

COMPLEX STUDIES OF 1,2,4-TRIAZOLES

Murat BEYTUR

Kafkas University

Onur AKYILDIRIM

Kafkas University

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Heterocyclic aromatic compounds containing nitrogen and oxygen have gained great importance globally not only because of their prevalence in natural products, but also because of their biological (natural or synthetic antioxidants known as exogenous are believed to have positive effects on health and disease prevention (Harmankaya et al., 2020, 2021; Harmankaya & Harmankaya, 2022) photochemical, optoelectronic, theoretical, pharmacological properties and industrial importance (Beytur, 2020; Boy, Aras, et al., 2021; Boy, Türkan, et al., 2021; Koç et al., 2020; Kotan et al., 2020; Turhan Irak & Beytur, 2019; Uğurlu & Beytur, 2020). There are many studies showing that many metallo-biomolecules with N and S atoms in their structure play an important role in the coordination of metals in their active sites. Metallo-organic chemistry (Sertçelik & Durman, 2020; Sertçelik, 2021; Sertçelik et al., 2018; Sugeçti & Büyükgüzel, 2021) has an important area of research as new metal-based compounds with antibacterial and antifungal activities are needed (Scozzafava & Supuran, 2000). The presence of 1,2,4-triazole structure in ligand systems has contributed significantly to science. Recent studies of the coordination structure of 1,2,4-triazole allow the formation of polydentate binding sites, which increases the stability of the complex formed due to chelation, the effect of substituents carrying donor atoms (Burke et al., 2004; Haasnoot, 2000; Klingele & Brooker, 2003).

In recent years, many studies have been done on organotin(IV) complexes due to their important industrial and biological applications. Organotin(IV) complexes provide coordination with hetero-donor atoms through intermolecular and intramolecular interactions due to their low level of vacant 5d atomic orbitals and electron accepting ability of Sn atoms (Chandrasekhar et

al., 2002; Chaudhary et al., 2006). There are also few studies on the photo- and electroluminescent properties of Zn and Cd triazole coordination compounds (Chen et al., 2006).

The nickel complexes of 1,2,4-triazole-derived amido-functionalized N-heterocyclic carbene ligands were synthesized and structurally characterized. In particular, $[1-(R)-4-N-(\text{furan-2-ylmethyl})\text{-acetamido-1,2,4-triazol-5-ylidene}]_2\text{Ni}$ [$R=\text{Et}$, $i\text{-Pr}$ and Bn] complexes were obtained by direct reaction of the corresponding triazolium chloride salts by treatment with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of K_2CO_3 as the base. Density functional theory (DFT) studies performed on these complexes revealed the highly polar character of the NHC-Ni σ -bond interaction with the corresponding molecular orbital having the maximum contribution (59-69 %) from the NHC ligand fragments while providing the minimum contribution (4 %) from the central nickel atom (Kumar et al., 2015).

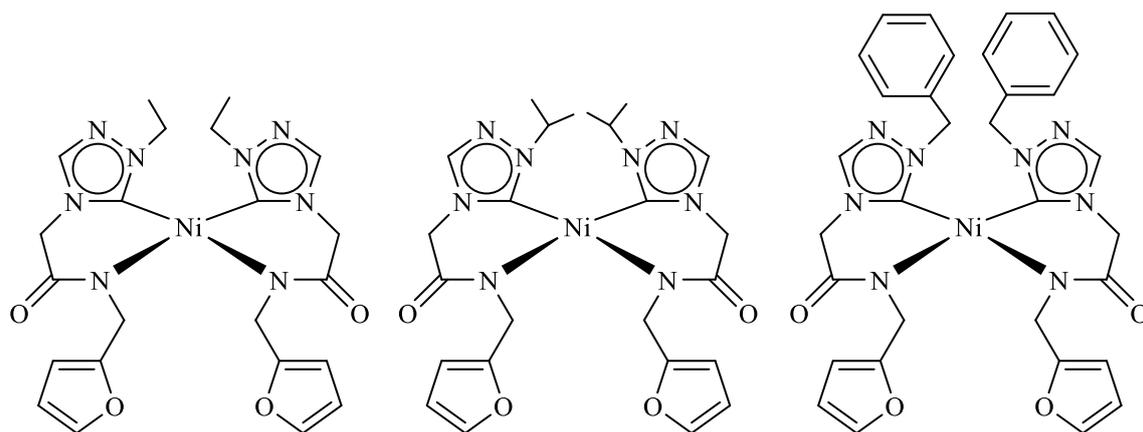


Figure 1. The nickel complexes of 1,2,4-triazole derived amido-functionalized N-heterocyclic carbene ligands (Kumar et al., 2015).

Cu(II) complexes were synthesized by reacting the at a ratio 1:1 M of newly prepared 3-R-1,2,4-triazole Schiff bases [$R=\text{H}$, CH_3 and C_2H_5] with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the presence of sodium acetate trihydrate at reflux temperature. Not all synthesized complexes are electrolytes in N,N -dimethylformamide. CuO nanoparticles were synthesized by thermal decomposition of newly prepared Cu(II) triazole Schiff base complexes as solid precursors. The synthesized CuO nanoparticles were characterized using HR-TEM, FT-IR, XRD and optical properties. All Schiff bases, their Cu(II) complexes and CuO nanoparticles showed moderate activity against both pathogenic bacterial strains (*Escherichia coli* & *Staphylococcus aureus*) and weak antifungal activity (*Aspergillus flavus* & *Candida albicans*) (Aly et al., 2015).

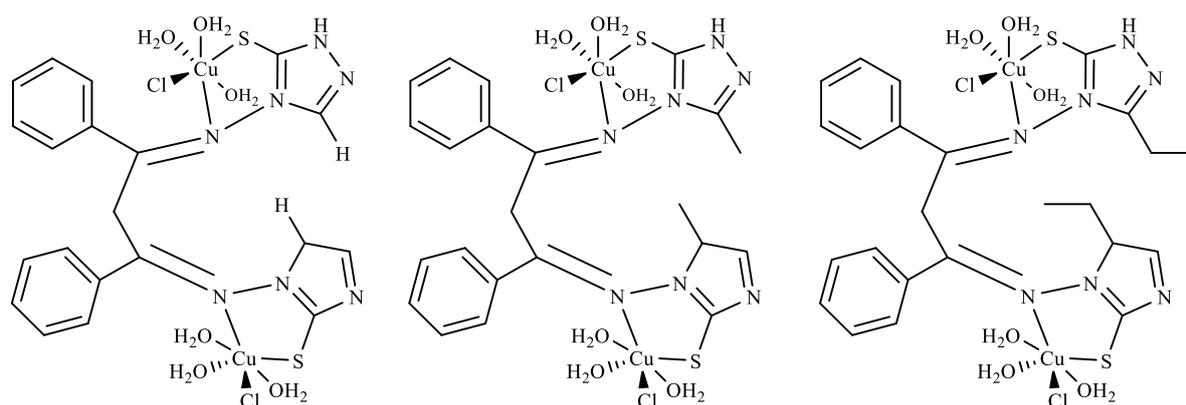


Figure 2. Cu (II) complexes of 3-R-4-amino-5-mercapto-1,2,4-triazole Schiff bases (Aly et al., 2015).

The novel triorganotin of Schiff base (E)-4-amino-3-(2-(2-hydroxybenzylidene)hydrazinyl)-1H-1,2,4-triazol-5(4H)-thion with the general formula R_3SnL complexes derived from the condensation of 4-amino-3-hydrazino-5-mercapto-4H-1,2,4-triazole and 2-hydroxybenzaldehyde was synthesized by the sodium salt method. Spectroscopic characterization showed that in these 1:1 monomeric derivatives, that the deprotonated hydrazino-Schiff base behaves as a monoanionic bidentate coordinated along the ophenolic and nasometine and the polyhedron around the tin atom shows that it has a distorted trigonal-bipyramidal geometry. NBO analysis was performed to analyze intramolecular and intermolecular interactions leading to stabilization in the studied systems. A detailed vibration assessment was successfully performed for all complexes, and the comparative analysis between the experimental and simulated IR vibration frequencies of both complexes shows a good correlation between them. Boundary MOs have been defined for the complexes. Here, the HOMO is concentrated on the ligand moiety, and the LUMO center is concentrated around the tin atom. The synthesized complexes have showed either equivalent or better in vitro antifungal activity as compared to Schiff base with reference to Amphotericin B against *Aspergillus flavus* and *Fusarium oxysporum*. In silico, docking studies on the active site of cytochrome P450 14- α -demethylase were also performed (Joshi et al., 2019).

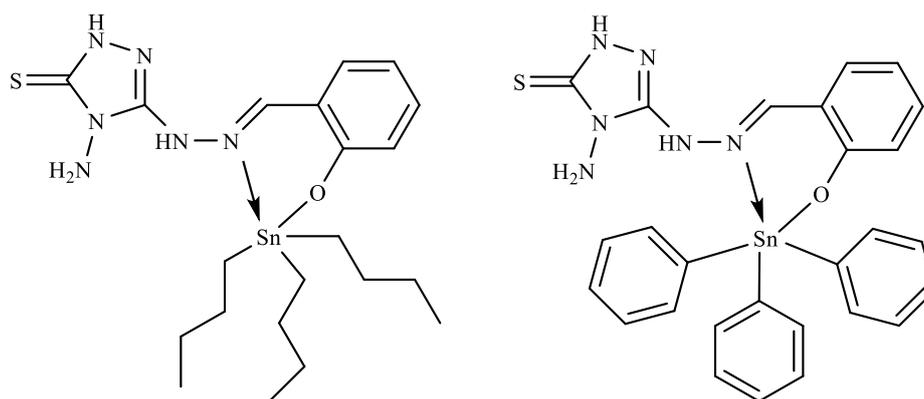


Figure 3. Triorganotin(IV) complexes of o-hydroxy schiff base (Joshi et al., 2019).

Reaction of 3-(Pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole with salicylaldehyde or benzaldehyde gives rise to a new 1,2,4-triazole derivatives. Reactions of ligands with zinc acetate in ethanol, two new complexes are obtained with the azomethine or dihydrotriazine indolizine form of the ligands. The structures of the synthesized complexes were investigated by X-ray analysis. The complexes showed strong green-blue luminescence in the solid state. Zinc complexes synthesized with high thermal stability and high luminescence are expected to be an important agent for organic light production (Gusev et al., 2011).

