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Synthesis, characterization and a few noticeable properties of Ni(II) complexes embedded with azo (-N=N-) and azomethine (-C=N-) ligands: A brief review

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Transition metal complexes incorporating conjugated or non-conjugated azo-

azomethine ligands are emergent class compounds in organometallic and catalytic

chemistry. Metal complexes with structurally tuneable azo-azomethine ligands

have versatile properties and numerous applications in various fields of chemistry.

Predominantly, 3d, 4d, and a few 5d transition metal chelates of azo-azomethine ligands with variant features have been reported unequivocally. Geometrical

complexity characterizes the rich coordination chemistry of azo-azomethine

compounds due to their multiple denticities and the redox non-innocent ligands

and metal centres. A detailed literature survey revealed that no brief review has

yet been published on azo-imine chemistry with nickel metal. Therefore, the

present review article encompasses the research undertaken on the synthetic

strategies and coordinating behaviour of various azo-azomethine ligands with

nickel metal centres and a few significant properties of metal complexes.

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ABSTRACT

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1. Introduction

In 1834, Prof. Eilhardt Mitscherlich first reported azobenzene [1]. Subsequently, azo compounds are the major groups of industrially synthesized organic dyes. They are used in various fields of science, such as textile dyestuffs, ink-jet printers, LCDs, optical communication systems, nonlinear optics (NLO), and solar energy conversion [2–7]. Transition metal complexes of azo ligands have piqued the interest of researchers due to their intriguing properties relating to coordination mode versatility, catalytic activity, C-H activation. [8-12] photophysical bond and photochemical properties, [13-15] liquid crystals, [16-17] electron transfer, and biological properties [18-24] Azo-Schiff base compounds incorporating azo (-N = N)and azomethine (-C=N-) units can be coordinated to the metal in different ways, depending on their structures and the nature of the metals. In a few cases, the azo group participates in metal coordination; on the other side, the azo group acts as a spectator unit [25-27]. There are a few interesting conjugated azo-imine ligands where imine (>C=N) groups come from the Nheterocyclic backbone [28-29]. Moreover, the metal complexes of the azo-imine (-N=N-C=N-) function have significant properties, e.g., isomerization, metal-assisted organic transformation, and catalytic and biological activity [30]. In the last two decades, a group of researchers has widely explored the synthetic method of different azo-imine ligands, and their coordination modes with various transition metals for their a few interesting properties, as delineated before [30].

Whatever, the nickel acts as a borderline of Lewis acid and binds to both soft and hard atoms of ligands easily to give ample coordination complexes with diverse geometry. Nickel complexes have applicability in various physical, chemical, and biological phenomena. Nickel has enormous importance in organometallic and catalytic chemistry. As a result of its

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intriguing features and activities, nickel complexes with multidentate azo-imine ligands as the donor have garnered considerable interest in chemical synthesis [31-34] Recently, many bioactive Ni(II) complexes with heterocyclic azo dye ligands were reported for their potential biochemical properties. The complexes showed excellent antimalarial, antimicrobial, anticancer, and anti-inflammatory properties [35-39]. Azo-azomethine compounds and their nickel complexes have been tested in several fields, such as pharmacological, [40-41] thermal, [42] catalytic, [27, 43-44] molecular docking, biological activity, [45-46] photoswitching behavior, [47-48] C-N bond formation [49].

From this background, I have tried a comprehensive literature review of previously reported research highlighting nickel complexes' emergent properties and coordination chemistry incorporating azo-azomethine ligands.

2. Results and discussion

The ligand incorporating azo (-N=N-) and azomethine (-C=N-) groups is a distinct class of organic ligands with multiple denticities. So, their distinctiveness has developed in coordination chemistry as a preferred scaffold. Several researchers have designed and synthesized new nickel chelate complexes with azo-imine ligands and explored their discrete properties. A brief description of the synthetic method, characterization procedure, and a few interesting properties of nickel complexes incorporating bi, tri, and tetradentate azo-azomethine ligands have been provided afterward. The characteristics of the delineated ligands and complexes are given in *Table 1*.

2.1. Nickel complexes with bidentate azo-azomethine ligands

Earlier in 2005, C. Sinha et al. synthesized a mononuclear bis-chelated Ni(II) complexes (2) by reaction of NiSO₄. $6H_2O$ and NH₄HCN with 1-alkyl-2-(arylazo)imidazoles azo-imine ligand (1), after X-ray quality crystals of the complex were isolated in DMF solvent. Various microanalytical tools were used for the characterization of the complex, including thermal and magnetic studies. The X-ray crystallographic data showed that the ligand (I) binds to the Ni(II) ion in bidentate mode with the azo-N and imidazole-N atoms, yielding a distorted octahedral complex, as shown in Scheme 1 [33].



Scheme 1. The synthetic route for mono-nuclear bis-chelate Ni(II) complex (2) with imidazole-based azo ligand (1)

In a separate study, distorted octahedral Ni(II) complexes (4) were synthesized in methanol by reacting Ni(ClO₄)₂.6H₂O with 1-alkyl-2-(naphthyl- \propto / β) –azo)imidazole (3) and solid ammonium thiocyanate (NH₄SCN) or sodium azide (NaN₃). The complexes (4) were characterized by elemental analysis, spectral data, magnetic studies, and molar conductance measurement. The X-ray structure confirmed the molecular structure

of the Ni(II) chelate complexes (4). In the bis-chelate complexes, the Ni(II) ion is surrounded by the ligands (3) through the imidazole N, azo-N, and the N-atoms of two pseudohalide ions (see Scheme 2). The two pseudohalide ligands coordinated in a cis fashion with Ni(II) ion due to greater repulsion of the pendant naphthyl group stereochemical arrangements is cistrans-cis. The complexes are non-electrolyte in nature [50].



Scheme 2. The synthetic route for azo-imine Ni(II) complexes (4) of bidentate 1-alkyl-2-(naphthyl- \propto/β -azo)imidazole (3)

Another stable complex (6) of Ni(II) was synthesized in an ethanolic solution with an optimal pH by the reaction of nickel chloride salt with a novel heterocyclic Schiff base azo ligand (5). The structure elucidation of this heteroleptic complex (6) was performed by elemental analysis, including magnetic moment, molar conductivity, IR, and AAS. In complex (6), the azo-N and azo-methine-N atoms of the ligand (5) are mutually coordinated to metal cores, resulting in an octahedral complex (see Scheme 3) [51].



Scheme 3. The synthetic route for octahedral Ni(II) complex (6) with new heterocyclic azo-imine ligand (5)

S. M. Mahdi et al. reported a square planar Ni(II) complex (8) of a newly synthesized azo-Schiff base ligand (7). The ligand and the complex were identified with elemental analysis and various spectral techniques

such as UV, FT-IR, ¹H NMR, etc. The analytical data suggested that the bidentate ligand (7) binds to the metal centre with an azo-N and phenolic-O atom adjacent to the azo group to form a mononuclear complex (8), as

shown in Scheme 4. It was also corroborated that the non-coordination of the imine (-C=N-) group during

chelation and the complex is neutral due to the direct coordination of chloride ion with Ni(II) ion [52].



Scheme 4. The synthetic route for mononuclear Ni(II) complex (8) with (N, O) bidentate azo-azomethine ligand (7)

In another report in a methanol-ethanol solvent, $Ni(OAC)_2.4H_2O$ was mixed with new Schiff base ligands (9 & 10) to obtain a monomer and an oligomer nickel complex (11 & 12) (see Scheme 5). The ligands and their complexes were characterized by CHN analysis, spectral studies, ¹H &

 13 C NMR, mass spectra, etc. The magnetic measurement of the complexes indicated that the first complex (11) is diamagnetic and has a square planar structure, but the second one (12) is paramagnetic and consistent with tetrahedral geometry [53].



Scheme 5. The synthetic route for diamagnetic & paramagnetic Ni(II) complexes (11 & 12) with azo-Schiff base ligands (9 & 10)

In a novel report, a Schiff-base ligand (13) with an azo chromophore group was synthesized by condensation. The azo-azomethine ligand (13) was then treated with NiCl₂. $6H_2O$ in methanol solvent with constant stirring results in an orange-coloured Ni(II) complex (14) (see Scheme 6). The spatial arrangement of the mononuclear

square-planar nickel complex (14) was determined by elemental analysis, ¹H-NMR, UV–Vis, IR spectroscopy, and X-ray powder diffraction. In the complex, the metal is coordinated with the azomethine-N and deprotonated phenolic-O atoms of the azo-azomethine ligand [54].



Scheme 6. The synthetic route for genotoxic azo-azomethine square planar Ni(II) complex (14) with azo-Schiff base ligand (13)

Later on, a diamagnetic Ni(II) complex (16) was synthesized with a high yield by reacting an azo-imine ligand (15) with Ni(OAc)₂.4H₂O salt in ethanol. The structure elucidation of compounds was done using elemental analysis and different spectral techniques. The

azomethine-N and phenolate-O atoms of the ligands coordinate with the Ni(II) ion and form a bis-chelate complex (16). The azo group is pendant after chelation (see Scheme 7). Measured magnetic moment value of complex exhibited square planar geometry [55].



Scheme 7. The synthetic route for bio-active square planar Ni(II) complex (16) with azabicyclo octane based ligand (15)

In another report, Z. Rezvani et al. 2005, synthesized a series of azo-Schiff base ligands (17) homologous and their Ni(II) complexes (18) in an ethanol-chloroform solution. The ligands (17) and complexes (18) were characterized by elemental analyses and various spectral

data. The X-ray crystal structure authenticated the (N, O) bidentate coordination mode of the ligands (see Scheme 8). The geometry of the bis-chelate complexes is nearly square-planar [56].



Scheme 8. The synthetic route for glass forming square planar Ni(II) complex (18) with azo-Schiff base ligands (17)

Recently, M.C. Prabhakara and his group synthesized pyrazole-based azo ligand (19) and the corresponding Ni(II) complex (20) by the addition of metal and ligand (1:2) in hot ethanol with a few drops of Et_3N base. The structure of the synthesized ligand and complex was systematically characterized by various analytical and spectroscopic

techniques. The physical measurement and analytical data of the ligand and its metal complex showed that the azo-N and pyrazole-O atoms of the ligand coordinated with metal ions to form a bis-chelate diamagnetic Ni(II) complex with square planar geometry (see Scheme 9) [57].



Scheme 9. The synthetic route for diamagnetic square planar Ni(II) complex (20) with pyrazole-based azo ligand (19)

In a notable study, a novel Ni (II) complex (22) of the azo dye ligand (21) derived from sulfamethoxazole was synthesized and characterized by different analytical and spectroscopic techniques. The analytical data of the complex revealed that the nickel metal reacts with the ligand to form a bis-chelate complex. Spectral analysis and magnetic susceptibility measurements suggested the square planar geometry for the Ni (II) complex (**21**). Based on this physicochemical evidence, the following structure was proposed for the metal complex, as shown in Scheme 10. The magnetic moment value indicated that the complex was diamagnetic, which satisfied the square planar geometry around the Ni(II) ion [58].



Scheme 10. The synthetic route for diamagnetic square planar Ni(II) complex (22) with azo dye ligand (21) containing sulfamethoxazole moiety

In another case, Saeid Amani et al. synthesized two new azo Schiff base ligands (23) and (24) and the corresponding Ni(II) complexes (25 & 26) as a solid powder. Elemental analyses and spectroscopic elucidation indicate that the metal centre is coordinated with phenolate-O and nearer azomethine-N atom to form a mononuclear complex (25 and (26), as shown in Scheme 11. The magnetic moment measurements of two Ni(II) complexes show the square-planar geometry of complexes [59].

Recently, Saeid Amani and his coworkers reported another Ni(II) complex (28) integrating a bi-dentate azoazomethine ligand (27). According to various analytical and spectral data, it was revealed that the chelation of the ligand to the Ni(II) ion occurs through deprotonated b phenolic-O and azomethine-N atoms of the ligand and proposed a mononuclear square planar complex (see Scheme 12) [60].

In another novel synthesis, Ni(II) complex (**30**) was prepared by stirring hexahydrate nickel chloride with azo-Schiff base ligand (**29**) in ethanol. The square planar geometry of the Ni(II) complex was suggested through elemental analysis, FT-IR, and UV-Vis spectra. The spectral data have shown that the bidentate mode of ligand involves the azomethine-N and phenolic-O atoms [61]. The azo group appeared free in the binuclear nickel complex, as shown in the Scheme 13.



Scheme 11. The synthetic route for two mononuclear bio-active Ni(II) complexes (25 & 26) with azo-Schiff base ligand (23 & 24)



Scheme 12. The synthetic route for bis-chelate square planar Ni(II) complex (28) with (NO) bidentate azoazomethine ligand (27)



Scheme 13. The synthetic route for bis-chelate square planar Ni(II) complex (30) with azo-azomethine ligand (29)

Further, A. S. Burlov and his coworkers have synthesized nickel complexes (32) by refluxing Ni(OAc)₂.4H₂O with newly synthesized azomethine ligands (31) containing azobenzene groups in the ortho positions of the amine fragment. In the Ni(II) complexes, the central Ni-atom is coordinated with the ligand through the azomethine-N, and the azo-N atom produces bis-chelate Ni(II) complexes, as shown in Scheme 14. The azo (-N=N-) group appeared free in the complexes. FT-IR, ¹H NMR, Magnetochemistry, and X-ray absorption spectroscopy provided the information needed to deduce the square planar structures of the diamagnetic Ni(II) complexes [62].



Scheme 14. The synthetic route for diamagnetic and paramagnetic Ni(II) complexes (31) with two different azo-Schiff base ligands (32)

In 2019, S. D. Power et al. reported a synthetic route for the preparation of azo oxime-based Schiff base ligand (**33**), as well as its Ni(II) complex (**34**). The compounds were successfully characterized by UV-vis, FT-IR, ¹H NMR, PXRD, elemental analysis, and ESR spectroscopy. The spectral study revealed that the noncoordination of azo-N and the Ni(II) ion in the complex is surrounded by the ligands through the two phenolate-O and two imine-N atoms, resulting in a bis-chelate square planar complex (see Scheme 15). The molar conductance value suggested the nonelectrolyte nature of the complex [63].

In another study, a novel azo ligand (35) with an imine group in the heterocyclic ring was synthesized by diazotization, and its non-electrolyte metal complex (36) with NiCl₂.6H₂O in an ethanolic medium was also prepared and characterized by conventional analytical techniques and spectral methods. Spectral analysis and magnetic susceptibility data show that the Ni(II) ion is in a square planar environment (see Scheme 16) [45].



Scheme 15. The synthetic route for Ni(II) complex (33) with azo oxime-based Schiff base ligands (34)



Scheme 16. The synthetic route for azo-imine Ni(II) complex (36) with thiazole-based azo-imine ligand (35)

In a report by E. S. Madhi et al., a solid divalent nickel complex (38) was prepared by the reaction between a suitable amount of hydrated metal chlorides and an N-based azo-Schiff base ligand (37), operated at ambient temperature for several hours. The structural picture of the octahedral complexes was generated with the help of UV-Vis, FTIR,

ESI-MS, and magnetic moment measurement, which provided the suggested geometries. The spectral data confirmed the donation by the azo-methine section and phenolic ring in (N, O) bidentate fashion, leaving the azo group free from coordination [64], as shown in Scheme 17.



Scheme 17. The synthetic route for azo-imine Ni(II) complex (38) with novel Azo-Schiff base thiazole-based ligand (37)

N. Rabi et al. synthesized potentially bioactive Ni(II) chelates (40) with newly designed azo-imine ligands (39). Various physical and spectroscopic methods were used to elucidate the structure of ligands and complexes. The azo-N and phenolate-O atoms of the pyridine moiety of the bidentate ligand bind to metal ions, and two water molecules coordinate to the Ni(II) centre, indicating the complexes' octahedral geometry (see Scheme 18). All the complexes (40) are non-electrolytes and have good thermal properties [65].

In an investigation by K. J. Al-Adilee et al. clearly reported the synthetic method of a new mono-azo dye ligand (41) containing thiazole and pyridine, two heterocyclic rings, and its Ni(II) chelate complex (42). All the compounds were checked by microanalysis and different spectral techniques. The electronic spectral studies showed that the ligand behaves as a bidentate chelator and is coordinated through its N-atom of the azo group, farthest from the thiazole ring, and the N-atom of the thiazole molecule with the Ni(II) ion (see Scheme 19). The high magnetic moment value of the Ni(II) complex suggested a regular octahedral geometry and sp³d² hybridization. The complex is non-ionic due to the presence of two chloride (Cl⁻) ions in the coordination sphere, as authenticated by the high molar conductance value of the complex [66].



Scheme 18. The synthetic route for bioactive octahedral Ni(II) complex (40) with a novel azo-imine ligand (39)



Scheme 19. The synthetic route for bis-chelate Ni(II) complex (42) with thiazole and pyridine based mono azo dye ligand (41)

In current research, a non-electrolyte octahedral Ni(II) complex (44) integrating a novel bi-dentate heterocyclic azo ligand (43) based on a naphthalene ring was synthesized and described by elemental analysis and conventional electronic spectral studies. The analytical data revealed that the ligand

coordinated with the Ni(II) ion through azo-N, the deprotonated phenolic-O atom of the naphthalene ring, and two water molecules coordinated with the metal centre as shown in Scheme 20. [67]



Scheme 20. The synthetic route for octahedral Ni(II) complex (44) of naphthalene-based (NO) bidentate azo ligand (43)

A series of nickel complexes (**46-48**), as shown in Scheme 21, embedded in notable azo-imine ligands were synthesized by the reaction of 2-(arylazo)-pyridine (45) ligands with three nickel metal precursors in methanol and dichloromethane and characterized unequivocally with various spectroscopic techniques, Xray crystallography, and DFT by S. Goswami et al [68].

Interestingly, nickel complexes exhibited three different types of coordination features. Crystallographic data showed that complex (46) adopts nearly octahedral coordination around the nickel centre, which is surrounded by three bi-dentate azo-imine ligands. The complex behaves as a (1:2) electrolyte in CH_3CN solvent. Likewise, in complex (47), which adopted octahedral geometry, only two chloride ligands satisfied the hexa-coordination of nickel instead of a third azo-imine ligand. Contrariwise, the geometry of complex (48) is distorted tetrahedral. Later, two complexes are non-electrolyte in nature. Magnetic susceptibility measurements indicated that complexes 46 and 47 are paramagnetic, but the complex (48) is diamagnetic. Furthermore, the electrochemical study revealed that ligands in all complexes are highly redox

active, while the metal ion behaves as a redox-innocent centre.



Scheme 21. The synthetic route for ligand-centreed redox-active Ni(II) complexes (46-48) with conjugated azo-imine ligand (45)

Recently, K. J. Al-Adilee groups have synthesized the Ni(II) complex (50) with a new heterocyclic azoimine ligand (49) obtained by refluxing ligand and nickel chloride salt in hot ethanol and ammonium acetate buffer solution. All the compounds were characterized by spectroscopic and analytical methods. In the spectral studies and X-ray data, the magnetic susceptibility value proposed the high-spin paramagnetic octahedral geometry [69]. The Ni(II) ion coordinated through the ligand azo-N and imine-N atoms of the imidazole ring affords a bis-chelate complex, as shown in Scheme 22.

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Scheme 22. The synthetic route for bis-chelate Ni(II) complex (50) of (NN) bi-dentate heterocyclic azo-imine ligand (49)

Likewise complex (18), another bis-chelate Ni(II) complexes (52) incorporating a homologous series of azo-azomethine ligands (51) were synthesized and

characterized undoubtedly. Single crystal X-ray structure authenticated the slightly distorted tetrahedral structure of the Ni(II) complex (see Scheme 23) [70].



Scheme 23. The synthetic route for bis-chelate Ni(II) complex (52) of homologous series of azo-azomethine ligand (51)

In a report by S. H. Abid et al., a Ni(II) complex (54) was prepared by the combination of hydrated nickel halide with an azo-Schiff base ligand (53). The spatial arrangement of ligand around Ni(II) ions was pictured by ¹HNMR, UV-Vis, FT-IR, and mass spectra data and suggested the coordination mode of the ligand with metal, as shown in Scheme 24. [71]

Recently, another azo-Schiff base ligand (55) and its octahedral Ni(II) complex (56) were synthesized by the addition of nickel salt with the ligand (1:2) in ethanol. The

spatial arrangement of the complex was determined by the elemental and spectral techniques, which suggested the (N, O) bidentate coordination mode of the azo ligand. The non-coordination of the azomethine-N atom is also evident (see Scheme 25) [72].



Scheme 24. The synthetic route for anti-tumour Ni(II) complex (54) with azo-Schiff base ligand (53)



Scheme 25. The synthetic route for octahedral Ni(II) complex (56) with azo-Schiff base ligand (55)

In one of the novel syntheses, T. Akitsu et al. have reported an organic/inorganic hybrid material containing a chiral Schiff base complex (58) of bivalent nickel. The complex (58) was prepared by the reaction of nickel (II) acetate tetrahydrate with the ligand (57) in methanol. The elemental analysis and spectral techniques, such as FT-IR and UV-Vis, unveiled the square planar structure of this Ni(II) complex. The two trans-azo groups reside in a pendant with each other (see Scheme 26) [73].



Scheme 26. The synthetic route for Ni(II) complex (58) with chiral azo-Schiff base ligand (57)

2.2. Nickel complexes with tri-dentate azoazomethine ligands

Earlier in 2000, S. Goswami et al. synthesized the Nickel(II) complex (**60**) by the refluxing a notable azo-imine ligand, 2-[(Arylamido)phenylazo]pyridine (**59**), with NiCl₂.6H₂O (a ratio of 2:1) in methanol with a few drops of triethylamine. The structure of the green-colored complex was confirmed with the help of combustion analysis, UV–Vis, and IR spectra, and its structure was confirmed by X-ray crystallography data. The deprotonated tridentate ligands bind to Ni(II) in a tridentate (N, N, N) fashion, resulting in an octahedral bis-chelate of the azo-imine complex. (see Scheme 27). The effective magnetic moment value indicated the paramagnetic nature of complexes due to the presence of two unpaired electrons [67].

Further, this group has designed and synthesized an N-donor tridentate azo-imine bridging ligand (61). Next, the reaction of hydrated NiCl₂.6H₂O salt with the ligand (61) in methanol in the presence of Et_3N produced an intense blue crystal of a complex (62) with an excellent yield. The synthesized compounds were characterized by elemental analysis and various spectral techniques. The single-crystal X-ray structure resolved the structure of the dinickel (II) complex (62). Each Ni(II) ion in the bridging complex is surrounded by an N₅Cl environment with highly distorted octahedral geometry (see Scheme 28). The dinickel complex (62) is paramagnetic and ferromagnetically coupled with two nickel centres, making this complex intriguing [49].



Scheme 27. The synthetic route for paramagnetic octahedral Ni(II) complex (60) with (phenylazo)pyridine based azo-imine ligand (59)



Scheme 28. The synthetic route for bimetallic octahedral Ni(II) complex (62) with diamine azo ligand (61)

In 2004, P. P. Hankare's group reported the synthesis of a unique homo-bimetallic Ni(II) complex (64) that was achieved by the reaction of a hot ethanolic solution of hydrated nickel chloride salt with heterocyclic azo-azomethine ligand (63) in a reaction mixture heated for a few hours. The structure elucidation was done by AAS, IR, magnetic susceptibility, UV-Vis, XRD, elemental, and gravimetric analysis. The two ligand (63) units coordinated with two metal centres, each utilizing its own three donor sites, in which one azo-N, one azomethine-N atom, and one phenolic oxygen in the vicinity of the azo-methine moiety permitted the chelation in complex (see Scheme-29). The electronic spectra and magnetic moment values indicated the square planar structure of the complex [75].

Later, S. Goswami et al. synthesized a new Ni(II) complex (66) by the reaction of a newly designed azo pincer type 2,6-bis(phenylazo)pyridine ligand (65) with $[Ni(H_2O)_6]$ Cl₂ in THF solution. The complex (66) was isolated as a green solid and characterized by elemental and spectral data. X-ray crystallography data identify the distorted octahedral of the Ni(II) complex (66) (see Scheme 30), in which the coordination sphere Ni(II) centre is surrounded by a NNN tridentate ligand (65), two chlorides (Cl⁻), and a molecule (H_2O) . Magnetic moment water measurement revealed the paramagnetic nature of the Ni(II) complex [76, 77].



Scheme 29. The synthetic route for bimetallic octahedral Ni(II) complex (64) with diamine azo ligand (63)



Scheme 30. The synthetic route for azo-imine Ni(II) complex (66) with bis-azo pincer ligand (65) to the hemiliability nature of coordinated redox-active

2-(arylazo)-1,10-phenanthroline (67) is another redox-active tridentate azo-aromatic pincer ligand reported by Nanda D. Paul and coworkers [34]. They have examined the redox-induced hemilabile coordination behavior of ligands (67). The reaction of ligands with hydrated NiCl₂ afforded brown-colored neutral complexes (68) with a high yield, whereas the reaction with Ni(ClO₄)₂.6H₂O yielded di-cationic redcolored complexes (69). On the other hand, the reaction of the ligand with a low valent Ni(0) precursor, Ni(COD)₂, produced homoleptic neutral complexes (70). X-ray data revealed that the NNN tridentate ligands (67) are bound to the Ni(II) centre in bidentate mode with an octahedral environment around the central nickel ion. In these complexes, the azo-chromophore moiety remains pendant. On the contrary, complexes (70) are hexacoordinated, in which two ligands bind to the Ni(0) centre in a (NNN) tridentate mode, as shown in Scheme 31. Complexes (68 & 69) are paramagnetic due to the high-spin electronic configuration of the Ni(II) ions. Notably, the complexes undergo reversible interconverted due

to the hemiliability nature of coordinated redox-active azo-aromatic ligands (67). R. Mukherjee et al. designed a new potentially tridentate 2-pyridine carboxamide ligand attached

tridentate 2-pyridine carboxamide ligand attached azo-functionality (71) by refluxing with 2-(phenylazo)aniline with pyridine-2-carbonyl chloride in dry THF/Et₃N solvent in an inert atmosphere. This tridentate ligand reacts with Ni(OAc)₂.4H₂O in methanol, affording black, shining crystals of the bis-Ni(II) complex (72). The Ni(II) centre in the mercomplex (72) is coordinated with the ligand by two pyridyl-N, two deprotonated amido-N, and two azo-N atoms in a cis-trans-cis fashion as shown in Scheme 32. The coordination environment surrounding the Ni(II) ion is a six-coordinated distorted octahedral geometry. The structure of the complex (72) was validated using X-ray crystallography data. Due to the integration of other donor groups, EPR and DFT calculations ascertained how subtle changes to pyridine amide ligand electronics influence the locus of oxidation in Ni(II) complexes of such ligands of varying denticities [31].



Scheme 31. The synthetic route for Ni(II) complexes (68, 69 & 70) with redox-active azo-aromatic pincer ligand (67)



Scheme 32. The synthetic route for six-coordinate Ni(II) complexes (72) with azo-containing pyridine amide ligand (71)

In another report S. Chattopadhyay et al., [32] have synthesized and characterized a new azo-Salen type ligand (73) and corresponding Ni(II) complexes (74). X-ray structure confirmed that the two deprotonated ligands (73) coordinated to the Ni(II) ion through the phenolic-O, azo-N, and aldimine-N atom in (N, N, O) tridentate fashion and forms a bis-chelate octahedral compound as shown in Scheme 33. