indicated that the complex was in close association with the DNA. Δ and Λ-[Ru(bpyMe<sub>2</sub>)<sub>2</sub>(dpq)]<sup>2+</sup> bind through different modes, the Δ isomer by intercalation and the Λ isomer by partial intercalation. The results indicate that the extended methyl groups in the 4 and 4' positions on the bpyMe<sub>2</sub> ligand are critical in eliciting different enantiomeric interactions with the walls of the DNA grooves<sup>135</sup>.

A new complex Mo(CO)<sub>4</sub>(2,2'-pq) {where 2,2'-pq = 2-(2'pyridyl)quinoxaline} was synthesized and characterized. The octahedral geometry of the metal centre is distorted due to the bending of the axial carbonyls from the ligand 2,2'-pq. This bending is associated with the extensive solvatochromism of the MLCT band of complex Mo(CO)<sub>4</sub>(2,2'-pq) were also studied<sup>136</sup>. Preparation and properties of cyclopalladated complexes of d dibenzo[f,h]quinoxaline with ethylenediamine were reported by Cherezova et al<sup>137</sup>.

Synthesis, characterization and DNA binding properties of a series of mixed metal complexes coupling Ru light absorbers to Pt reactive metal sites through polyazine bridging ligands have been prepared<sup>138</sup>. They have the general formula [(tpy)RuCl(BL)PtCl<sub>2</sub>]PF<sub>6</sub> {B=2,3-bis(2-pyridyl) quinoxaline (dpq), 2,3-bis(2-pyridyl)benzoquinoxaline (dpb); tpy=2,2': 6',2''-terpyridine)}. These system possess electron rich Ru metal centers bound to five polyazine nitrogens and one chloride ligand. This leads to complexes with low energy Ru-BL charge transfer bands that are tunable with BL. The chlorides bound to Pt(II) centre are substantially labile and has the ability to covalently bind to DNA.

The novel quinoxaline substituted (E,E)-dioxime (H<sub>2</sub>L) containing a hexaoxadiaza macrobicycle has been synthesized and the mononuclear Ni(II) complex with a metal:ligand ratio of 1:2 was prepared. The above hydrogen bridged complex was converted into its BF<sub>2</sub><sup>+</sup> capped analogue by reaction with BF<sub>3</sub>·Et<sub>2</sub>O. The reaction of the BF<sub>2</sub><sup>+</sup> bridged complex with KPF<sub>6</sub>

gave a hetero trinuclear complex. Structures for the dioxime and its complexes are proposed in accordance with elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR, IR and MS spectral data<sup>139</sup>.

A Cu(I) complex [Cu(dpq)<sub>2</sub>](ClO<sub>4</sub>) {dpq is dipyrido-[3,2-d:2',3'-f]-quinoxaline} is prepared and characterized. The cationic complex has the Cu(I) center bonded to two N,N-donor dpq ligands giving a distorted tetrahedral geometry. The crystal structure displays extensive π-π stacking interactions involving the planar aromatic rings of dpq. The complex is diamagnetic and exhibits a MLCT band at 442 nm in MeCN and a perchlorate stretch at 1088 cm<sup>-1</sup> in the IR spectrum in KBr phase. It shows a quasi reversible cyclic voltammetric response at 0.17 V (ΔEp = 120 mV) at 50 mV s<sup>-1</sup> in DMF for the Cu(II)/Cu(I) couple. The complex shows efficient nuclease activity on treatment with supercoiled DNA in presence of hydrogen peroxide. Mechanistic studies have shown minor groove binding of the complex and the involvement of hydroxyl radicals in the DNA cleavage reactions<sup>140</sup>. Metal assisted red light induced efficient DNA cleavage by dipyridoquinoxaline-Cu(II) complex was reported by Dhar et al<sup>141</sup>.

The synthesis and characterization of new Cu(II), Zn(II), Cd(II) and Pb(II) complexes of quinoxaline moieties linking the macrocyclic units are reported<sup>142</sup>. The 1:2 and 1:3 (metal:ligand) complexes of 2,3-bis(diphenylphosphine)quinoxaline dioxide with Ce(III), Nd(III) and Sm(III) nitrates were synthesized and characterized by IR spectroscopy<sup>31</sup>P NMR and X-ray diffraction. In all complexes, the ligand coordinated through the P=O groups and is characterized by the chelate coordination with the metal. The behavior of the complexes in solutions of CHCl<sub>3</sub> and CH<sub>3</sub>CN is studied<sup>143</sup>.

The variable temperature <sup>1</sup>H and <sup>13</sup>C NMR and EPR spectra of the stable radical anions [Os<sub>3</sub>(CO)<sub>10</sub>(μ<sup>3</sup>-η<sup>2</sup>-L)(μ-H)] {LH=quinoxaline} was reported. They also reported the DFT calculations of the stable triosmium cluster<sup>144</sup>. The selective paramagnetic relaxation of oligonucleotide proton resonance of d(GTCGAC)<sub>2</sub> and d(GTGCAC)<sub>2</sub> by Ni(phen)<sub>2</sub>(L)<sup>2+</sup> { L=dpq} has been examined to obtain structural insight into the non covalent binding of the metal complex to DNA<sup>145</sup>.

Ternary Cu(II) complexes [CuLL'](ClO<sub>4</sub>), where L is NSO donor Schiff base (2-(methylthio)phenyl) salicylaldehyde and L' is dipyridoquinoxaline (dpq) are prepared and structurally characterized by X-ray crystallography. [CuL(dpq)](ClO<sub>4</sub>) show axial sulfur ligation. The one electron paramagnetic complexes exhibit axial electron paramagnetic resonance (EPR) spectra in dimethylformamide glass at 77 K. The complex shows photocleavage activity when irradiated with a monochromatic UV light of 312 nm. The dpq complex also cleaves SC DNA on visible light irradiation at 436, 532 and 632.8 nm but with a longer exposure time and higher complex concentration. The quinoxaline ligand exhibits significant photosensitizing effect assisted by the Cu(II) center<sup>146</sup>.

Ni(II) complexes of a various quinoxaline containing dioxyclams were reported<sup>147</sup>. The DNA binding and oxidative cleaving ability of these complexes were studied. They observed that the Ni(II) complexes cleave DNA in the presence of oxone and depends on both the nature and the orientation of the quinoxaline moieties.

The ternary Cu(II) complexes [Cu(salgly)L], [Cu(salala)L] and [Cu(salphe)L] { L=dipyridoquinoxaline (dpq), salgly, salala and salphe are tridentate Schiff base ligands derived from the condensation of salicylaldehyde with glycine, L-alanine and L-phenylalanine respectively} are prepared and their nuclease activity were studied. The complexes are redox active and exhibit a quasi reversible Cu( II)/Cu(I) couple in DMF. They show catalytic activity in the oxidation of ascorbic acid by molecular oxygen. The ability of the complexes to bind calf thymus (CT) DNA is also examined. Complexes show oxidative DNA cleavage activity in the presence of mercaptopropionic acid as a reducing agent. All the complexes show hydrolytic cleavage activity in the absence of light or any reducing agent<sup>148</sup>.

Thomas et al<sup>149</sup> reported new ternary Cu(II) complexes of formulations [Cu(Ph-tsc)B] {B=dipyridoquinoxaline (dpq), Ph-H<sub>2</sub>tsc=salicylaldehyde-N(4)-phenylthiosemicarbazone) and [Cu(Me-tsc)(phen)] (Me-H<sub>2</sub>tsc, salicylaldehyde-N(4)-methylthiosemicarbazone}. They also studied their DNA binding and cleavage properties including the mechanisms

The reaction of 2,3-quinoxalinedithiol with 2,6-bis(bromomethyl) pyridine leads to the isolation of a macrocyclic ligand precursor, bis(2-thio-3-mercaptoquinoxalino)-2,6-dimethylpyridine (L) was reported by Anacona<sup>150</sup>. The reaction of transition metal ions with L gives [M(L)<sub>x</sub>]X complexes (M=Mn(II), Co(II), Cu(II), Ag(I), Zn(II) or Cd(II) and X = Cl<sup>-</sup> or Br<sup>-</sup>). The compounds were characterized by physical and spectroscopic measurements which indicated that the ligand is probably acting as a pentadentate NS<sub>4</sub> chelating agent.

Ternary Cu(II) complex [Cu(L-met)B(Solv)](ClO<sub>4</sub>) { L-Hmet = L-methionine and B is N,N-donor heterocyclic base dipyrido[3,2-d:2',3'-f]quinoxaline (dpq)} prepared and its DNA binding and photo induced DNA cleavage activity studied. The complex displayed significant binding propensity to the calf thymus DNA. Control cleavage experiments using pUC19 supercoiled DNA and distamycin indicate minor groove binding<sup>151</sup>.

Hwang et al<sup>152</sup> reported the synthesis, electrochemical and photophysical properties of four red emitting Ir(III) complexes using the cyclometalated quinoxaline ligands and one nitrogen chelate ligand, such as pyridylpyrazolate or triazolate. The synthesized complexes exhibit high emission quantum yields and short phosphorescence radiative life times in the range of several microseconds that are suitable for serving as red

emitting materials for PLED and OLED. Single crystal X-ray diffraction studies of [(dpqx)<sub>2</sub>Ir(fppz)] revealed distorted octahedral geometry.

The design of a series of luminescent Re(I) polypyridine biotin complexes containing different spacer arms, [Re(N-N)(CO)<sub>3</sub>(py-4-CH<sub>2</sub>-NH-biotin)](PF<sub>6</sub>) (py-4-CH<sub>2</sub>-NH-biotin=4-(biotinamidomethyl)-pyridine; N-N=dipyrido[3,2-f,2',3'-h]quinoxaline, dpq), [Re(N-N)(CO)<sub>3</sub>(py-3-CO-NH-en-NH-biotin)](PF<sub>6</sub>) (py-3-CO-NH-en-NH-biotin=3-(N-((2-biotinamido)ethyl)amido)pyridine, N-N=dpq) and [Re(N-N)(CO)<sub>3</sub>(py-4-CH<sub>2</sub>-NH-cap-NH-biotin)](PF<sub>6</sub>) (py-4-CH<sub>2</sub>-NH-cap-NH-biotin=4-(N-((6-biotin amido)hexanoyl)aminomethyl)pyridine; N-N=dpq). The interactions of these biotin containing complexes with avidin have been studied by 4'-hydroxyazobenzene-2-carboxylic acid (HABA) assays, emission titrations, and competitive association and dissociation assays. On the basis of the results of these experiments, homogeneous assays for biotin and avidin have been designed<sup>153</sup>.

Study on the minor groove recognition of B-DNA d(GTCGAC)<sub>2</sub> by racemic d,l-[Co(phen)2dpq]<sup>3+</sup> {phen and dpq stand for 1,10-phenanthroline and dipyrido [3,2-d:2,3-f]quinoxaline} was carried out with one, two-dimensional (1D, 2D) nuclear magnetic resonance (NMR) methodologies and molecular simulations. NMR investigations revealed that the metal complex intercalates into the DNA base stack from minor groove orientation with dpq as intercalator and dpq ligand participated in the nucleobase stack<sup>154</sup>.

The self assembly of ligand-metal-ligand sandwich complexes involving a novel quinoxaline-containing crown ether was studied by electrospray ionization mass spectrometry (ESI-MS). Donor-acceptor  $\pi$ -stacking interactions between the electron poor quinoxaline group of quinoxaline containing crown ether and electron rich benzene groups from benzo or dibenzo-18-crown-6 were found to significantly enhance the formation of mixed-ligand sandwich complexes. The relative intensities of the sandwich complexes were greatest with the alkali metals Na<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> as well as with the ammonium ion in equimolar concentrations with the macrocycles<sup>155</sup>.

The electrochemistry and spectroelectrochemistry of four quinoxalinoporphyrins containing metal(II) ions and one free-base quinoxalinoporphyrin dissolved in nonaqueous media have been reported. The compounds are represented as (P)M and (PQ)M, {where P = 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin, PQ = 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)quinoxalino[2,3-b]porphyrin and M = Ni(II), Cu(II), Zn(II) or Pd(II)}. The average HOMO-LUMO gap for the (P)M and (PQ)M derivatives is 2.26±0.09 V and 2.14±0.08 V, respectively are smaller than the average separation of 2.33±0.13 V for the corresponding derivatives of tetraphenylporphyrin. The electrochemistry and UV-Vis. spectroelectrochemical data indicate that moderate

communication exists between the quinoxaline unit and the porphyrin  $\pi$ -ring system<sup>156</sup>.

The DNA-binding affinities and the spectral properties of a series of Ru(II) polypyridyl complexes, [Ru(bpy)<sub>2</sub>(dmdpq)]<sup>2+</sup>, [Ru(bpy)<sub>2</sub>(dpq)]<sup>2+</sup>, [Ru(bpy)<sub>2</sub>(dcdpq)]<sup>2+</sup> {bpy = 2,2'-bipyridine; dpq=dipyrido[3,2-d:2',3'-f]quinoxaline; dmdpq=di-methyl-dpq; dcdpq=di-cyano-dpq} have been experimentally and theoretically examined. The DNA binding constants K<sub>b</sub> of the complexes were determined systematically with spectrophotometric titration. The density functional theory (DFT) and time dependent DFT (TDDFT) calculations were carried out for the above complexes. The experimental results show that the complexes bind to DNA in intercalation mode<sup>157</sup>.

Schramm et al<sup>158</sup> reported the ruthenium amidinate complexes of diamino substituted pyrazinoquinoxalines. The structure of the derived complexes was studied by X-ray diffraction. Ternary Cu(II) complexes [Cu(L-lys)B(ClO<sub>4</sub>)](ClO<sub>4</sub>) {where B is a heterocyclic base dipyrido[3,2-d:2',3'-f]quinoxaline (dpq)} was prepared and its DNA binding and photo induced DNA cleavage activity was studied (L-lys = L-lysine)<sup>159</sup>. The complex displayed good binding propensity to the calf thymus DNA. The complex shows efficient DNA cleavage activity on UV (365 nm) or visible light (694 nm ruby laser) irradiation via a mechanistic pathway involving formation of singlet oxygen as the reactive species. The amino acid L-lysine bound to the metal shows photosensitizing effect at red light. The dpq ligand displays red light-induced photosensitizing effects in copper-bound form.

The Fe(III), Al(III), Ga(III) and Cr(III) complexes of a bidentate ligand, 3-hydroxy-2-methyl-4(1H)-pyridinone directly attached to the fluorescent 2,3-dimorpholinoquinoxaline at C-6 position was reported<sup>160</sup>. The ratio between the bidentate ligand and metal ions were found to be 3:1. The fluorescence was efficiently quenched by the metal complex formation. The fluorescence was recovered by removal of Fe(III) with the N-benzoyl analogue of a naturally occurring siderophore, desferrioxamine B.

The synthesis and luminescence study of a new platinum quinoxaline complex was reported. The complex, [(DPQ)Pt(acac)] {where DPQ=2, 3-diphenylquinoxaline, acac=2, 4-pentanedione}. Organic light emitting diode (OLED) with a configuration of [ITO/NPB(21 nm) /NPB=7% (DPQ)Pt(acac)(17.5 nm) /BCP(7 nm)/ Alq 3(21 nm)/ Mg:Ag(10:1)(120 nm)/Ag(10 nm)] (ITO: indium tin oxide; NPB: 4, 4'-bis[N-(1-naphthyl)-N- phenyl-amino] biphenyl; BCP: 2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline; Alq 3: tris(8-hydroxyquinoline) aluminum) shows a red emission at 632 nm<sup>161</sup>. They also reported a new iridium quinoxaline complex, [Ir(DPQ)<sub>2</sub>(acac)] (DPQ=2,3-diphenylquinoxaline, acac= acetoacetone). The complex was characterized by elemental analysis, <sup>1</sup>H NMR and mass spectroscopy. The UV-Vis. absorption and photoluminescence of the complex were

investigated. The complex shows strong <sup>1</sup>MLCT and <sup>3</sup>MLCT absorption at 476 and 625 nm, respectively. OLED with a configuration of [ITO/NPB (30 nm)/NPB: 7% Ir(DPQ)<sub>2</sub>(acac)(25 nm)/PBD (10 nm)/Alq3 (30 nm)/Mg: Ag (10:1)(120 nm)/Ag(10 nm)] were fabricated by using this complex as the triplet emissive dopant in NPB. The power efficiency of the device indicates that [Ir(DPQ)<sub>2</sub>(acac)] is a promising electrophosphorescent material<sup>162</sup>.

Zou et al<sup>163</sup> reported the synthesis and characterization of Co(II), Ni(II), Cu(II) and Cd(II) complexes with 2,3-bis[3-(2-pyridyl)pyrazolmethyl]-quinoxaline. These results show that the nuclearity of metal complexes may be tuned by ligand modifications and the nature of ligands, metal ions, counter anions and solvent molecules play important roles in the formation of coordination compounds.

Synthesis and characterization of the new complex W(CO)<sub>4</sub>(2,2'-pq) {2,2'-pq = 2-(2'-pyridyl)quinoxaline} was reported. The structure resembles those of W(CO)<sub>4</sub>(phen) and W(CO)<sub>4</sub>(bpy), some distortions that stem from 2,2'-pq's asymmetry are present. The solvatochromic behaviour of the complex is anticipated by DFT/CPCM calculations and is investigated in detail by absorption and NMR spectroscopy. The <sup>1</sup>H NMR data of 2,2'-pq and W(CO)<sub>4</sub>(2, 2'-pq) reveal an increase of the solvent influence to the chemical shifts of the diimine ligand after its coordination to the metal and suggest two different types of solvent effects for the complex and the ligand respectively<sup>164</sup>.

The synthesis, characterization, photophysical, electrochemical and avidin-binding properties of luminescent Re(I) amidodipyridoquinoxaline biotin complexes were reported (10)<sup>165</sup>. All the complexes exhibited <sup>3</sup>MLCT emission in fluid solution at room temperature and in alcohol glass at 77 K. Luminescence titration experiments showed that these complexes exhibited emission enhancement and life time extensions upon binding to avidin and anthracene labeled avidin have been displayed.

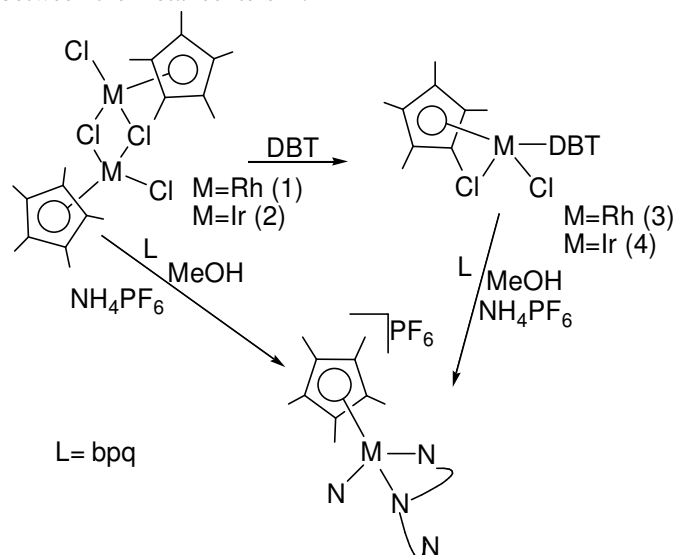
Balashev et al<sup>166</sup> reported a comparative study of platinum complexes of dipyrido[f,h]quinoxaline (dpq), 6,7-dicyanodipyrido[f,h]quinoxaline (dicnq), dibenzo[f,h]quinoxaline and 6,7-dicyanodibenzo[f,h]quinoxaline. Saravanakumar et al<sup>167</sup> reported the synthesis, NMR and crystal structure data of novel electron-deficient quinoxaline anellated imidazol-2-ylidene precursors and their transition metal complexes.

A new vanadyl complex with the formula VO(L)<sub>2</sub> {L<sub>1</sub>=3-amino-6(7)-chloroquinoxaline-2-carbonitrile N<sub>1</sub>,N<sub>4</sub>-dioxide, has been synthesized and characterized by elemental analyses, conductometry, fast atom bombardment mass spectroscopy (FAB-MS), electronic, Fourier transform infrared (FTIR), Raman, nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) spectroscopies. The complex

give rise to more potent *in vitro* cytotoxins than the free ligand<sup>168</sup>.

New cationic Ir(III) complex of 2-(2-quinolonyl)quinoxaline has been reported<sup>169</sup>. UV-Vis., photoluminescence, cyclic voltammetry and theoretical calculations were used for studying the photophysical and electrochemical properties and also excited state properties. The excited state of complexes is complicated and contains triplet<sup>3</sup> MLCT, triplet ligand-to-ligand charge transfer (<sup>3</sup>LLCT) and ligand-centered cyclometal (<sup>3</sup>LC) transitions simultaneously.

Li et al reported neutral Ru(II) based emitting materials containing DBQ (dibenzo[f,h]quinoxaline)<sup>170</sup>. Synthesis and characterization of complexes of the type  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\text{poly-py})]$  {where M=Rh and Ir, poly-py = poly pyridyl ligands} were reported by Govindaswamy et al (scheme 4)<sup>171</sup>. Syntheses, characterization and magnetic properties of  $[\text{Mn}^{\text{II}}(\text{DMeDPQ})(\mu\text{1,5-dca})_2]_n$  have been described {where DMeDPQ=6,7-dimethyl-2,3-di(2-pyridyl) quinoxaline, dca = dicyanamide} the structure of the complex is polymeric and consists of one dimensional double chains. DMeDPQ behave here as bidentate chelating ligand. The one dimensional double chain structure is formed due to the dual existence of two single and two double end to end ( $\mu\text{1,5-}$ , EE) dca ligands. The variable temperature magnetic susceptibility measurements reveal that dicyanamide mediates a weak antiferromagnetic interaction between the metal centers<sup>172</sup>.



Scheme 4

#### Synthesis of complexes of the type $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\text{poly-py})]$

Veroni et al<sup>173</sup> reported the monodentate complexation of 2-(2'-pyridyl)quinoxaline (pq) to a metal centre through N<sub>4</sub>. Photochemical exchange of the THF ligand in  $\text{W}(\text{CO})_5\text{THF}$  by pq yields  $\text{W}(\text{CO})_5(\text{N}_4\text{-pq})$ , where the potentially bidentate pq ligand coordinates in an unusual monodentate fashion. Complex  $\text{W}(\text{CO})_5(\text{N}_4\text{-pq})$  is isolated and fully characterized on the basis of NMR, IR, UV-Vis. and emission spectroscopy. The structure

of the complex was determined by X-ray analysis. The preference to N<sub>4</sub> as coordination site is discussed in terms of electronic interactions. Solutions of the complex emits dually at 77 K while they are moderately unstable at room temperature.

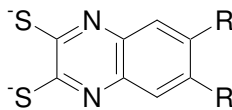
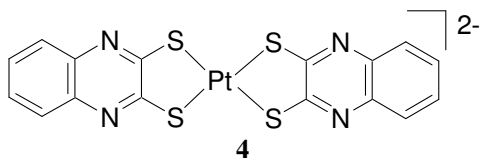
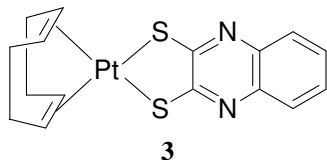
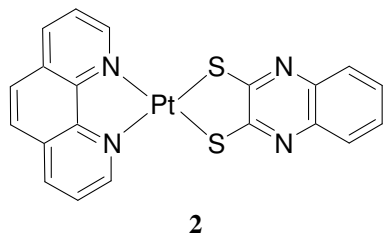
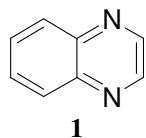
Ternary Cu(II) complexes  $[\text{Cu}(\text{L}_1)\text{B}](\text{ClO}_4)$  and  $[\text{Cu}(\text{L}_2)\text{B}](\text{ClO}_4)$  { HL<sub>1</sub> and HL<sub>2</sub> are tridentate NSO and ONO donor Schiff bases and B is a heterocyclic base, viz. dipyrido[3,2-d:2',3-andlt;-f]quinoxaline (dpq)} were prepared and their DNA binding and photoinduced DNA cleavage activity was studied. The complexes display good binding tendency to calf thymus DNA. They cleave supercoiled pUC19 DNA to its nicked circular form when treated with 3-mercaptopropionic acid (MPA) by formation of hydroxyl radicals as the cleavage active species under dark reaction conditions. The photoinduced DNA cleavage activity of the complexes was investigated using UV radiation of 365 nm and red light of 633, 647.1, and 676.4 nm (CW He-Ne and Ar-Kr mixed gas ion laser sources) in the absence of MPA. Enhancement of the cleavage activity on photoexposure at the d-d band indicates the occurrence of metal-assisted photosensitization processes involving the LMCT and d-d band in the ternary structure<sup>174</sup>.

## Conclusion

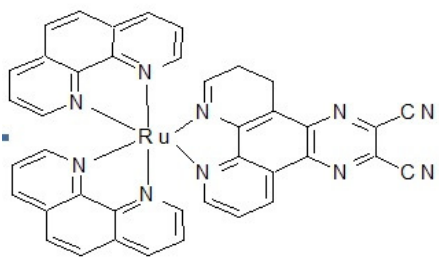
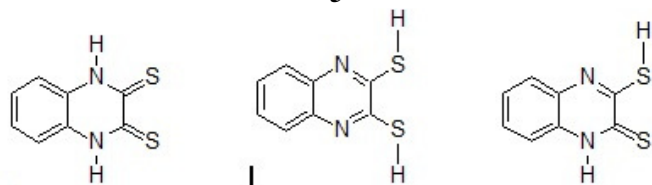
Currently thousands of papers are available on metal complexes. An attempt has been made to present salient facts related to works done on various quinoxaline derivative metal complexes. The review highlights various synthetic methods employed in addition to the conventional methods, experimental condition, distinct spectro-analytical and physico-chemical methods involved in the characterization of mono, bi and trimetallic, homo bimetallic, mixed metal and mixed ligand complexes of quinoxaline derivatives. Various transitions involved, types of complexes, coordination mode and geometries of the complexes were arrived from the studies. The review pointed out that the complexes exhibit various physico-chemical properties. They act as luminescent materials, hybrid coordination polymers, photo conducting materials, catalysts, DNA binding and cleaving agents, etc. The results indicate Quinoxaline and its derivatives as very important and biologically active system. The data together with several varieties of results reported in this review promise bright future for Quinoxaline derivative metal complexes. We hope this review will throw more light on quinoxaline derivative metal complexes. Finally this review gives indepth knowledge in understanding coordination chemistry and may be useful in the design of metal complexes as therapeutics.

## Acknowledgment

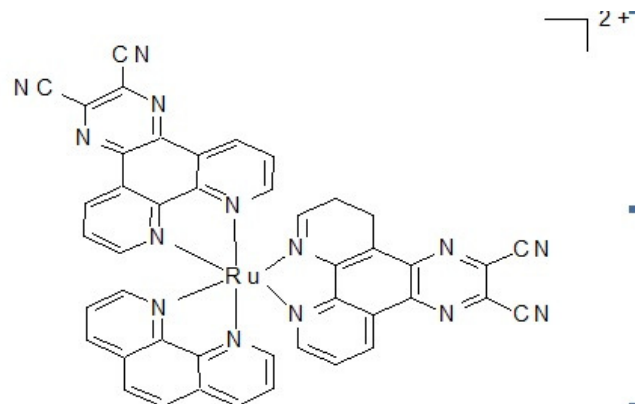
We thank Council of Scientific and Industrial Research (CSIR), New Delhi for the financial support in the form of a research project (Scheme No: 01(2453)/11/EMR-II).



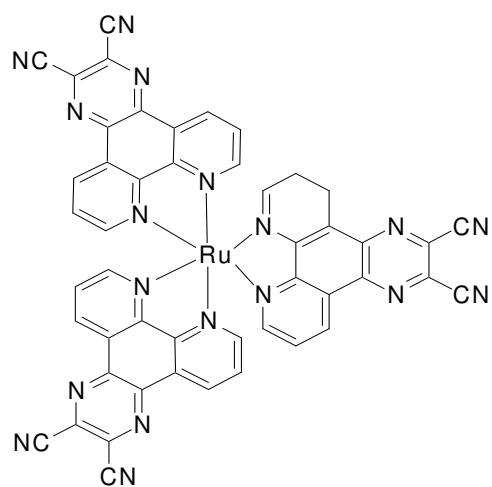
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 Me dmqdt



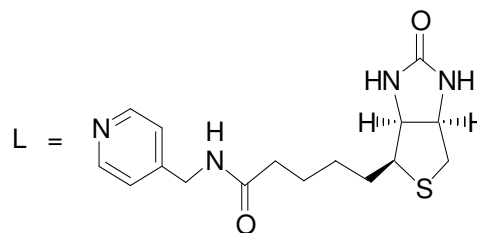
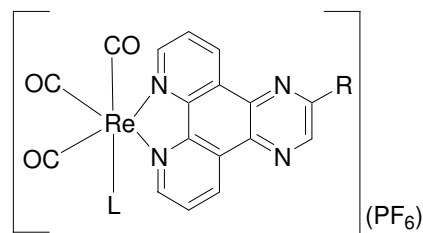
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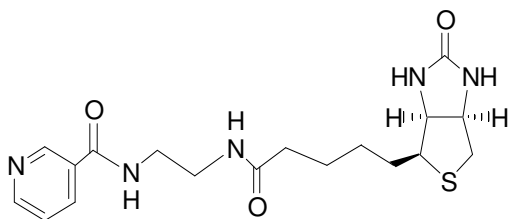
2+



2+

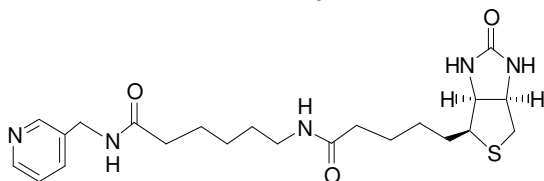


py-4-CH<sub>2</sub>-NH-biotin  
 R = CONHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (1), H (1a)



py-3-CO-NH-en-NH-biotin

R = CONHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (2), H (2a)



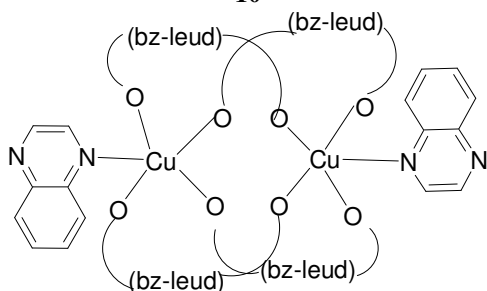
py-4-CH<sub>2</sub>-NH-cap-NH-biotin

R = CONHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (3), H (3a)



py  
R = CONHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (4), H (4a)

10



11

## References

- Black D. St. C. and Hartshorn A., Ligand design and synthesis, *J Coord Chem Rev*, **9**, 219 (1973)
- Cheeseman G.W.H., Recent Advances in Quinoxaline Chemistry, *Adv Heterocycl Chem*, **2**, 203 (1963)
- Constable E.C. and Steel P., *N,N'*-Chelating biheteroaromatic ligands; a survey, *J Coord Chem Rev*, **2**, 93 (1989)
- Torre M.H., Gambino D., Araujo D.J., Cerecetto H., González M., Lavaggi M.L., Azqueta M., De Cerain A.L., Vega A.M., Abram U. and Costa-Filho A.J., Design and evaluation of "3 + 1" mixed ligand oxorhenium and oxotechnetium complexes bearing a nitroaromatic group with potential application in nuclear medicine oncology, *Eur J Med Chem*, **40**, 473 (2005)
- Kim Y.B., Kim Y.H., Park J.Y. and Kim S.K., Synthesis and biological activity of new quinoxaline antibiotics of echinomycin analogues, *Bioorg Med Chem Lett*, **14**, 541 (2004)
- Schenfelder D., Slumm D., Bhola G. and Niclas N.J., *Pharmazie*, **43**, 837 (1998)
- Paul F.F., Lang S.A., Yang L. and Cufcik T., *J Med Chem*, **2**, 973 (1960)
- Sasee K., Wegle R., Unterslenhoefer. and Grews G. F., *Angew Chem*, **72**, 973 (1960)
- Refat M.S., El-Deen I.M., Anwer Z.M. and El-Ghol S., Spectroscopic studies and biological evaluation of some transition metal complexes of Schiff-base ligands derived from 5-arylozo-salicylaldehyde and thiosemicarbazide, *J Coord Chem*, **62**, 1709 (2009)
- Wang P.H., Keck G.J., Lien E.J. and Lai M.C., Design, synthesis, testing, and quantitative structure-activity relationship analysis of substituted salicylaldehyde Schiff bases of 1-amino-3-hydroxyguanidine tosylate as new antiviral agents against coronavirus, *J Med Chem*, **33**, 608 (1990)
- Ziegler J., Shurela T., Pasierb L., Kelly C., Elamin A., Cole K.A., Wright D.W., The Propionate of Heme Binds N<sub>4</sub>O<sub>2</sub> Schiff Base Antimalarial Drug Complexes, *Inorg Chem*, **39**, 3731 (2000)
- Chang D.W., Ko S.J., Dai L. and Baek, Multifunctional quinoxaline containing small molecules with multiple electron-donating moieties: Solvatochromic and optoelectronic properties, *J Synthetic Metals*, **162**, 1196 (2012)
- Mighani H. and Ghaemy M., Synthesis and characterization of organosoluble polyamides from quinoxaline based diamine, *Chin J Polym Science*, **28**, 147 (2010)
- Aldakov D., Palacios M. and Anzenbacher P., Benzothiadiazoles and Dipyrrolyl Quinoxalines with Extended Conjugated Chromophores-Fluorophores and Anion Sensors, *Chem Mater*, **17**, 5238 (2005)
- Kozyrev A., Suresh V., Senge M., Shibata M., Dougherty T. and Pandey R., Syntheses and Spectroscopic Studies of Novel Chlorins with Fused Quinoxaline or Benzimidazole Ring Systems and the Related Dimers with Extended Conjugation, *Tetrahedron*, **56**, 3353 (2000)
- Zarrouk A., Hammouti B., Touzani R., Al-Deyab S. S., Zertoubi M., Dafali A. and Elkadiri S., *Int J Electrochem Sci*, **6**, 4939 (2011)
- Huang T., Whang W., Shen J.Y., Wen Y., Ke T., Chen L. and Wu C., *Adv Funct Mater*, **16**, 1449 (2006)



18. Zmujdzin A., *Chem Abstr*, **81**, 77966 (1974)
19. Vogel A.I., Vogel's text book of practical organic chemistry, 5<sup>th</sup> ed. 1190 (1989)
20. Kurasawa Y. and Takada A., *Heterocycles*, **23**, 2083 (1985)
21. Thirumurugan P., Muralidharan D. and Perumal P.T., The synthesis and photophysical studies of quinoxaline and pyridopyrazine derivatives, *Dyes and Pigments*, **81**, 245 (2009)
22. Thakuria H. and Das G., One-pot efficient green synthesis of 1,4-dihydro-quinoxaline-2,3-dione derivatives, *J. Chem Sci*, **118**, 425 (2006)
23. Ayres G.H. and Annand R.R., Spectrophotometric Study of Cobalt and Nickel Complexes with 2,3-Quinoxaline dithiol, *Anal Chem*, **35**, 33 (1963)
24. Ayres G.H. and Mc Corry R.W., Spectrophotometric Determination of Platinum with 2,3-Quinoxalinedithiol, *Anal Chem*, **36**, 133 (1964)
25. Billing D.E., Underhill A.E., Adams D.M., Morris D.M., *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*. 902 (1966)
26. Dutt N.K., Sanayal G.S. and Nag K., *Anal Chim Acta*, **41**, 331 (1968)
27. Billing D.E., Underhill A.E., Transition-metal quinoxaline complexes. Part IV. Cobalt(II) derivatives, *J Chem Soc A: Inorg Phys and Theo Chem*, **5** (1968)
28. Billing D.E., Underhill A.E., Transition-metal quinoxaline complexes. Part V. Nickel(II) derivatives, *J Chem Soc A: Inorg Phys and Theo Chem*, **8** (1968)
29. Geary W.J., Transition-metal complexes of the 2,3-dipyridylquinoxalines. Part II. Cobalt(II), nickel(II), and copper(II) halide derivatives of 2,3-di-(6-methyl-2-pyridyl)quinoxaline, *J Chem Soc A: Inorg Phys and Theo Chem*, 2118 (1969)
30. Geary W.J., Transition-metal complexes of the 2,3-dipyridylquinoxalines. Part I. Cobalt(II), nickel(II), and copper(II) halide derivatives of 2,3-di-(2-pyridyl)quinoxaline, *J Chem Soc A: Inorg Phys and Theo Chem*, 71 (1969)
31. Kidani Y., Matsuo M. and Koike H., Studies on the Metal Complexes of Indoloquinoxaline Derivatives. I.: Syntheses of Hydroxyindoloquinoxaline Derivatives, *Yakugaku Zasshi*, **90**, 54 (1970)
32. Kidani Y., Matsuo M. and Koike H., Studies on the Metal Complexes of Indoloquinoxaline Derivatives. II: Spectrophotometric Determination of the Stability Constants of Hydroxyindoloquinoxaline Metal Complexes *Yakugaku Zasshi*, **90**, 452 (1970)
33. Matsuo M., Kidani Y. and Koike H., Studies on the Metal Complexes of Indoloquinoxaline Derivatives. III.: Metal Complexes of 1-and 4-Hydroxyindoloquinoxaline, *Yakugaku Zasshi*, **90**, 601 (1970)
34. Seyhan M. and Ocakeioglu B., About metal complexes of substituted heterocyclic formazans and Azomethines, *Monatshefte für Chemie*. **101**, 829 (1970)
35. Colton D.F. and Geary W.J., Transition-metal complexes of the 2,3-dipyridylquinoxalines. Part III. Cobalt(II), nickel(II), and copper(II) halide derivatives of 6-methyl-2,3-di-(2-pyridyl)quinoxaline and 6,7-dimethyl-2,3-di-(2-pyridyl)quinoxaline, *J Chem Soc A: Inorg Phys and Theo Chem*, 2457 (1971)
36. Carmichael W.M. and Edwards D. A., Complexes of molybdenum(IV) chloride with potentially bridging nitrogen donor ligands, *J Inorg Nucl Chem*, **34**, 1181 (1972)
37. Colton D.F. and Geary W.J., Transition-metal complexes of the 2,3-dipyridylquinoxalines. Part IV. Cobalt(II), nickel(II), and copper(II) halide derivatives of 6-methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline and 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline, *J Chem Soc Dalton Trans*, **4**, 547 (1972)
38. Colton D.F. and Geary W.J., Transition metal complexes of the 2,3-dipyridylquinoxalines—V[1]: Cobalt(II), nickel(II) and copper(II) halide derivatives of 6-nitro-2,3-di(2-pyridyl)quinoxaline, and the low frequency infrared spectra of some other dipyrldylquinoxaline complexes, *J Inorg Nucl Chem*, **36**, 1499 (1974)
39. Rignedoli, G. Peyronel, and Malavasi W., A comparative study of the cationic, neutral and anionic nickel(II) complexes of quinoxaline-2,3-dithiol, *J Inorg Nucl Chem*, **38**, 1963 (1976)
40. Chasan D.E., Pytlewski L.L., Owens C. and Karayannis N. M., Quinoxaline 1-oxide complexes with transition metal chlorides[1], *J Inorg Nuc Chem*, **38**, 1799 (1976)
41. Chasan D.E., Pytlewski L.L., Owens C. and Karayannis N.M., 3d Metal perchlorate complexes with quinoxaline 1-oxide[1], *J Inorg Nucl Chem*, **39**, 585 (1977)
42. Chasan D.E., Pytlewski L.L., Owens C., and Karayannis N.M., Quinoxaline 1,4-dioxide complexes with transition metal chlorides [1], *Inorg Chim Acta*, **24**, 219 (1977)
43. Chasan D.E., Pytlewski L.L., Owens C. and Karayannis N.M., Quinoxaline 1,4-dioxide complexes with 3d metal perchlorates[1] *J Inorg Nucl Chem*, **40**, 1019 (1978)
44. Rillema D.P. and Mark K.B., The low-lying excited state in ligand pi-donor complexes of ruthenium(II): mononuclear and binuclear species, *Inorg Chem*, **21**, 3849 (1982)
45. Coelho L., Toma H.E. and Malin J.M., Pentacyanoferrate(II) complexes of pyrimidine and quinoxaline, *Inorg Chem*, **22**, 2703 (1983)

46. Case F.H., Schilt A.A. and Simonzadeh N., Synthesis and Chelation Properties of Hydrazones Derived from Isoquinoline-1-carboxaldehyde, 2-Quinoxalinecarboxaldehyde, 4-Isoquinolyldiazine, and 2-Quinoxalyl hydrazine, *Anal Chem*, **56**, 2860 (1984)
47. Siedle A.R., Mann K.R., Bohling D.A., Flipovid G., Toren P.E., Palensky F.J., Newmark R.A., Duerst R.W., Stebbings W.L, Mishmash H.E. and Melancon, Redox, ligand-exchange, oligomerization, and hydrosilation chemistry of trans-dichloro(ethylene)(phenazine)platinum, *Inorg Chem*, **24**, 2216 (1985)
48. Rillema P.D., Toghdiri D.G., Jones D.S., Keller C.D., Worl L.A., Meyer T.J., Revy R.A., Structure and redox and photophysical properties of a series of ruthenium heterocycles based on the ligand 2,3-bis (2-pyridyl) quinoxaline, *Inorg Chem* **26**, 578 (1987)
49. Sahai R. and Rillema D.P., A novel hetero-oligomer containing one ruthenium(II) and three platinum(II) metal centres bridged by 2,3-bis(2-pyridyl)quinoxaline, *J Chem Soc, Chem Comm*, **14**, 1133 (1986)
50. Sahai R., Morgan L. and Rillema P.D., Ruthenium(II) cluster complexes: a series of homooligonuclear complexes based on bidentate bridging ligands, *Inorg Chem*, **27**, 3495 (1988)
51. Wallace A.W., Murphy Jr. W.R. and Petersen J.D., Electrochemical and photophysical properties of mono- and bimetallic ruthenium(II) complexes, *Inorg Chim Acta*, **166**, 47 (1989)
52. Carlton L., Belciug M.P., The <sup>15</sup>N NMR spectra of some dihydrobis(triphenylphosphine)rhodium(III) complexes of aromatic N-donor carboxylates, *J Organomet Chem*, **378**, 469 (1989)
53. Lumme P.O. and Lindroos S., Infrared, thermal and structural properties of first transition series metal chloride and perchlorate complexes of quinoxaline, *Thermochim Acta*, **162**, 375 (1990)
54. Allan J.R., Paton A.D. and Turvey K., Thermal, electrical and structural properties of chloro complexes of cobalt, nickel, copper and zinc with 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline, *Thermochim Acta*, **164**, 177 (1990)
55. Akasheh T.S., Jibril I. and Shraim A.M., Ligand-metal interactions and excited state properties in ruthenium (II)-diimine complexes, *Inorg. Chim Acta*, **175**, 171 (1990)
56. Gordon K.C. and McGarvey J.J., Resonance Raman evidence for photogeneration of a class II mixed-valence excited state of a binuclear copper(I) complex in solution, *Chemical Physics Lett*, **173**, 443 (1990)
57. Dodsworth E.S. and Lever A.B.P., Solvatochromism of dinuclear complexes: an alternative explanation, *Inorg Chem*, **29**, 499 (1990)
58. Brent MacQueen D. and Petersen J.D., Competitive hydrogen production and emission through the photochemistry of mixed-metal bimetallic complexes, *Inorg Chem*, **29**, 2313 (1990)
59. Baiano J.A., Carlson D.L., Wolosh G.M., DeJesus D.E., Knowles C.F., Szabo E.G. and Murphy Jr. W.R., Bimetallic complexes of rhenium(I). Preparation of Re(BL)(CO)3Cl and [Re(CO)3Cl]2(BL) (BL = 2,3-bis(2-pyridyl)pyrazine, 2,3-bis(2-pyridyl)quinoxaline, and 2,3-bis(2-pyridyl)benzo[g]quinoxaline), *Inorg Chem*, **29**, 2327 (1990)
60. Richter M. M. and Brewer K. J., Synthesis and characterization of osmium(II) complexes incorporating polypyridyl bridging ligands, *Inorg Chim Acta*, **180**, 125 (1991)
61. Carlson D.L., Murphy Jr. W.R., Tuning of excited state reduction potentials via expanded  $\pi$ -systems. Synthesis and characterization of [Ru(2,3-di(2'-pyridyl)benzo(g)quinoxaline)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, *Inorg Chim Acta*, **181**, 61 (1991)
62. Boyde S., Garner C.D., Electrochemistry of tris(quinoxaline-2,3-dithiolato)molybdate(IV) in acidic solution; multi-electron ligand-based redox activity, *J Chem Soc Dalton Trans*, 713 (1991)
63. Ye Q.Y. and Nakano Y., Frauenholf G.R., Whitcomb D.R., Tukasagawa F., Tetradentate dithiooxamide ligands and their nickel complexes. Synthesis, characterization, and crystal structure of a mononuclear neutral complex, Ni((c-C<sub>5</sub>H<sub>9</sub>)NHC(S)C(S)N(CH<sub>2</sub>)<sub>2</sub>NC(S)C(S)NH(c-C<sub>5</sub>H<sub>9</sub>)), *Inorg Chem*, **30**, 1503 (1991)
64. Baiano J.A. and Murphy Jr. W.R., Nonradiative decay in rhenium(I) monometallic complexes of 2,3-di-2-Pyridylpyrazine, *Inorg Chem*, **30**, 4594 (1991)
65. Yoblinski B.J., Stathis M. and Guarr T.F., Ligand-bridged rhenium(I) complexes: an electrochemical and photophysical study, *Inorg Chem*, **31**, 5 (1992)
66. Richter M. M. and Brewer K. J., Spectroscopic, electrochemical, and spectroelectrochemical investigations of mixed-metal osmium(II)/ruthenium(II) bimetallic complexes incorporating polypyridyl bridging ligands, *Inorg Chem*, **31**, 1594 (1992)
67. Feng D., Wang M. and Wang B., Complexes of quinoxaline-2,3-dicarboxylic acid with lanthanides *Polyhedron*, **11**, 1109. (1992)
68. Molnar S.M., Neville K. R., Jensen G.E. and Brewer K.J., Utilization of substituted polyazine bridging ligands to tune the spectroscopic and electrochemical properties of bimetallic ruthenium complexes, *Inorg Chim Acta*, **206**, 69 (1993)
69. Kasselouri S., Garoufis A., Katehanakis A., Kalkanis G., Perlepes S. P. and Hadjiliadis N., 1:1 Metal

- complexes of 2-(2'-pyridyl)quinoxaline, a ligand unexpectedly formed by the reaction between 2-acetylpyridine and 1,2-phenylenediamine, *Inorg Chim Acta*, **207**, 255 (1993)
70. Richter M.M, and Brewer K.J., Investigation of the spectroscopic, electrochemical, and spectroelectrochemical properties of osmium(II) complexes incorporating polyazine bridging ligands: formation of the Os/Os and Os/Ru mixed-valence complexes, *Inorg. Chem*, **32**, 2827 (1993)
71. Richter M.M. and Brewer K.J., Osmium(II)/ruthenium(II) trimetallics incorporating polyazine bridging ligands: isovalent near-IR absorbers with unique electrochemical behavior, *Inorg Chem*, **32**, 5762 (1993)
72. Ohzeki K., Nukatsuka I., Ichimura K., Kumagai F. and Kogawa M., Pre Concentration of Nickel(II) in White Wine Using Quinoxaline-2,3-dithiol and a Finely Divided Anion-Exchange Resin for the Determination by Solid-Phase Spectrophotometry concentration of Nickel(II) in White Wine Using Quinoxaline-2,3-dithiol and a Finely Divided Anion-Exchange Resin for the Determination by Solid-Phase Spectrophotometry, *Microchemical Journal*, **49**, 256 (1994)
73. Anderson P.A., Strouse G.F, Treadway J.A., Keene F.R. and Meyer T.J., Black MLCT Absorbers, *Inorg Chem*, **33**, 3863 (1994)
74. Parsons B. J., Beaumont P. C., Navaratnam S., Harisson W. D., Akasheh T. S. and Othman M., Laser flash photolysis and pulse radiolysis studies of ruthenium complexes, *Inorg Chem*, **33**, 157 (1994)
75. Molnar S. M., Jensen G. E., Vogler L. M., Jones S. W., Laverman L., Bridgewater J. S., Richter M. M. and Brewer K. J., Photochemical properties of mixed-metal supramolecular complexes *Journal of Photochemistry and Photobiology, A: Chemistry*, **80**, 315 (1994)
76. Vogler L. M., Franco C., Jones S. W. and Brewer K. J., Ruthenium chromophores containing terpyridine and a series of polyazine bridging ligands, *Inorg Chim Acta*, **221**, 55 (1994)
77. Kasselouri S., Garoufis A., Paschalidou S., Perlepes S. P., Butler I. S. and Hadjiliadis N., Preparation, structural and physical studies of mercury(II) halide complexes with the N,N'-chelating biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline, *Inorg Chim Acta*, **227**, 129 (1994)
78. Richter M. M., Jensen G. E. and Brewer K. J., A comparative study of the spectroscopy and oxidative spectroelectrochemistry of a series of homo- and heterobimetallic Ru(II) and Os(II) polypyridine complexes, *Inorg Chim Acta*, **230**, 35 (1995)
79. Yurdaknl S., Güllüolu T. M. and Kantam Z., Vibrational spectra and gas phase structures of fluorine fluorosulfate (FOSO<sub>2</sub>F) and chlorine fluorosulfate (ClOSO<sub>2</sub>F), *J Mol Struct*, **348**, 111 (1995)
80. Perlepes S. P., Spyridoula K., Achilleas G., Lutz F., Bau R. and Hadjiliadis N., Reaction of the biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline (L) with zinc(II) and cadmium(II) halides: Preparation and characterization of the 1 : 1 complexes, *Polyhedron*, **14**, 1461 (1995)
81. Baiano J. A., Kessler R. J., Lumpkin R. S., Munley M. J. and Murphy Jr. W. R., Nonradiative Decay in Rhenium(I) Monometallic Complexes of 2,3-Di(2-pyridyl)pyrazine and 2,3-Di(2-pyridyl)quinoxaline, *J. Physical Chem*, **99**, 17680 (1995)
82. Garoufis A., Perlepes S. P., Vreugdenhil A., Butler I. S. and Hadjiliadis N., Synthesis and characterization of 1:2 metal complexes of the biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline (L) and the X-ray structure of [CuL<sub>2</sub>](PF<sub>6</sub>), *Inorg Chim Acta*, **240**, 673 (1995)
83. Kilpatrick L., Rajagopalan K. V., Hilton J., Basti N.R., Stiefen E. I., Pilato R. S. and Spiro T. G., Resonance Raman Spectroscopic Characterization of the Molybdopterin Active Site of DMSO Reductase, *Biochemistry*, **34**, 3032 (1995)
84. Cummings S. C. and Eisenberg R., Luminescent Platinum(II) Complexes of Quinoxaline-2,3-dithiolate, *Inorg Chem*, **34**, 2007 (1995)
85. Garoufis A., Perlepes S. P., Schreiber A., Bau R. and Hadjiliadis N., Mercury(II)-carbon bond cleavage due to the coordination of the metal by 2-(2'-pyridyl)quinoxaline (L): preparation and characterization of [Hg<sub>2</sub>I<sub>4</sub>L<sub>2</sub>] derived from the reaction of CH<sub>3</sub>HgI and L, *Polyhedron*, **15**, 177 (1996)
86. Gordon K. C., Al-Obaidi A. H. R., Jayaweera P. M., McGarvey J. J., Malone J. F. and Bell S. E. J., Raman spectroelectrochemical studies and crystal structure of a binuclear copper(I) complex with a bridging diimine ligand, *J. Chem. Soc. Dalton Trans*, 1591 (1996)
87. Milkevitch M., Brauns E. and Brewer K. J., Spectroscopic and Electrochemical Properties of a Series of Mixed-Metal d<sup>6</sup>,d<sup>8</sup> Bimetallic Complexes of the Form [(bpy)<sub>2</sub>M(BL)PtCl<sub>2</sub>]<sup>2+</sup> (bpy = 2,2'-Bipyridine; BL = dpq (2,3-Bis(2-pyridyl)quinoxaline) or dpb (2,3-Bis(2-pyridyl)-benzoquinoxaline); M = Os<sup>II</sup> or Ru<sup>II</sup>), *Inorg Chem*, **35**, 1737 (1996)
88. Nallas G. N. A. and Brewer K. J., Electrocatalytic reduction of carbon dioxide by mixed-metal trimetallic complexes of the form {[ (bpy)<sub>2</sub>Ru(BL)<sub>2</sub>IrCl<sub>2</sub> ]<sup>5+</sup> where bpy=2,2'-bipyridine and BL=2,3-bis(2-pyridyl)quinoxaline (dpq) or 2,3-bis(2-pyridyl)benzoquinoxaline (dpb), *Inorg Chim Acta*, **253**, 7 (1996)
89. Scott S. M. and Gordon K. C., Spectroelectrochemical studies of ruthenium(II) diimine complexes with polypyridyl bridging ligands, *Inorg Chim Acta*, **254**, 267

- (1997)
90. Brauns E., Jones S. W., Clark J. A., Molnar S. M., Kawanishi Y. and Brewer K. J., Electrochemical, Spectroscopic, and Spectroelectrochemical Properties of Synthetically Useful Supramolecular Light Absorbers with Mixed Polyazine Bridging Ligands, *Inorg Chem*, **36**, 2861 (1997)
91. Kaiwar S. P., Hsu J. K., M.Liable-Sands L., Rheingold A. L. and Pilato R. S., Synthesis and Properties of Heterocyclic Substituted 1,2-Enedithiolates of Nickel, Palladium, and Platinum, *Inorg Chem*, **36**, 4234 (1997)
92. Nag P. K., Yue W., Gong X. and Chan W. K., *Materials Research Society Symposium – Proceedings*, **488**, 581 (1997)
93. Ng P. K., Gong X., Wong W. T. and Chan W. K., Quinoxaline-based conjugated polymers containing ruthenium(II) bipyridine metal complex, *Macromol Rapid Commun*, **18**, 1009 (1997)
94. Waterland M. R., Simpson T. J., Gordon K. C. and Burrell A. K., Spectroelectrochemical studies and excited-state resonance-Raman spectroscopy of some mononuclear rhenium(I) polypyridyl bridging ligand complexes. Crystal structure determination of tricarbonylchloro[2,3-di(2-pyridyl)quinoxaline]rhenium(I), *Dalton Trans*, 185 (1998)
95. Abbott L. C., Arnold C. J., Ye T. -Q., Gordon K. C., Perutz R. N., Hester R. E. and Moore J. N., Ultrafast Time-Resolved UV-Visible and Infrared Absorption Spectroscopy of Binuclear Rhenium(I) Polypyridyl Complexes in Solution, *J Physical Chem A*, **102**, 1252 (1998)
96. Kasselouri S., Garoufis A., Perlepes S. P., Lutz F., Bau R., Goubatsis S. and Hadjiliadis N., Preparation and characterization of the dinuclear complexes  $[\text{Fe}_2\text{Cl}_4\text{L}_2]$  and  $[\text{Fe}_2\text{Cl}_4\text{L}_2]\text{Cl}_2$  (L = 2-(2'-pyridyl) quinoxaline), *Polyhedron*, **17**, 1281 (1998)
97. Moliner N., Muñoz M. C., Van Koningsbruggen P. J. and Real J. A., Spin crossover in six-coordinate  $[\text{Fe}(\text{L})_2(\text{NCX})_2]$  compounds with L = DPQ = 2,3-bis-(2'-pyridyl)-quinoxaline, ABPT = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole and X = S, Se: synthesis, magnetic properties and single crystal studies, *Inorg Chim.Acta*, **274**, 1 (1998)
98. Tomaszewski L., Ding Z., Fermín D. J., Caçote H. M., Pereira C. M., Silva F. and Girault H. H., Spectroelectrochemical study of the copper(II) transfer assisted by 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline at the water|1,2-dichloroethane interface, *Journal of Electroanalytical Chemistry*, **453**, 171 (1998)
99. Collins J. G., Sleeman A. D., Aldrich-Wright J. R., Greguric I. and Hambley T. W., A  $^1\text{H}$  NMR Study of the DNA Binding of Ruthenium(II) Polypyridyl Complexes, *InorgChem*, **37**, 3133 (1998)
100. Page S. E., Gordon K. C. and Burrell A. K., Altering the Balance between Ligand-Based Radical Anion Formation and Dechelation in Electrochemically Reduced Binuclear Copper(I) Complexes: A Resonance Raman Spectroelectrochemical Study, *Inorg Chem*, **37**, 4452 (1998)
101. Bodini M. E., Del Valle M. A., Copia G. E. and Soto C., Voltammetric study of the redox chemistry of 2,3-dihydroxy-quinoxaline and its zinc complexes in non-aqueous medium, *Polyhedron*, **17**, 2109 (1998)
102. Rani D. S., Raju V. J. and Ananthakshmi P. V., Synthesis and structural studies of first row transition metal complexes of a new bi-ambidentate ligand, *Indian J Chem A*, **38**, 385 (1999)
103. Garoufis A., Kasselouri S., Boyatzis S. and Raptopoulou C. P., Preparation, crystal structure and solution studies of  $[\text{Mn}_2\text{L}_2\text{Cl}_4(\text{H}_2\text{O})_2]$ , where L=2-(2'-pyridyl)quinoxaline, *Polyhedron*, **18**, 1615 (1999)
104. Simao D., Lopes E. B., Santos I. C., Gama V., Henriques R. T. and Almeida M., Charge transfer salts based on  $\text{Cu}(\text{qdt})_2$ ,  $\text{Ni}(\text{qdt})_2$  and  $\text{Au}(\text{qdt})_2$  anions, *Synth Metals.*; **102**, 1613 (1999)
105. Collins J. G., Binding of the  $\Delta$ - and  $\Lambda$ -Enantiomers of  $[\text{Ru}(\text{dmphen})_2\text{dpq}]^{2+}$  to the Hexanucleotide  $\text{d}(\text{GTTCGAC})_2$ , *Inorg Chem*, **38**, 5502 (1999)
106. Xu Z. and Wang M., *Spectroscopy and Spectral Analysis*, **19**, 331 (1999)
107. Joy V. T. and Srinivasan T. K. K., Surface-Enhanced Raman Scattering Study of Quinoxaline-2,3-dithiol and Disodium Bis(quinoxaline-2,3-dithiolato)nickelate(II) Adsorbed on Silver Surface, *J Phys Chem B*, **103**, 6509 (1999)
108. Helton M. E., Gruhn N. E., McNaughton R. L. and Kirk M. L., Control of Oxo-Molybdenum Reduction and Ionization Potentials by Dithiolate Donors, *Inorg Chem*, **39**, 2273 (2000)
109. Garoufis A., Kasselouri S. and Raptopoulou C. P., Six- and five-coordinated complexes of Co(II) with 2-(2'-pyridyl)quinoxaline. Crystal structures of the complexes  $[\text{CoLCl}_2(\text{DMF})]$  and  $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$  *Inorg Chem Commun*, **3**, 251 (2000)
111. Pratihari P. L., Polarographic Studies on interaction of 2-Aminoquinoxaline with Cd(II) in Alkanols, Formamide, Dimethyl Formamide and Dimethyl Sulphoxide Solvent Mixture, *Asian J Chem*, **12**, 1146 (2000)
112. Waterland M. R., Flood A. and Gordon K. C., Metal-to-ligand charge-transfer excited-states in binuclear

- copper(I) complexes. Tuning MLCT excited-states through structural modification of bridging ligands. A resonance Raman study, *J Chem Soc Dalton Trans.* 121 (2000)
113. Gürsoy S., Koçak M., Bekarolu O., Synthesis and Characterization of a New 2,2'-Azoquinoline and its Complexes with Platinum and Palladium, *Monatshefte für Chemie*, **131**, 181 (2000)
114. Gok Y., Bilgin A., Ertepinar H. and Nisanoglu E., Synthesis and Characterization of novel tetraoximes and their poly metal complexes, *Indian J Chem Sect A*, 1280 (2000)
115. Jung O. -S., Park S. H., Kim Y. J., Lee Y. -A., Jang H. G. and Lee U., Synthesis, structure, and thermal behavior of discrete Co(II), Ag(I), and Pd(II) complexes with 2,3-bis(2-pyridyl)quinoxaline. Insight into coordination modes, *Inorg Chim Acta*, **312**, 93 (2001)
116. Gholamkhash B., Koike K., Negishi N., Hori H. and Takeuchi K., Synthesis and Characterization of Ruthenium(II) Molecular Assemblies for Photosensitization of Nanocrystalline TiO<sub>2</sub>: Utilization of Hydroxyl Grafting Mode, *Inorg Chem*, **40**, 756 (2001)
117. Mostafa S. I., Perlepes S. P. and Hadjiliadis N., New Dinuclear Transition Metal Complexes with the [M<sub>2</sub>(μ-dhbq)]<sup>n+</sup> Core and 2-(2'-Pyridyl)quinoxaline (L) as a Terminal Ligand: Preparation and Characterization (dhbq<sup>2-</sup> = the Dianion of 2,5-Dihydroxy-1,4-benzoquinone; M = AgI, MnII, CoII, NiII, CuII, RuII, PdII, FeIII, RhIII; n = 0, 2, 4), *Zeitschrift für Naturforschung - Section B Journal of Chemical Sciences*, **56**, 394 (2001)
118. Proudfoot E. M., Mackay J. P. and Karuso P., Probing Site Specificity of DNA Binding Metallointercalators by NMR Spectroscopy and Molecular Modeling, *Biochemistry*, **40**, 4867 (2001)
119. Montalban A. G., Sakellariou E. G., Riguet E., McCubbin Q. J., Barrett A. G. M. and Hoffman B. M., Phenanthroline-appended porphyrazines: synthesis and conversion into solitaire Ru(II) complexes, *Inorg Chim Acta*, **317**, 143 (2001)
120. Amin A. S. and El-Sayed G. O., Colorimetric Microdetermination of Mercury(II) with Some Quinoxaline Azo Compounds in Presence of an Anionic Surfactant, *Monatshefte für Chemie*, **132**, 587 (2001)
121. Bu X. -H., Liu H., Du M., Wong K. M. -C., Yam V. W. -W. and Shionoya M., Novel Boxlike Dinuclear or Chain Polymeric Silver(I) Complexes with Polypyridyl Bridging Ligands: Syntheses, Crystal Structures, and Spectroscopic and Electrochemical Properties, *Inorg Chem*, **40**, 4143 (2001)
122. Islam A., Sugihara H., Hara K., Singh L. P., Katoh R., Yanagida M., Takahashi Y., Murata S. and Arakawa H., *Journal of Photochemistry and Photobiology A: Chemistry*, **145**, 135 (2001)
123. D'Alessandro D. M., Kelso L. S. and Keene F. R., Stereochemical Influences on Intervalence Charge Transfer in Homodinuclear Complexes of Ruthenium, *Inorg Chem*, **40**, 6841(2001)
124. Ambroise A., and Mariya B. G., Ruthenium(II) Complexes of 6,7-Dicyanodipyridoquinoxaline: Synthesis, Luminescence Studies, and DNA Interaction, *Inorg Chem*, **39**, 4264 (2000)
125. Wu C., Lu C., Zhuang H. and Huang. J., Hybrid Coordination Polymer Constructed from β-Octamolybdates Linked by Quinoxaline and Its Oxidized Product Benzimidazole Coordinated to Binuclear Copper(I) Fragments, *InorgChem*, **41**, 5636 (2002)
126. Abdel-Shafi A. A., H. Khalil M. M., Abdalla H. H. and Ramadan R. M., Ruthenium, osmium and rhodium-2,3-bis(2'-pyridyl)quinoxaline complexes, *Trans Met Chem*, **27**, 69 (2002)
127. Naskar J. P., Chowdhury S., Drew M. G. B. and Datta D., Chemistry of the copper(I)-water bond. Some new observations, *New J Chem*, **26**, 170 (2002)
128. Mizuno T., Wei W. -H., Eller L. R. and Sessler J. L., Phenanthroline Complexes Bearing Fused Dipyrrolyquinoxaline Anion Recognition Sites: Efficient Fluoride Anion Receptors, *J Am Chem Soc*, **124**, 1134 (2002)
129. Seneviratne D. S., Uddin M. J., Swayambunathan V., Schlegel H. B. and Endicott J. F., Characteristics and Properties of Metal-to-Ligand Charge-Transfer Excited States in 2,3-Bis(2-pyridyl)pyrazine and 2,2'-Bypyridine Ruthenium Complexes. Perturbation-Theory-Based Correlations of Optical Absorption and Emission Parameters with Electrochemistry and Thermal Kinetics and Related Ab Initio Calculations, *Inorg Chem*, **41**, 1502 (2002)
130. Amin A. S., Microdetermination of Zinc(II) in alloys and ores by visible spectrophotometric technique using 2,3-dichloro-6-(2-hydroxynaphthylazo)- quinoxaline in presence of mixed surfactants, *Anal Lett*, **35**, 585 (2002)
131. Bu X. -H., Liu H., Du M., Wong K. M. -C. and Yam V. W. -W., Coordinative versatility of 2,3-bis(2-pyridyl)-5,8-dimethoxyquinoxaline (L) to different metal ions: syntheses, crystal structures and properties of [Cu(I)L]<sub>2</sub><sup>2+</sup> and [ML]<sup>2+</sup>(M=Cu(II), Ni(II), Zn(II) and Co(II)), *Inorg Chim Acta*, **333**, 32 (2002)
132. Flood A., Girling R. B., Gordon K. C., Hester R. E., Moore J. N. and Polson M. I. J., Revealing the chromophoric composition of multichromophoric polypyridyl complexes of Re(I) and Os(II): a resonance Raman study, *Journal of Raman Spectroscopy*, **33**, 434 (2002)

133. Shao C., Sun W. -H., Li Z., Hu Y. and Han L., Ethylene oligomerization promoted by group 8 metal complexes containing 2-(2-pyridyl)quinoxaline ligands, *Catalysis Communications*, **3**, 405 (2002)
134. Sherborne J. R., Page S. E., Flood A., Polson M. I. J. and Gordon K. C., Resonance Raman Spectroelectrochemistry, using a Raman OTTL Cell, of Molybdenum Tetracarbonyl Complexes with Polypyridine Ligands, *Asian J Spectros*, **6**, 169 (2002)
135. Xu Z. -D., Liu H., Wang M., Xiao S. -L., Yang M. and Bu X. -H., Manganese(II) complex of 6,7-dicyanodipyridoquinoxaline with antitumor activities: synthesis, crystal structure and binding with DNA, *J Inorg Biochem*, **92**, 149 (2002)
136. Pellegrini P. P. and Aldrich-Wright J. R., Evidence for chiral discrimination of ruthenium(II) polypyridyl complexes by DNA, *Dalton Trans*, 176 (2003)
137. Veroni I., Rontoyianni A. and Mitsopoulou C. A., Synthesis and characterization of a novel complex: Mo(CO)<sub>4</sub>[2-(2'-pyridyl)quinoxaline]. An insight based on experimental and theoretical data, *Dalton Trans*, 255 (2003)
138. Cherezova E. A., Taraskina T. V., Kulikova M. V. and Balashev K.P., Preparation and Properties of Cyclopalladated Complexes of Dibenzo[a,c]phenazine and Dibenzo[f,h]quinoxaline with Ethylenediamine, *Russian J Gen Chem*, **73**, 1160 (2003)
139. Williams R., Toft N. H., Winkel B. and Brewer K., Synthesis, Characterization, and DNA Binding Properties of a Series of Ru, Pt Mixed-Metal Complexes, *Inorg Chem*, **42**, 4394 (2003)
140. Ocak U., Kantekin H., Gok Y. and Misir M. N., The synthesis and characterization of a new (E,E)-dioxime and its homo- and heterotrimeric complexes containing a hexaoxadiazia macrobicyclic moiety, *New J Chem*, **27**, 1251 (2003)
141. Reddy P. A. N., Santra B. K., Nethaji M. and Chakravarty A. R., Synthesis, crystal structure and nuclease activity of bis(dipyridoquinoxaline)copper(I) perchlorate, *Indian J Chem sect A*, **42**, 2185 (2003)
142. Dhar S., Senapati D., Reddy P. A. N., Das P. K. and Chakravarty A. R., Metal-assisted red light-induced efficient DNA cleavage by dipyridoquinoxaline-copper(II) complex, *Chem Comm*, **9**, 2452 (2003)
143. Arca M., Bencini A., Berni E., Caltagirone C., Devillanova F. A., Isaia F., Garau A., Giorgi C., Lippolis V., Perra A., Tei L. and Valtancoli B., Coordination Properties of New Bis(1,4,7-triazacyclononane) Ligands: A Highly Active Dizinc Complex in Phosphate Diester Hydrolysis, *Inorg Chem*, **42**, 6929 (2003)
144. Matrosov E. I., Starikova Z. A., Khodak A. A. and Nifant'ev E. E., *Russian J Inorg Chem*, **48**, 1851 (2003)
145. Nervi C., Gobetto R., Milone L., Viale A., Rosenberg E., Rokhsana D. and Fiedler J., Spectroscopic and Computational Investigations of Stable Radical Anions of Triosmium Benzoheterocycle Clusters, *Chemistry –A European Journal*, **9**, 5749 (2003)
146. Bhattacharya P., Lawson H. and Barton J., <sup>1</sup>H NMR Studies of Nickel(II) Complexes Bound to Oligonucleotides: A Novel Technique for Distinguishing the Binding Locations of Metal Complexes in DNA, *Inorg Chem*, **42**, 8811 (2003)
147. Reddy P. A. N., Santra B. K., Nethaji M. and Chakravarty A. R., Metal-assisted light-induced DNA cleavage activity of 2-(methylthio)phenylsalicylaldehyde Schiff base copper(II) complexes having planar heterocyclic bases, *J Inorg Biochem*, **98**, 377 (2004)
148. Hegedus L. S., Greenberg M. M., Wendling J.J. and Bullock J. P., Synthesis of 5,12-Dioxocyclam Nickel (II) Complexes Having Quinoxaline Substituents at the 6 and 13 Positions as Potential DNA Bis-Intercalating and Cleaving Agents, *J Org Chem*, **68**, 4179 (2003)
149. Reddy P.A.N., Nethaji M. and Chakravarty A. R., Hydrolytic Cleavage of DNA by Ternary Amino Acid Schiff Base Copper(II) Complexes Having Planar Heterocyclic Ligands, *Eur J Inorg Chem*, **7**, 1440 (2004)
150. Thomas A.M., Naik A.D., Nethaji M. and Chakravarty A.R., Synthesis, crystal structure and photo-induced DNA cleavage activity of ternary copper(II)-thiosemicarbazone complexes having heterocyclic bases, *Inorg Chim Acta*, **357**, 2315 (2004)
151. Martell J. R. T. and Sanchez I., Metal complexes of a new ligand derived from 2,3-quinoxalinedithiol and 2,6-bis(bromomethyl)pyridine, *J Chilean Chem Soc*, **50**, 375 (2005)
152. Patra A. K., Dhar S., Nethaji M. and Chakravarty A. R., Metal-assisted red light-induced DNA cleavage by ternary L-methionine copper(II) complexes of planar heterocyclic bases, *Dalton Trans*, 896 (2005)
153. Hwang F. M., Chen H. Y., Liu C. S. C. F., Shu, Wu F., Cou, Peng P. T. and Lee S. M., Iridium(III) Complexes with Orthometalated Quinoxaline Ligands: Subtle Tuning of Emission to the Saturated Red Color, *Inorg Chem*, **44**, 1344 (2005)
154. Lo K. K. -W. and Hui W. -K., Design of Rhenium(I) Polypyridine Biotin Complexes as a New Class of Luminescent Probes for Avidin, *Inorg Chem*, **44**, 1992 (2005)
155. Wu Y., Chen. H. and Xiong Z. Y., Racemic d,l-[Co(phen)<sub>2</sub>dpq]<sup>3+</sup>-DNA interactions: Investigation into the basis for minor-groove binding and recognition, *J Inorg Biochem*, **99**, 1126 (2005)

156. Sherman C. L., Brodbelt J. S., Marchand A. P. and Poola B., Electrospray Ionization Mass Spectrometric Detection of Self-Assembly of a Crown Ether Complex Directed by  $\pi$ -Stacking Interactions, *Journal of the American Society for Mass Spectrometry*, **16**, 1162 (2005)
157. Ou Z., Shao W. E. J., Burn P. L., Sheehan C. S., Walton R., Kadish K. M. and Crossley M. J., Electrochemical and spectroelectrochemical properties of building blocks for molecular arrays: reactions of quinoxalino[2,3-b]porphyrins containing metal(II) ions, *Journal of Porphyrins and Phthalocyanines*, **9**, 151 (2005)
158. Liu X. W., Li J., Deng H., Zheng K. C., Mao Z. W. and Ji L. N., Experimental and DFT studies on the NA-binding trend and spectral properties of complexes  $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$  (L = dmdpq, dpq, and dcdpq), *Inorg Chim Acta*, **358**, 3311 (2005)
159. Schramm F., Walther D., Görls H., Käpplinger C. and Beckert R., Trifluoromethylaryl-substituted quinoxalines: Unusual ruthenium-amidininate complexes and their suitability for anellation reactions, *Zeitschrift für Naturforschung – Section B Journal of Chemical Sciences*, **60**, 843 (2005)
160. Patra A. K., Nethaji M. and Chakravarty A. R., Red-light photosensitized cleavage of DNA by (L-lysine) (phenanthroline base) copper(II) complexes, *Dalton Trans*, 2798 (2005)
161. Katoh A., Ogino K. and Saito R., Synthesis of new 3-hydroxy-4(1H)-pyridinone directly attached to quinoxaline and its fluorescence property upon complexation to metal ions *Heterocycles*, **65**, 2195 (2005)
162. Zhang G. -L., Chuai Y. -T., Guo H. -Q. and Zou D. -C., Synthesis and electrophosphorescence of a red platinum (II) quinoxaline complex, *Acta Physico-Chimica Sinica*, **21**, 1407 (2005)
163. Zhang G. -L., Guo H. -Q., Chuai Y. -T. and Zou D. -C., Synthesis and luminescence of a new red triplet iridium quinoxaline complex, *Acta Chimica Sinica*, **63**, 143 (2005)
164. Zou R. -Q., Liu C. -S., Huang Z., Hu T. -L. and Bu X. -H., Syntheses, structure, and properties of the metal complexes with 3-(2-pyridyl)pyrazole-based ligands: Tuning the complex structures by ligand modifications, *Crystal Growth and Design*, **6**, 99 (2006)
165. Veroni I., Makedonas C., Rontoyianni A. and Mitsopoulou C. A., An experimental and DFT computational study of a novel zerovalent tetracarbonyl tungsten complex of 2-(2'-pyridyl)quinoxaline, *J Organomet Chem*, **691**, 267 (2006)
166. Lo K. K., Tsang K. H. and Sze K., Utilization of the Highly Environment-Sensitive Emission Properties of Rhenium(I) Amidodipyridoquinoxaline Biotin Complexes in the Development of Biological Probes, *Inorg Chem*, **45**, 1714 (2006)
167. Balashev K. P., Ivanov M. A., Taraskina T. V. and Cherezova E. A., Spectroscopic and electrochemical properties of mixed-ligand cycloplatinated complexes based on 2-(2-thienyl)pyridine and 2-phenylpyridine with 1,10-phenantroline and its 1,4-diazine derivatives, *Russian J Gen Chem*, **76**, 781 (2006)
168. Saravanakumar S., Kindermann M. K., Heinicke J. and Köckerling M., Influence of anellation in N-heterocyclic carbenes: Novel quinoxaline-anellated NHCs trapped as transition metal complexes, *Chem Comm*, **6**, 640 (2006)
169. Vieites M., Noblí P., Torre M. H., Cerecetto H., Lavaggi M. L., Costa-Filho A. J., Azqueta A., de Cerain A. L., Monge A., Parajón-Costa B., González M. and Gambino D., Selective hypoxia-cytotoxins based on vanadyl complexes with 3-aminoquinoxaline-2-carbonitrile-N1,N4-dioxide derivatives, *J Inorg Biochem*, **100**, 1358 (2006)
170. Zhao Q., Liu S., Shi M., Wong C., Yu M., Li L., Li F., Yi T. and Huang C., Series of new cationic iridium(III) complexes with tunable emission wavelength and excited state properties: structures, theoretical calculations, and photophysical and electrochemical properties, *Inorg Chem*, **45**, 6152 (2006)
171. Li E. Y., Cheng Y. -M, Hsu C. -C., Chou P. -T., Lee G. -H., Lin I. -H., Chi Y. and Liu C. -S., Neutral Ru II-based emitting materials: A prototypical study on factors governing radiationless transition in phosphorescent metal complexes, *Inorg Chem*, **45**, 8041 (2006)
172. Govindaswamy P. and Kollipara M. R., Syntheses and characterization of  $\eta^5$ -pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes containing polypyridyls, *J Coord Chem*, **59**, 663 (2006)
173. Hsu G. -Y., Misra P., Cheng S. -C., Wei H. -H. and Mohanta S., Syntheses, structures, and magnetic properties of dicyanamide bridged one-dimensional double chain and discrete dinuclear complexes of manganese(II) derived from 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline or 2,4,6-tri(2-pyridyl)-1,3,5-triazine, *Polyhedron*, **25**, 3393 (2006)
174. Veroni I., Mitsopoulou C. A. and Lahoz F. J., An experimental and DFT computational study of a novel zerovalent tetracarbonyl tungsten complex of 2-(2'-pyridyl)quinoxaline, *J Organometallic Chem*, **69**, 5967 (2006)
175. Dhar S., Nethaji M. and Chakravarty A. R., DNA cleavage on photoexposure at the d-d band in ternary copper(II) complexes using red-light laser, *Inorg Chem*, **45**, 11043 (2006)