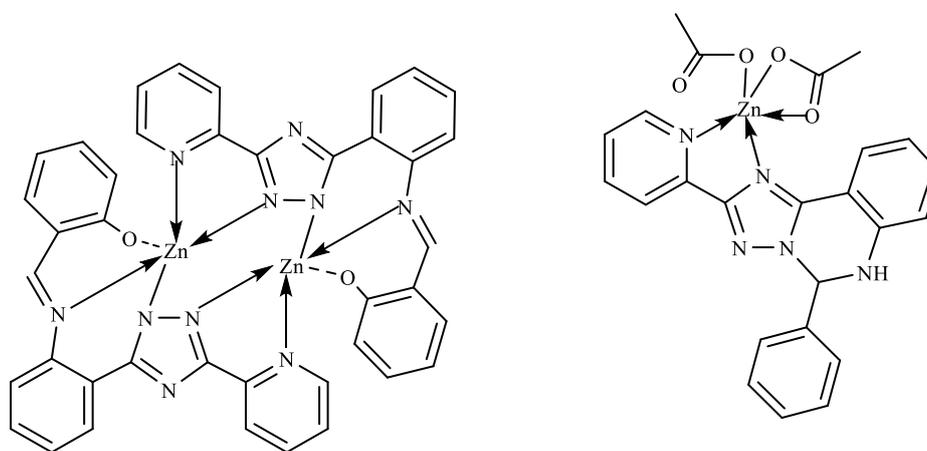


Figure 4. Zn complexes of 1,2,4-triazole (Gusev et al., 2011)

Novel triorganotin (IV) complexes with Schiff base (E)-4-amino-3-(2-(4-hydroxybenzylidene)hydrazinyl)-1H-1,2,4-triazol-5(4H)-thion were synthesized. It has been characterized using analytical and multiple spectroscopic techniques such as 2D-HMQC, FT-IR/Raman, NMR (^1H , ^{13}C , ^{119}Sn), ESI-MS spectrometry. A skewed tetrahedral geometry was determined in the Schiff base ligand. The atomic charges on the selected atoms were calculated

and the reactive regions on the surface of the molecules were evaluated by means of the molecular electrostatic potential map (MEP). A comparative analysis of the calculated vibrational frequencies with the experimental vibrational frequencies was performed and significant bands were determined. The *in vitro* antifungal activity of triorganotin (IV) complexes and Schiff base ligand were tested to investigate their potential antifungal activities. The results of *in vitro* antifungal studies against selected strains showed that both complexes showed potent inhibitory activity. Obtained bioactivity results were confirmed by *in-silico* molecular docking studies. Organotin complexes have attracted attention for their significant antifungal activities, but can also be considered as potential alternatives to platinum drugs used in various chemotherapies due to their low toxicity and high selectivity (Joshi et al., 2020).

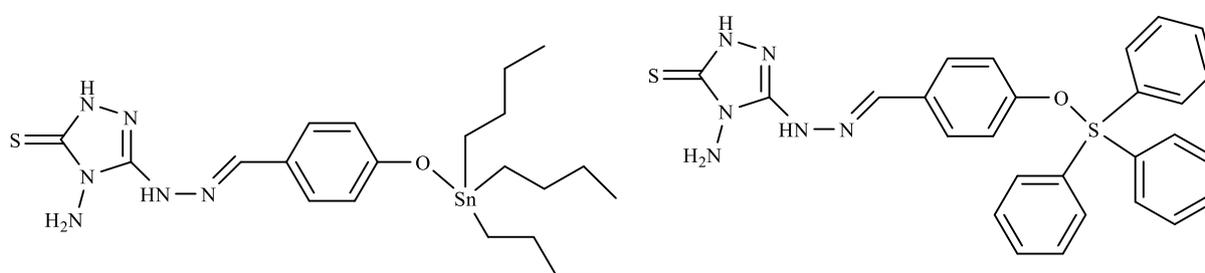


Figure 5. Triorganotin(IV) complexes of p-hydroxy schiff base (Joshi et al., 2020)

Ligands 4-phenyl-2H-1,2,4-triazol-3-thione (Hpht), 3,30-dithiobis (4-phenyl-1,2,4-triazole) (dbpht) and $[\text{Ni}](\text{pht})_2(\text{en})_2$ and $[\text{Cd}_2(1\text{-pht})_2(\text{pht})_2(\text{bpy})_2]$ (3) complexes were synthesized and characterized by various physicochemical methods. In complex Ni, the nickel center is bonded via the triazole ring nitrogen, while in complex Cd, cadmium is bonded via thiolato sulfur, forming a dimeric structure via thiolato bridging. Complexes are stabilized by various intermolecular and intramolecular hydrogen bonds. The DFT results of the optimized molecular geometry of all compounds were obtained and compared with the experimental X-ray diffraction results. Thermogravimetric analysis properties of the complexes were investigated. Its photoluminescent properties indicate that complex Cd is non-fluorescent and complex Ni has characteristic fluorescent emissions that make it a desirable target for photophysical studies and electronic applications (Dani et al., 2014).

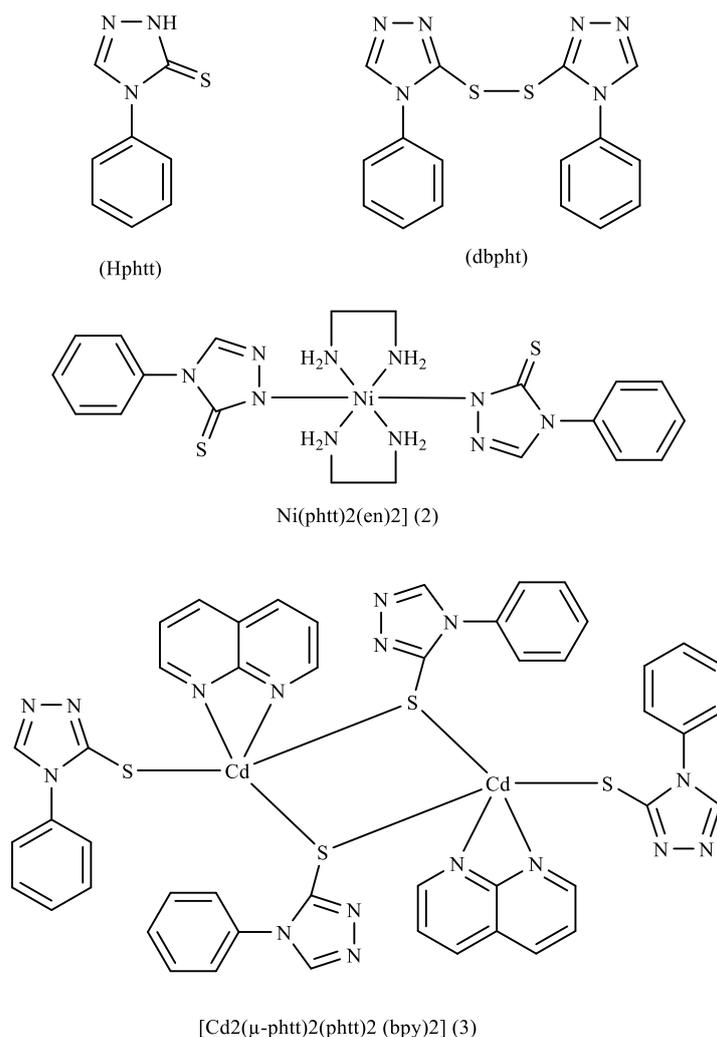


Figure 6. Syntheses of ligand and its complexes (Dani et al., 2014).

[Ni^{II}(dpp)₂(L)₂] (1), [Ni^{II}(eda)₂(L)₂] (2) and [Ni^{II}(deda)₂(L)₂] (3) complexes were synthesized by reacting 3-pyridinyl-4-amino-5-mercapto-1,2,4-triazole with diamines and nickel (II) salt (dpp=1,3-diaminopropane, eda=ethanediamine, deda=N,N-dimethyl ethylenediamine). Three new complexes were structurally characterized by the single crystal X-ray diffraction method. Inhibitory activity of the complexes was tested *in vitro* against jack bean urease. Molecular docking was investigated to insert complexes into the crystal structure of jack bean urease at the active site to determine the possible mode of binding. The synthesized complexes exhibited inhibitory activities as a potent urease inhibitor. Studies of molecular docking and urease inhibitory activities of complexes against Jack bean urease have valuably led to the development of a new urease inhibitor (Xu et al., 2014).

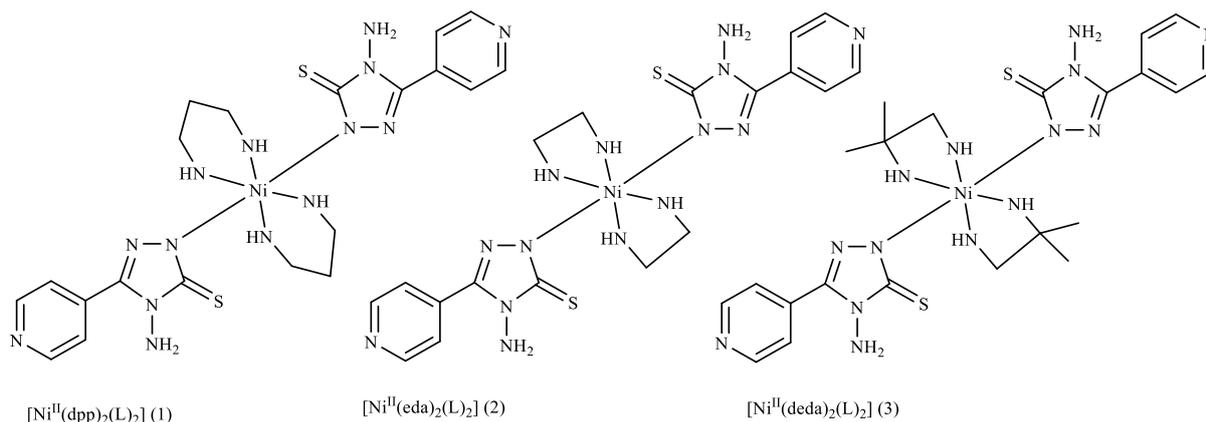


Figure 7. $[\text{Ni}^{\text{II}}(\text{dpp})_2(\text{L})_2]$ (1), $[\text{Ni}^{\text{II}}(\text{eda})_2(\text{L})_2]$ (2) and $[\text{Ni}^{\text{II}}(\text{deda})_2(\text{L})_2]$ (3) complexes synthesized 3-pyridinyl-4-amino-5-mercapto-1,2,4-triazole (Xu et al., 2014).

Synthesis of three new Pd(II) complexes, $[\text{Pd}(\text{eptu})_2]$, $[\text{Pd}(\text{Hmtrz})_4]\text{Cl}_2$ and $[\text{Pd}(\text{Hmthd})_4]\text{Cl}_2 \cdot 2\text{CHCl}_3$ were investigated spectral and crystal structure research. Single crystal X-ray structures showed a warped square planar geometry with four coordinates around the Pd(II) center in these complexes. The thiourea ligand Heptu binds to the metal ion via nitrogen and sulfur atoms and behaves like a non-negative bidentate in complex $[\text{Pd}(\text{eptu})_2]$. Triazole (Hmtrz) and thiadiazole (Hmthd) ligands act as neutral monodentate coordinated to the metal ion via the thion sulfide in complexes. It is observed that the transition of hydrogen from sulfur to nitrogen in the ligand framework in complexes $[\text{Pd}(\text{Hmtrz})_4]\text{Cl}_2$ and $[\text{Pd}(\text{Hmthd})_4]\text{Cl}_2 \cdot 2\text{CHCl}_3$ causes the ligand to form thion and coordination to the metal center in both complexes. The complexes are stabilized by inter molecular and intramolecular hydrogen bonding (Bharati et al., 2016).

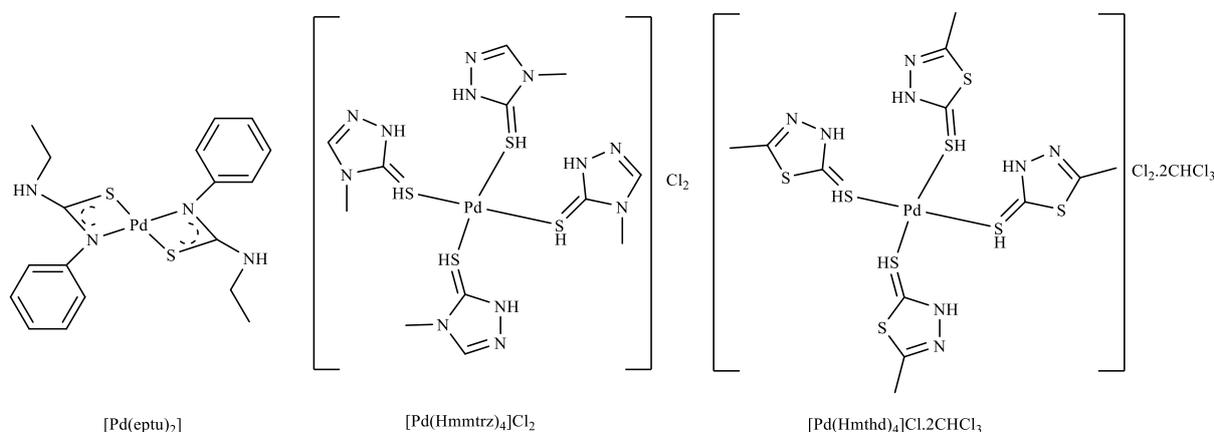


Figure 8. $[\text{Pd}(\text{eptu})_2]$, $[\text{Pd}(\text{Hmtrz})_4]\text{Cl}_2$ and $[\text{Pd}(\text{Hmthd})_4]\text{Cl}_2 \cdot 2\text{CHCl}_3$ Pd(II) complexes (Bharati et al., 2016).

Two mononuclear mixed ligand complexes $[\text{Ni}(\text{en})_2(\text{ppdtt})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{en})_2(\text{ppdtt})_2] \cdot 2\text{H}_2\text{O}$ were synthesized with Hppdtt =4-phenyl-5-pyridine-4-yl-2,4-dihydro-1,2,4-triazol-3-thion and ethylenediamine (en). The studied compounds were characterized by elemental analysis, UV-Vis, IR, magnetic susceptibility, ESR, cyclic voltammetry and single crystal X-ray studies. The geometry of complexes 1 and 2 is distorted octahedral. Complexes 1 and 2 were determined to exhibit quasi-reversible redox behavior due to an electron transfer oxidation reduction. Complexes 1 and 2 crystallized in orthorhombic and monoclinic. Various types of extended hydrogen bonding provided spaces for lattice water containment in the three-dimensional supramolecular framework of the complexes (Dulare et al., 2011).

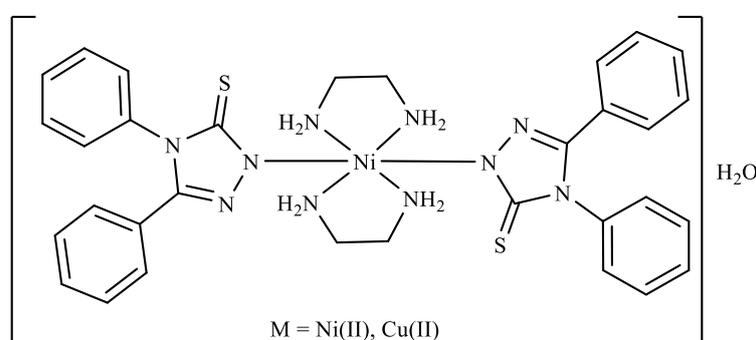


Figure 9. Two mononuclear mixed ligand complexes $[\text{Ni}(\text{en})_2(\text{ppdtt})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{en})_2(\text{ppdtt})_2] \cdot 2\text{H}_2\text{O}$ (Dulare et al., 2011).

The new mixed ligand complexes $[\text{Ni}(\text{aptt})_2(\text{en})_2]$, $[\text{Ni}(\text{apytt})_2(\text{en})_2] \cdot \text{CHCl}_3$ and $[\text{Ni}(\text{athtt})_2(\text{en})_2]$ with 4-amino-5-phenyl-2H-1,2,4-triazol-3-thion (Haptt), 4-amino-5-(pyridin-3-yl)-4,5-dihydro-3H-1,2,4-triazole-3-thione (Hapytt) and 4-amino-5-thiophene-2H-1,2,4-triazol-3-thione (Hathtt) were prepared complexes containing en as secondary ligand. These complexes were synthesized by reacting nickel (II) acetate and triazole ligand followed by adding ethylenediamine or $[\text{Ni}(\text{en})_2(\text{NCS})_2]$ precursor and triazole ligand. Metal complexes were characterized with the help of elemental analysis, IR, magnetic susceptibility and single crystal X-ray data. All complexes bond with two nitrogen atoms of two triazole ligands and four nitrogens of two ethylenediamine, and the resulting complexes have distorted octahedral geometry. Due to the hard character of nickel (II), triazole ligands behave like a non-negative monodentate bound through the triazole nitrogen. The complexes contain extended hydrogen bonding that provides the supramolecular framework (Bharty et al., 2014).

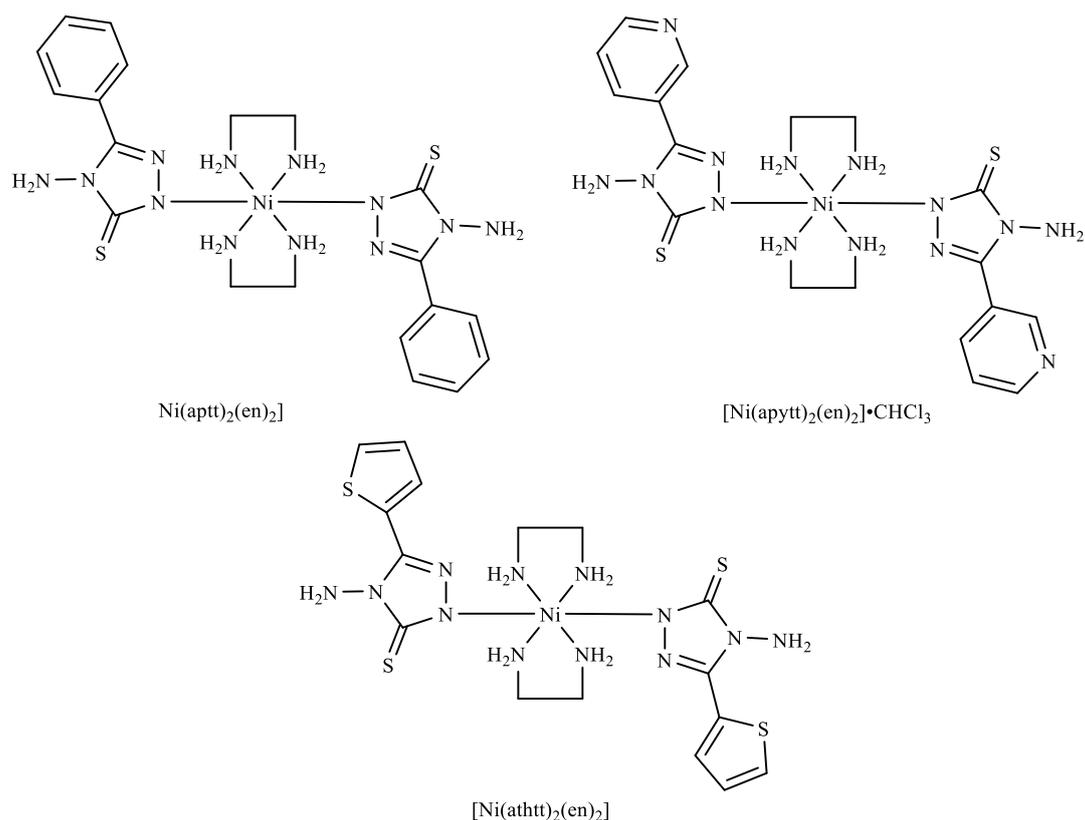


Figure 10. Ni complexes $\text{Ni}(\text{aptt})_2(\text{en})_2$, $[\text{Ni}(\text{apytt})_2(\text{en})_2] \cdot \text{CHCl}_3$ and $[\text{Ni}(\text{athtt})_2(\text{en})_2]$ (Bharty et al., 2014).

Five new mononuclear Pt (II) complexes with ligands 5-perfluoroalkyl-1,2,4-oxadiazolyl-pyridine and 3-perfluoroalkyl-1,2,4-triazolyl-pyridine have been reported. The structures of the synthesized complexes were characterized by a combination of elemental analysis, atomic absorption spectrometry, IR, ^1H NMR and molar conductivities. In complexes 2a and 3a, 5-perfluoroalkyl-1,2,4-oxadiazole ligands are monodentately bound to the Pt (II) ion through the pyridine ring, where the metal geometry is square planar. The 3-perfluoroalkyl-1,2,4-triazole ligands also act monodentately to the Pt(II) ion via the N2 atom of the 1,2,4-triazole ring. Five new complexes and synthesized new ligands were tested in vitro. Complexes containing the 1,2,4-triazole ring were found to be active against three interlocking tumor cell lines, but other complex was found to be much more active than ligand 2 (Rubino et al., 2016).

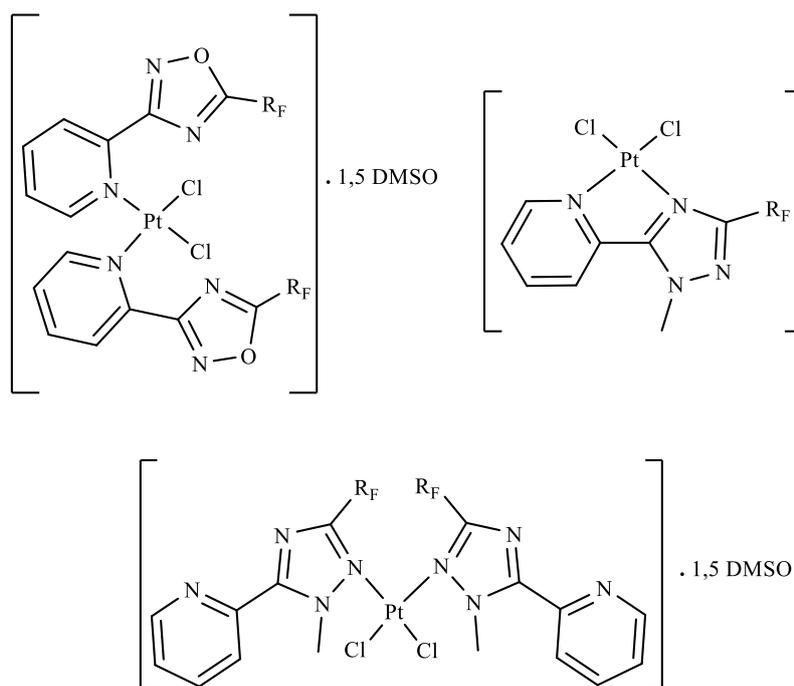


Figure 11. platinum complexes containing oxadiazole and 1,2,4-triazole moiety (Rubino et al., 2016).

The novel series of silver complexes with coumarin-substituted 1,2,4-triazole-based NHC ligands were synthesized and characterized to examine and compare their antioxidant and antihemolytic activities. Ionic 1,2,4-triazolium salts were prepared by the sequential N-alkylation method using allyl bromide and appropriately substituted 4-bromomethylcoumarine derivatives. Silver NHC complexes exhibited a linear coordination geometry with the monoclinic crystal system. The supramolecular association of the salt and the complexes proved moderate π - π stacking interactions between adjacent coumarin rings. Since the medicinal properties of silver (I) NHC complexes are well known, the existing complexes, potent antioxidant and antihemolytic properties have been studied. The bis-NHC coordinated silver hexafluorophosphate complexes showed significant DPPH radical scavenging activities (Geetha et al., 2020).

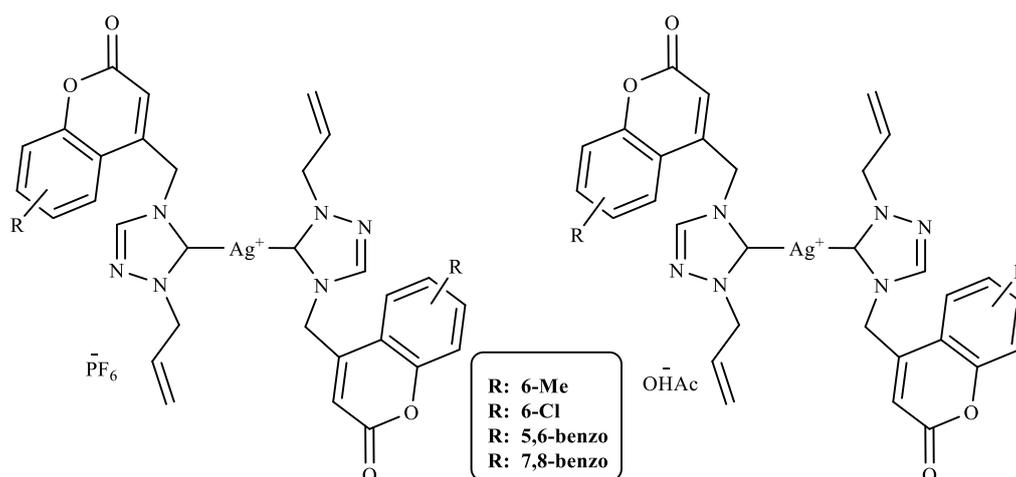


Figure 12. Coumarin and allyl substituted bis-NHC coordinated silver (I) complexes and NHC coordinated silver(I) acetate complexes (Geetha et al., 2020).

Metal complexes of cobalt (II), nickel (II) and copper (II) were synthesized with newly synthesized biologically active 1,2,4-triazole Schiff bases derived from the condensation of 3-substitute-4-amino-5-mercapto-1,2,4-triazole and 8-formyl-7-hydroxy-4-methylcoumarin. The synthesized 3-substitute-4-amino-(8-formyl-7-hydroxy-4-methylcoumarin)-5-mercapto-1,2,4-triazole Schiff bases act as tetradentate Schiff bases. The metals are coordinated to the azomethine nitrogen, lactonyl oxygen, phenolic oxygen, and sulfur atom. Analytical, IR, ESR, electronic, magnetic and thermal studies have confirmed the binding of Schiff bases to metal ions. Electrochemical investigation of Cu (II) and Ni (II) complexes can provide the degree of reversibility of an electron transfer reaction and they have a semi-reversible character. All complexes are limitedly soluble in common organic solvents, but more substantially soluble in DMF and DMSO, and are not electrolytes in DMF and DMSO. All these Schiff bases and complexes were also screened for antibacterial (*Escherichia coli*, *Staphylococcus aureus*, *Streptococcus pyogenes*, *Pseudomonas aeruginosa* and *Salmonella typhi*) and antifungal activities (*Aspergillus niger*, *Aspergillus flavus* and *Cladosporium*) by MIC method (Bagihalli et al., 2008).

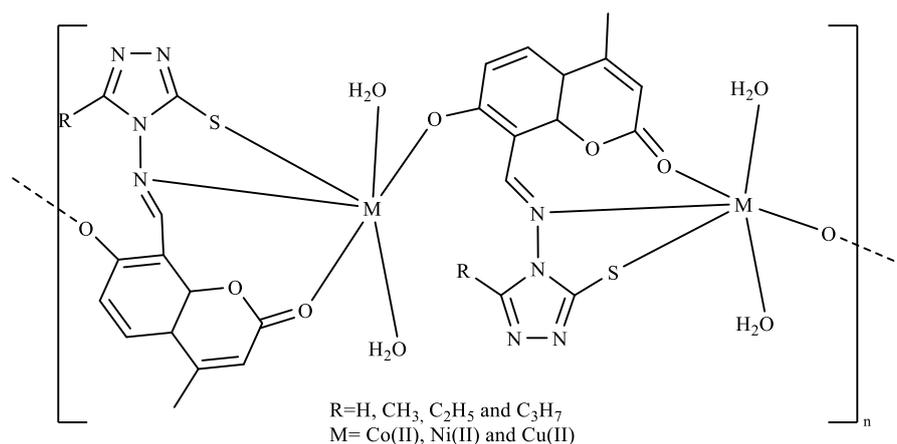


Figure 13. Proposed structure of metal(II) complexes (Bagihalli et al., 2008).

Two mononuclear and first binuclear palladium complexes containing the well-known 4-amino-3-methyl-1,2,4-triazol-5-thione moiety were synthesized and characterized. The molecular structures of the complexes were determined by X-ray diffraction studies. According to the crystal structures determined, it was found that the 1,2,4-triazole moiety acts as a bidentate chelating ligand through the sulfur and nitrogen atoms, while the deprotonated triazole moiety alone functions as a bridging agent between the two metal centers. It can simultaneously act as a bidentate chelating agent through the thiol sulfur atom and the hydrazine nitrogen atom to one metal center, and as a monodentate material through the endocyclic nitrogen atom to the other metal center. Single-crystal X-ray diffraction revealed that the packing mode of the heterocycle by the phenyl rings of the PPh₃ moiety is responsible for the interesting "sandwich" effect observed (Ghassemzadeh et al., 2010).

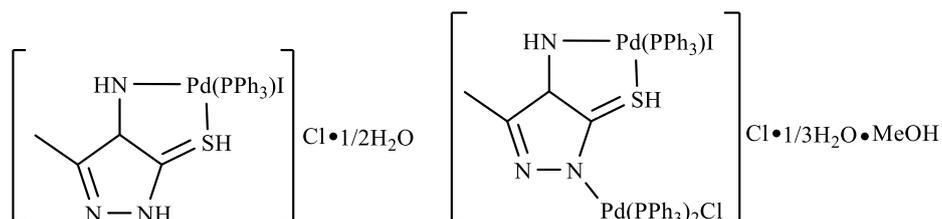


Figure 14. binuclear palladium complexes (Ghassemzadeh et al., 2010).

Synthesis, spectral characterization and luminescence properties of 3-(2-pyridyl)-1H-1,2,4-triazole-5-acetic acid ethyl ester (HL) and palladium (II) complexes were determined. The compounds Pd(L)₂ and Pd₄(L)₄Cl₄·2DMF were prepared by refluxing Pd(HL)Cl₂ in DMF. Molecular and crystal structures of Pd₄(L)₄Cl₄·2DMF were analyzed by single crystal X-ray diffraction analysis. The triazoles in Pd₄(L)₄Cl₄·2DMF were found to act as bidentate ligands

bridging the two palladium centers in two different ways. Therefore, the molecular structure consists of tetranuclear units of palladium ions. The luminescence properties of the ligand and its complexes are discussed (Khomenko et al., 2015).

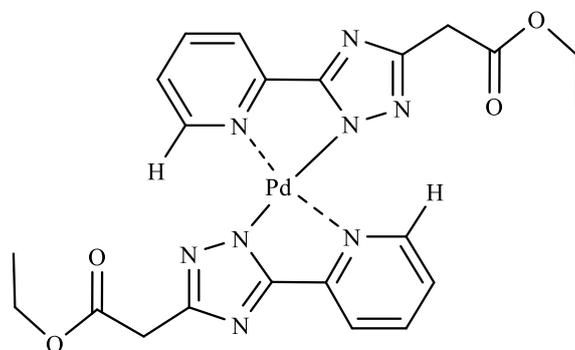


Figure 15. Structure proposed for Pd(L)₂ (Khomenko et al., 2015).

Two new diphenylboron containing 1,3,4-oxadiazole and two new zinc containing 1,2,4-triazole complexes were prepared in good yields by the coordination of 2-(2-hydroxyphenyl)-5-(3,4,5-trimethoxyphenyl)-1,3,4-oxadiazole and 1-phenyl-3-methyl-1,2,4-triazole with triphenylboron or zinc acetate under mild conditions. The molecular structures of the chelated diphenylboron complexes containing 1,3,4-oxadiazole were determined by X-ray single crystal diffraction. Excited-state intramolecular proton transfer (ESIPT) rearrangements observed in ligands containing 1,3,4-oxadiazoles with the inclusion of the spectroscopic properties of all compounds were analyzed using DFT and TD DFT calculations. All complexes were found to show significant fluorescence in both polar and non-polar solvents in the blue region of the spectrum. The displayed spectral properties make these complexes important for use as blue emitters in the design of light-emitting organic diodes (Mikhailov et al., 2019).

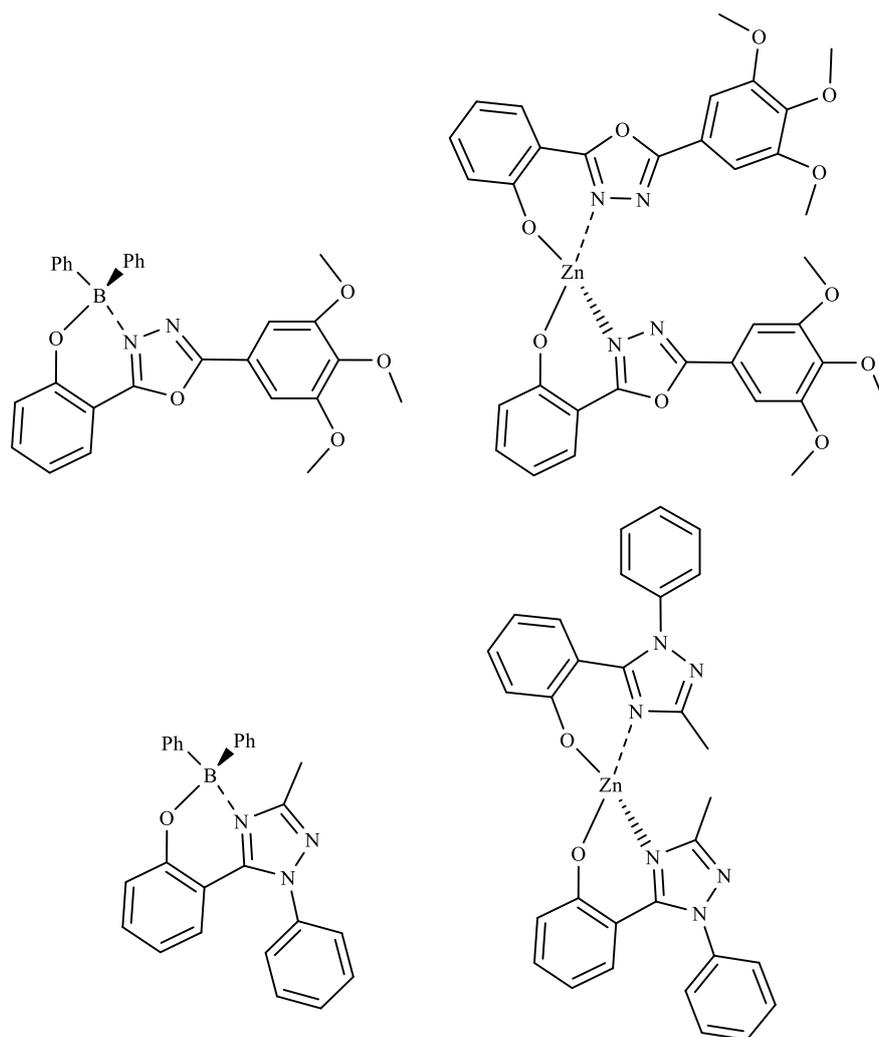


Figure 16. Two new diphenylboron containing 1,3,4-oxadiazole and two new zinc containing 1,2,4-triazole complexes (Mikhailov et al., 2019).

Two new complexes, 4-phenyl(phenyl-acetyl)-3-thiosemicarbazide (Hppt) and 4-amino-5-phenyl-1,2,4-triazole-3-thiolate (Haptt) with $[\text{Mn}(\text{ppt})_2(\text{o-phen})]$ and $[\text{Mn}(\text{apt})(\text{Cl})(\text{o-phen})_2] \cdot 2\text{Haptt} \cdot \text{H}_2\text{O}$ new ligand containing o-phenanthroline (o-phen) as coligand was synthesized. Both complexes are six coordinated and heteroleptic with distorted octahedral geometries around the metal center. The coordination sphere of complex $[\text{Mn}(\text{ppt})_2(\text{o-phen})]$ is filled with two amide carbonyl oxygens and a deprotonated hydrazine nitrogen atom of two mono-negative bidentate ppt ligands and two nitrogen atoms of o-phene; each forms three five-membered chelate rings. TGA of complexes $[\text{Mn}(\text{ppt})_2(\text{o-phen})]$ and $[\text{Mn}(\text{apt})(\text{Cl})(\text{o-phen})_2] \cdot 2\text{Haptt} \cdot \text{H}_2\text{O}$ shows that the metal is converted to metal oxide at very high temperature. In the solid state, the crystal structure of both complexes is stabilized by various intermolecular and intermolecular interactions. To investigate possible electrochemical applications of

complexes $[\text{Mn}(\text{ppt})_2(\text{o-phen})]$ and $[\text{Mn}(\text{aptt})(\text{Cl})(\text{o-phen})_2] \cdot 2\text{Haptt} \cdot \text{H}_2\text{O}$, they are immobilized on a glassy carbon electrode using Nafion. The cyclic voltammetry technique is used to characterize metal complex immobilized electrodes in basic medium. Both complexes show excellent electrocatalytic activity for electrochemical oxygen reduction (Bharty et al., 2019).

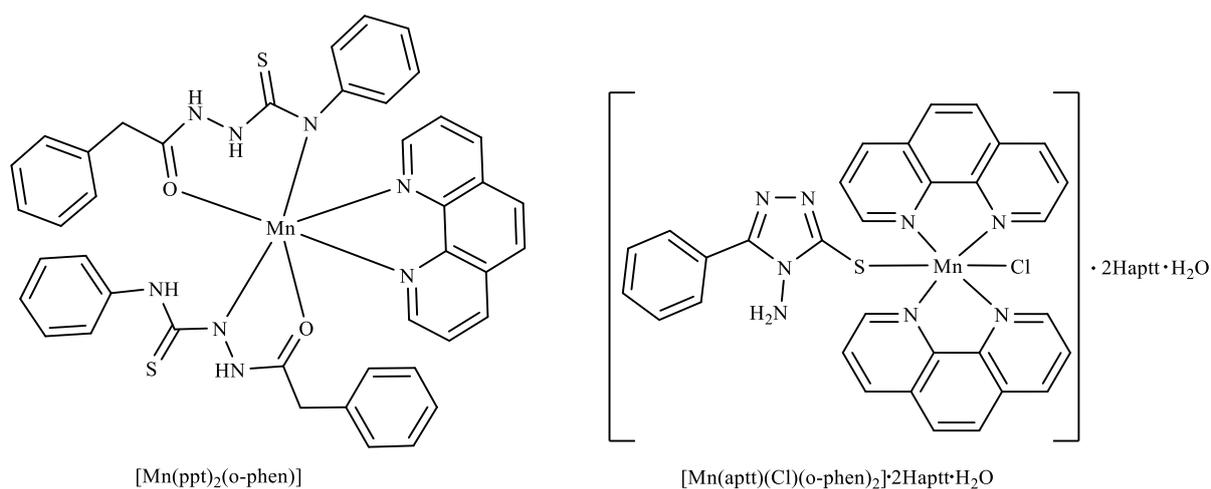


Figure 17. Two new complexes $[\text{Mn}(\text{ppt})_2(\text{o-phen})]$ and $[\text{Mn}(\text{aptt})(\text{Cl})(\text{o-phen})_2] \cdot 2\text{Haptt} \cdot \text{H}_2\text{O}$ (Bharty et al., 2019).

Cyclometallized Ir (III) complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{pyta})\text{Cl}]$ was successfully synthesized by reflux with 2-(1H-1,2,4-triazol-1-yl)-pyridine with Ir (III) dimer $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$. X-ray crystallographic study revealed that the Ir(III) ion is coordinated in a distorted octahedral geometry to a pyridine-triazole, one chloro, and two difluorophenylpyridine ligands. The crystal structure of the complex was determined and it was stated that in the solid state the complex adopts a distorted octahedral coordination environment. DFT calculations on the Ir (III) complex show that HOMO is mainly localized on the cyclometallising ligands and Ir 5d orbitals, while LUMO is located on the cyclometallising ligands, and the HOMO-LUMO energy gap is 3.86 eV. The contacts between the different units of the cyclometallized Ir(III) complex were investigated by analyzing the Hirshfeld surface and the molecular electrostatic potential surface plotted in the ground and triple excited states (Bain et al., 2020).

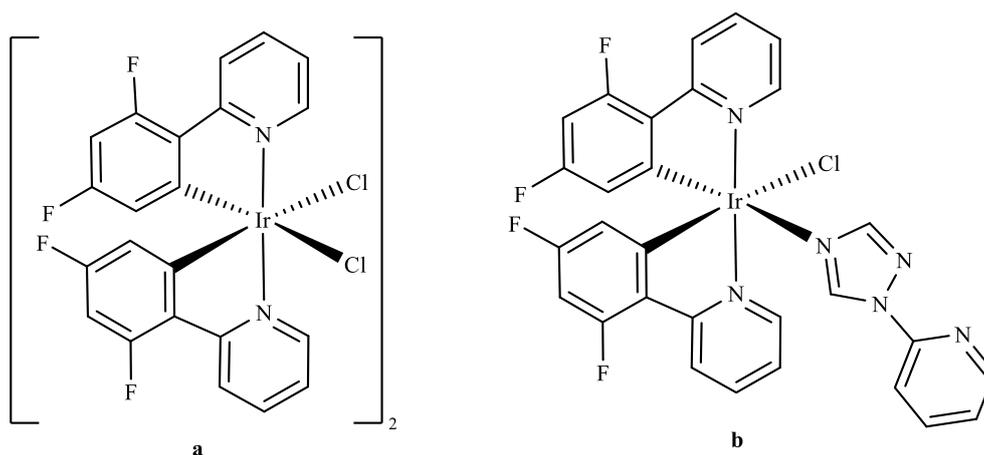


Figure 18. Cyclometallized Ir (III) complex $[\text{Ir}(\text{2,4-F}_2\text{ppy})_2(\text{pyta})\text{Cl}]$ (b) (Bain et al., 2020).

Two neutral heteroleptic iridium(III) complexes carrying substituted pyridine 1,2,4-triazoles as auxiliary ligands were synthesized as emitters for PhOLEDs and their properties were investigated. Although the pyridine-1,2,4-triazole complex family is well known in the literature, there are few studies on their investigation as emitters for OLEDs. While sky blue devices were prepared with the fluorinated complex, blue-green devices were created with the second complex (Dumur et al., 2013).

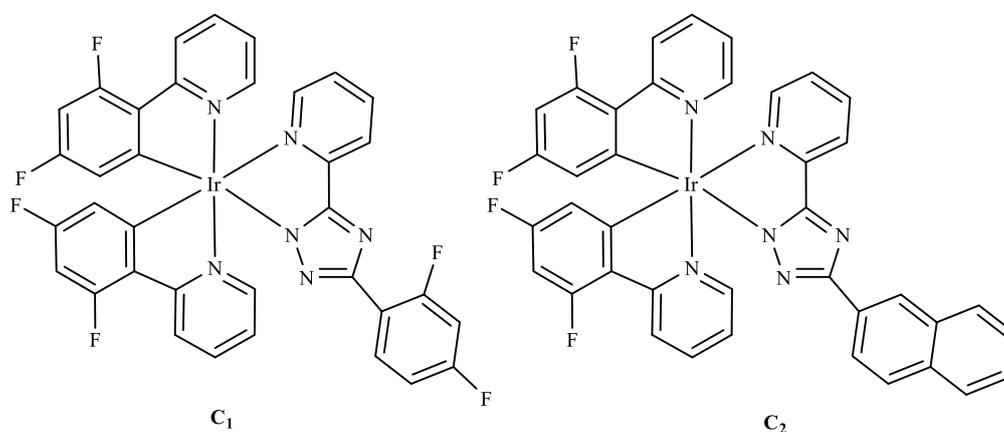


Figure 19. Two neutral heteroleptic iridium(III) complexes carrying substituted pyridine 1,2,4-triazoles (Dumur et al., 2013).

Luminescent europium complexes were obtained by the reaction of 1,2,4-triazole-3-carboxylic (trzc), pyridine-2,6-dicarboxamide (pdcam) and EuCl_3 solutions at different molar ratios. The synthesized europium complexes were characterized using elemental analysis, UV-vis, FT-IR spectroscopy, TGA, powder XRD studies, SEM and photoluminescence spectroscopic methods. With the aid of thermal stability data, the complexes were found to be relatively stable

at high temperature. The highest lifetime and intrinsic quantum efficiency among all complexes were determined for $[\text{Eu}(\text{pdcam})_2(\text{trzc})]\text{Cl}_3$. The anion detection properties of the studied Europium complexes were investigated in detail using absorption and emission spectral studies. $[\text{Eu}(\text{pdcam})_2(\text{trzc})]\text{Cl}_3$ (1) and $[\text{Eu}(\text{pdcam})(\text{trzc})_2]\text{Cl}_3$ (2) complexes were showed significant differences in luminescence upon hydrogen bonding to its F-ions. After adding different anions, UV-vis and photoluminescence spectra of Eu(III) complexes were also investigated. The anion sensing properties of europium complexes were investigated using absorption and emission spectral studies (Sengar & Narula, 2017).

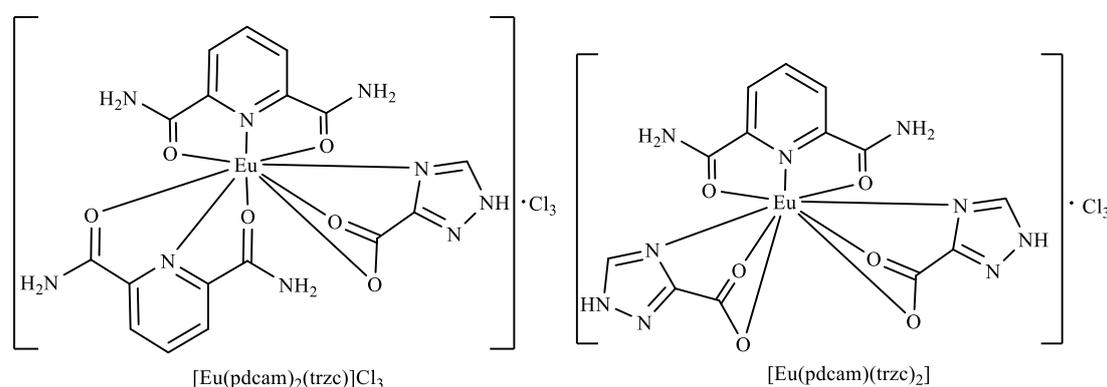


Figure 20. $[\text{Eu}(\text{pdcam})_2(\text{trzc})]\text{Cl}_3$ (1) and $[\text{Eu}(\text{pdcam})(\text{trzc})_2]\text{Cl}_3$ (2) complexes (Sengar & Narula, 2017).

A novel emissive mononuclear homoleptic Cu(I) complex of 5-tert-butyl-3-(6-methyl-2-pyridyl)-1H-1,2,4-triazole $[\text{Cu}(\text{bmptzH})_2](\text{ClO}_4)_2$ were obtained by reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)_2$ or $(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ with the bmptzH ligand. The structural and photophysical properties of the complexes have been well studied. It was observed that Complex 1 adopts a neutral bidentate chelation coordination mode using the N atom of the pyridyl ring of bmptzH and the 4-N atom of the 1,2,4-triazolyl ring, not the 2-N and a distorted N4 tetrahedral arrangement formed by the two bmptzH chelates. It has been shown that the Cu(I) complex is highly stable and exhibits good luminescence properties in solution and solid states at room temperature as a result of the incorporation of a methyl group in the ortho-position of the pyridyl ring (Luo et al., 2017).

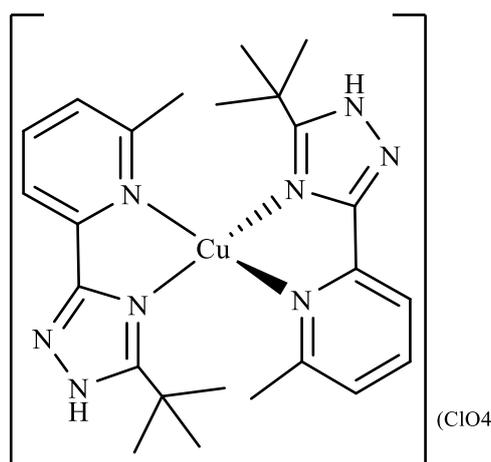


Figure 21. Cu(I) complex of 5-tert-butyl-3-(6-methyl-2-pyridyl)-1H-1,2,4-triazole [Cu(bmptzH)₂](ClO₄) (Luo et al., 2017).

New Fe(III) complexes were synthesized by the reactions of Schiff base derived from 3-substituted phenyl-4-amino-5-hydrazino-1,2,4-triazole and indoline-2,3-dione with ferric nitrate. All synthesized complexes were dissolved in DMSO and DMF; shows that they are not electrolytes due to their low molar conductivity values. Elemental analysis results of the complexes show that the structures are in 1:1 stoichiometry of the [FeLn(H₂O)(OH)]•xH₂O type. The structural and spectroscopic properties of the synthesized complexes were investigated on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic measurements, ¹H and ¹³H-NMR spectra and mass spectra. According to the magnetic moment and reflection spectral studies, an octahedral geometry is formed in all the prepared complexes. FT-IR, ¹H and ¹³H-NMR studies reveal that the ligand (Ln) is in the form of tautomeric enol in both cases with intramolecular hydrogen bonding. The complexes were found good antimicrobial activities when compared to their free ligands against *Staphylococcus aureus*, *Bacillus subtilis*, *Serratia marcescens*, *Pseudomonas aeruginosa* and *Escherichia coli*. When FRAP values are investigated, it shows that all compounds have ferric reducing antioxidant power (Kharadi, 2013).

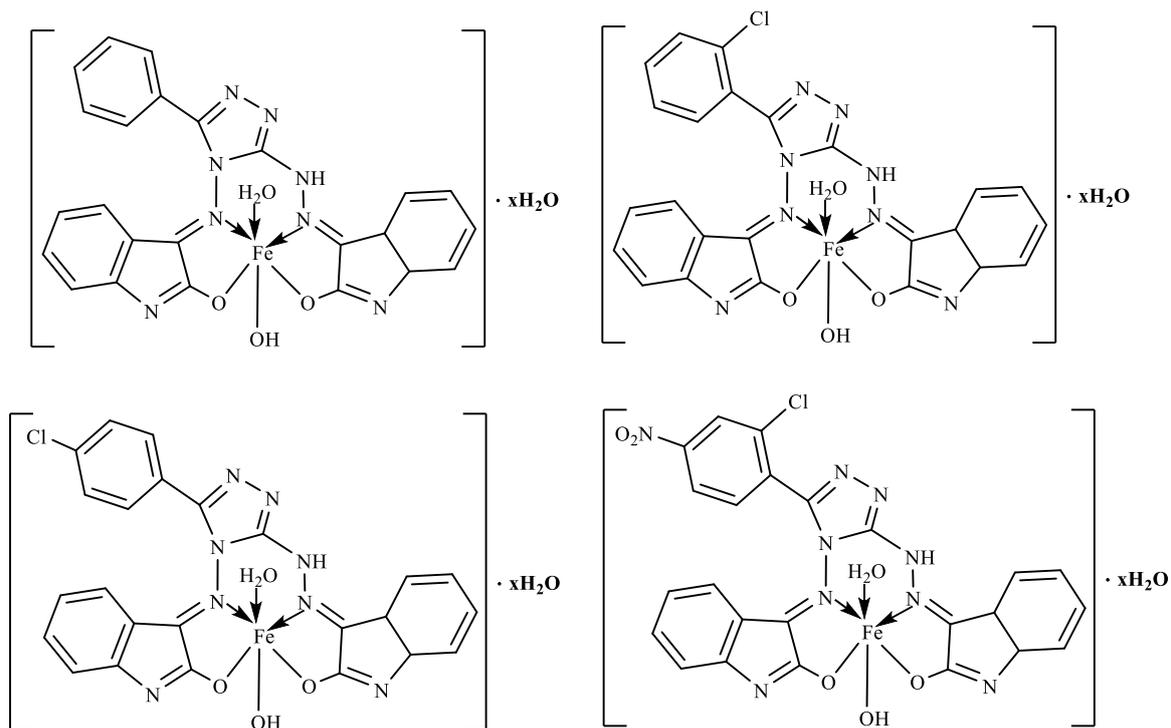


Figure 22. Fe(III) complexes synthesized Schiff base derived (Kharadi, 2013).

REFERENCES

- Aly, H. M., Moustafa, M. E., Nassar, M. Y., & Abdelrahman, E. A. (2015). Synthesis and characterization of novel Cu (II) complexes with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases: A new route to CuO nanoparticles. *Journal of Molecular Structure*, *1086*, 223–231. <https://doi.org/10.1016/j.molstruc.2015.01.017>
- Bagihalli, G. B., Avaji, P. G., Patil, S. A., & Badami, P. S. (2008). Synthesis, spectral characterization, in vitro antibacterial, antifungal and cytotoxic activities of Co(II), Ni(II) and Cu(II) complexes with 1,2,4-triazole Schiff bases. *European Journal of Medicinal Chemistry*, *43*(12), 2639–2649. <https://doi.org/10.1016/j.ejmech.2008.02.013>
- Bain, N. H. A. S., Ali, N. M., Juahir, Y., Hashim, N., Isa, I. M., Mohamed, A., Kamari, A., Anouar, E. H., Yamin, B. M., Tajuddin, A. M., & Baharudin, M. H. (2020). Synthesis, crystal structure, photophysical properties, DFT studies and Hirshfeld surface analysis of a phosphorescent 1,2,4-triazole-based iridium(III) complex. *Polyhedron*, *188*, 114690. <https://doi.org/10.1016/j.poly.2020.114690>
- Beytur, M. (2020). Fabrication of platinum nanoparticle/boron nitride quantum dots/6-methyl-2-(3-hydroxy-4-methoxybenzylidenamino)-benzothiazole (ILS) nanocomposite for electrocatalytic oxidation of methanol. *Journal of the Chilean Chemical Society*, *65*(3), 4929–4933. <https://doi.org/10.4067/s0717-97072020000204929>
- Bharati, P., Bharti, A., Nath, P., Kumari, S., Singh, N. K., & Bharty, M. K. (2016). Square planar Pd(II) complexes derived from 1-ethyl-3-phenylthiourea, 3-mercapto-4-methyl-1,2,4-triazole and 2-mercapto-5-methyl-1,3,4-thiadiazole: Syntheses, spectral, structural characterization and photoluminescence properties. *Inorganica Chimica Acta*, *443*, 160–169. <https://doi.org/10.1016/j.ica.2016.01.003>
- Bharty, M. K., Bharati, P., Bharti, A., Singh, A., Singh, S., & Singh, N. K. (2014). Syntheses, spectral and structural characterization of Ni(II) complexes of 4-amino-5-phenyl/3-pyridyl/thiophen-2H-1,2,4-triazole-3-thione. *Journal of Molecular Structure*, *1056–1057*, 326–332. <https://doi.org/10.1016/j.molstruc.2013.10.057>
- Bharty, M. K., Bharti, A., Chaurasia, R., Chaudhari, U. K., Kushawaha, S. K., Sonkar, P. K., Ganesan, V., & Butcher, R. J. (2019). Synthesis and characterization of Mn(II) complexes of 4-phenyl(phenyl-acetyl)-3-thiosemicarbazide, 4-amino-5-phenyl-1,2,4-triazole-3-thiolate, and their application towards electrochemical oxygen reduction reaction. *Polyhedron*, *173*, 114125. <https://doi.org/10.1016/j.poly.2019.114125>
- Boy, S., Aras, A., Türkan, F., Akyıldırım, O., Beytur, M., Sedef Karaman, H., Manap, S., & Yüksek, H. (2021). Synthesis, Spectroscopic Analysis, and in Vitro/in Silico Biological Studies of Novel Piperidine Derivatives Heterocyclic Schiff-Mannich Base Compounds. *Chemistry & Biodiversity*, *18*(12), e2100433. <https://doi.org/10.1002/cbdv.202100433>
- Boy, S., Türkan, F., Beytur, M., Aras, A., Akyıldırım, O., Karaman, H. S., & Yüksek, H. (2021). Synthesis, design, and assessment of novel morpholine-derived Mannich bases as multifunctional agents for the potential enzyme inhibitory properties including docking study. *Bioorganic Chemistry*, *107*, 104524. <https://doi.org/10.1016/j.bioorg.2020.104524>

- Burke, H. M., Gallagher, J. F., Indelli, M. T., & Vos, J. G. (2004). The synthesis and characterisation of Rh(III) complexes with pyridyl triazole ligands. *Inorganica Chimica Acta*, 357(10), 2989–3000. <https://doi.org/10.1016/j.ica.2004.03.003>
- Chandrasekhar, V., Nagendran, S., & Baskar, V. (2002). Organotin assemblies containing Sn–O bonds. *Coordination Chemistry Reviews*, 235(1), 1–52. [https://doi.org/10.1016/S0010-8545\(02\)00178-9](https://doi.org/10.1016/S0010-8545(02)00178-9)
- Chaudhary, A., Agarwal, M., & Singh, R. V. (2006). Organotin(IV) and organolead(IV) complexes as biocides and fertility regulators: Synthetic, spectroscopic and biological studies. *Applied Organometallic Chemistry*, 20(4), 295–303. <https://doi.org/10.1002/aoc.1037>
- Chen, X., Qiu, D., Ma, L., Cheng, Y., Geng, Y., Xie, Z., & Wang, L. (2006). Synthesis, Crystal Structure, Spectroscopy and Electroluminescence of Zinc(II) Complexes Containing Bidentate 2-(2-pyridyl)quinoline Derivative Ligands. *Transition Metal Chemistry*, 31(5), 639–644. <https://doi.org/10.1007/s11243-006-0040-2>
- Dani, R. K., Bharty, M. K., Paswan, S., Singh, S., & Singh, N. K. (2014). Mononuclear Ni(II) and dinuclear Cd(II) complexes of 4-phenyl-2H-1,2,4-triazole-3-thione and Mn(II) catalyzed disulphide bond formation in 3,3'-dithio bis (4-phenyl-1,2,4-triazole): Syntheses, structural characterization, thermal analysis and DFT calculation. *Inorganica Chimica Acta*, 421, 519–530. <https://doi.org/10.1016/j.ica.2014.06.037>
- Dulare, R., Bharty, M. K., Kushawaha, S. K., & Singh, N. K. (2011). Mononuclear mixed-ligand complexes with 4-phenyl-5-pyridin-4-yl-2,4-dihydro-1,2,4-triazole-3-thione and ethylenediamine: Syntheses, spectral and X-ray crystallographic characterization. *Journal of Molecular Structure*, 985(2–3), 323–329. <https://doi.org/10.1016/j.molstruc.2010.11.015>
- Dumur, F., Lepeltier, M., Graff, B., Contal, E., Wantz, G., Lalevée, J., Mayer, C. R., Bertin, D., & Gigmes, D. (2013). Blue and blue–green PhOLEDs prepared with neutral heteroleptic iridium(III) complexes comprising substituted pyridine-1,2,4-triazoles as the ancillary ligands. *Synthetic Metals*, 182, 13–21. <https://doi.org/10.1016/j.synthmet.2013.07.009>
- Geetha, B. M., Brinda, K. N., Achar, G., Małeck, J. G., Alwarsamy, M., Betageri, V. S., & Budagumpi, S. (2020). Coumarin incorporated 1,2,4-triazole derived silver(I) N-heterocyclic carbene complexes as efficient antioxidant and antihaemolytic agents. *Journal of Molecular Liquids*, 301, 112352. <https://doi.org/10.1016/j.molliq.2019.112352>
- Ghassemzadeh, M., Bahemmat, S., Mahmoodabadi, M., Rezaii-Rad, B., Monfared, H. H., Mottefakeri, E., & Neumüller, B. (2010). New mono- and binuclear Pd(II) complexes containing 1,2,4-triazole moieties. *Polyhedron*, 29(16), 3036–3045. <https://doi.org/10.1016/j.poly.2010.08.012>
- Gusev, A. N., Shul'gin, V. F., Konnic, O. V., Meshkova, S. B., Aleksandrov, G. G., Kiskin, M. A., Eremenko, I. L., & Linert, W. (2011). New Zn complexes based on 1,2,4-triazoles: Synthesis, structure and luminescence. *Inorganica Chimica Acta*, 376(1), 509–514. <https://doi.org/10.1016/j.ica.2011.07.009>

- Haasnoot, J. G. (2000). Mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivatives as ligands. *Coordination Chemistry Reviews*, 200–202, 131–185. [https://doi.org/10.1016/S0010-8545\(00\)00266-6](https://doi.org/10.1016/S0010-8545(00)00266-6)
- Harmankaya, A., & Harmankaya, S. (2022). Use of Herbs And Spices as Natural Antioxidants in Foods. In *Functional Foods and Nutraceuticals: Bioactive Compounds* (pp. 49–67).
- Harmankaya, A., Özcan, A., Dalginli, K., Erdağ, D., Aydın Dursun, Y., & Güngör, B. (2021). The Effect of Trolox on Oxidative Stress Index and Nitric Oxide Levels. *Journal of the Institute of Science and Technology*, 3262–3268. <https://doi.org/10.21597/jist.951122>
- Harmankaya, A., Özcan, A., Kaya, R., Özbey, Ç., Atakişi, O., & Dalginli, K. (2020). Effect of ACE Plus Selenium on Total Antioxidant/Oxidant Capacity and Nitric Oxide Levels in Rabbits. *Caucasian Journal of Science*. <https://doi.org/10.48138/cjo.830176>
- Joshi, R., Kumari, A., Singh, K., Mishra, H., & Pokharia, S. (2019). Synthesis, structural characterization, electronic structure calculation, molecular docking study and biological activity of triorganotin(IV) complexes of schiff base (E)-4-amino-3-(2-(2-hydroxybenzylidene)hydrazinyl)-1H-1,2,4-triazole-5(4H)-thione). *Journal of Molecular Structure*, 1197, 519–534. <https://doi.org/10.1016/j.molstruc.2019.07.066>
- Joshi, R., Kumari, A., Singh, K., Mishra, H., & Pokharia, S. (2020). Triorganotin(IV) complexes of Schiff base derived from 1,2,4-triazole moiety: Synthesis, spectroscopic investigation, DFT studies, antifungal activity and molecular docking studies. *Journal of Molecular Structure*, 1206, 127639. <https://doi.org/10.1016/j.molstruc.2019.127639>
- Kharadi, G. J. (2013). Antioxidant, tautomerism and antibacterial studies of Fe(III)-1,2,4-triazole based complexes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 110, 311–316. <https://doi.org/10.1016/j.saa.2013.03.068>
- Khomenko, D. M., Doroschuk, R. O., & Lampeka, R. D. (2015). Synthesis, characterization and luminescent properties of palladium complexes with 3-(2-pyridyl)-1H-1,2,4-triazole-5-acetic acid ethyl ester. *Polyhedron*, 100, 82–88. <https://doi.org/10.1016/j.poly.2015.06.036>
- Klinge, M. H., & Brooker, S. (2003). The coordination chemistry of 4-substituted 3,5-di(2-pyridyl)-4H-1,2,4-triazoles and related ligands. *Coordination Chemistry Reviews*, 241(1), 119–132. [https://doi.org/10.1016/S0010-8545\(03\)00049-3](https://doi.org/10.1016/S0010-8545(03)00049-3)
- Koç, E., Yüksek, H., Beytur, M., Akyıldırım, O., Akçay, M., & Beytur, C. (2020). Heterosiklik 4,5-dihidro-1H-1,2,4-triazol-5-on Türevinin Antioksidan Özelliğinin Erkek Ratlarda (Wistar albino) İn vivo Olarak Belirlenmesi. *Bitlis Eren Üniversitesi Fen Bilimleri Dergisi*, 9(2), 542–548. <https://doi.org/10.17798/bitlisfen.600412>
- Kotan, G., Gökce, H., Akyıldırım, O., Yüksek, H., Beytur, M., Manap, S., & Medetalibeyoğlu, H. (2020). Synthesis, Spectroscopic and Computational Analysis of 2-[(2-Sulfanyl-1H-benzo[d]imidazol-5-yl)iminomethyl]phenyl Naphthalene-2-sulfonate. *Russian Journal of Organic Chemistry*, 56(11), 1982–1994. <https://doi.org/10.1134/S1070428020110135>
- Kumar, A., Bheeter, L. P., Gangwar, M. K., Sortais, J.-B., Darcel, C., & Ghosh, P. (2015). Nickel complexes of 1,2,4-triazole derived amido-functionalized N-heterocyclic carbene ligands: Synthesis, theoretical studies and catalytic application. *Journal of*

- Organometallic Chemistry*, 786, 63–70.
<https://doi.org/10.1016/j.jorganchem.2015.03.007>
- Luo, Y.-S., Chen, J.-L., Zeng, X.-H., Qiu, L., He, L.-H., Liu, S.-J., & Wen, H.-R. (2017). A highly stable and luminescent mononuclear Cu(I) bis-{5- tert -butyl-3-(6-methyl-2-pyridyl)-1 H -1,2,4-triazole} complex. *Chinese Chemical Letters*, 28(5), 1027–1030.
<https://doi.org/10.1016/j.ccllet.2016.12.015>
- Mikhailov, I. E., Dushenko, G. A., Gurskii, M. E., Vikrischuk, N. I., Popov, L. D., Revinskii, Y. V., Lyssenko, K. A., & Minkin, V. I. (2019). Synthesis, structure, spectral and luminescence properties of the tetracoordinated diphenylboron and zinc complexes with 1,3,4-oxadiazole and 1,2,4-triazole ligands. *Polyhedron*, 166, 73–82.
<https://doi.org/10.1016/j.poly.2019.03.044>
- Sertçelik, M. & Durman, M. (2020). Synthesis, Characterization, and Antibacterial Activity of Cd(II) Complexes with 3-/4-Fluorobenzoates and 3-Hydroxypyridine as Co-Ligands. *Russian Journal of Inorganic Chemistry*, 65(9), 1351–1359.
<https://doi.org/10.1134/S0036023620090168>
- Rubino, S., Pibiri, I., Costantino, C., Buscemi, S., Girasolo, M. A., Attanzio, A., & Tesoriere, L. (2016). Synthesis of platinum complexes with 2-(5-perfluoroalkyl-1,2,4-oxadiazol-3yl)-pyridine and 2-(3-perfluoroalkyl-1-methyl-1,2,4-triazole-5yl)-pyridine ligands and their in vitro antitumor activity. *Journal of Inorganic Biochemistry*, 155, 92–100.
<https://doi.org/10.1016/j.jinorgbio.2015.11.020>
- Scozzafava, A., & Supuran, C. T. (2000). Carbonic Anhydrase and Matrix Metalloproteinase Inhibitors: Sulfonylated Amino Acid Hydroxamates with MMP Inhibitory Properties Act as Efficient Inhibitors of CA Isozymes I, II, and IV, and N -Hydroxysulfonamides Inhibit Both These Zinc Enzymes. *Journal of Medicinal Chemistry*, 43(20), 3677–3687.
<https://doi.org/10.1021/jm000027t>
- Sengar, M., & Narula, A. K. (2017). Luminescent lanthanide complexes based on pyridine-2,6-dicarboxamide and 1,2,4-triazole-3-carboxylic acid ligands as F⁻ anion sensor. *Sensors and Actuators B: Chemical*, 241, 567–576. <https://doi.org/10.1016/j.snb.2016.10.119>
- Sertçelik, M. (2021). Synthesis, spectroscopic properties, crystal structures, DFT studies, and the antibacterial and enzyme inhibitory properties of a complex of Co(II) 3,5-difluorobenzoate with 3-pyridinol. *Journal of Chemical Research*, 45(1–2), 42–48.
<https://doi.org/10.1177/1747519820924636>
- Sertçelik, M., Sugeçti, S., Büyükgüzel, E., Necefoğlu, H., & Büyükgüzel, K. (2018). *Diaquabis(N,N-dietilnikotinamid- l NI)bis(4-formilbenzoato- l O)kobalt(II) Kompleksinin Model Organizma Galleria mellonella L. (Lepidoptera: Pyralidae) Üzerindeki Toksikolojik ve Fizyolojik Etkileri*. 6.
- Sugeçti, S., & Büyükgüzel, K. (2021). Effects of Ni (II) p-hydroxybenzoate with caffeine on metabolic, antioxidant and biochemical parameters of model insect *Galleria mellonella* L. (Lepidoptera: Pyralidae). *Turkish Journal of Zoology*. <https://doi.org/10.3906/zoo-2110-6>
- Turhan Irak, Z., & Beytur, M. (2019). Theoretical Study on The Investigation of Antioxidant Properties of Some 4-Benzylidenamino-4,5-dihydro-1H-1,2,4-triazol-5-one

- Derivatives. *Journal of the Institute of Science and Technology*, 512–521. <https://doi.org/10.21597/jist.481990>
- Uğurlu, G., & Beytur, M. (2020). Theoretical studies on the structural, vibrational, conformational analysis and nonlinear optic property of 4-(methoxycarbonyl)-phenylboronic acid. *Indian Journal of Chemistry -Section A*, 9.
- Xu, Y.-P., Qin, J., Sun, S.-M., Liu, T.-T., Zhang, X.-L., Qian, S.-S., & Zhu, H.-L. (2014). Synthesis, crystal structures, molecular docking and urease inhibitory activity of nickel(II) complexes with 3-pyridinyl-4-amino-5-mercapto-1,2,4-triazole. *Inorganica Chimica Acta*, 423, 469–476. <https://doi.org/10.1016/j.ica.2014.09.012>

About The Authors

Murat BEYTUR completed his MSc and PhD degrees at Faculty of Science and Letters, Kafkas University, Kars, Turkey. He is working as an Associate Prof. Dr. in Department of Chemistry, Faculty of Science and Letters at Kafkas University in Turkey. His research interests include organic chemistry, biochemistry (antioxidant and antimicrobial properties), theoretical chemistry, biosensor/nanosensor and applications.

E-mail: muratbeytur83@gmail.com, ORCID: 0000-0002-7098-5592

Onur AKYILDIRIM completed his MSc and PhD degrees at Faculty of Science and Letters, Kafkas University, Kars, Turkey. He is working as an Associate Prof. Dr. in Department of Chemical Engineering, Faculty of Engineering and Architecture at Kafkas University in Turkey. His research interests include organic chemistry, biosensor/ nanosensor and applications.

E-mail: onurakyildirim@gmail.com, ORCID: 0000-0003-1090-695X

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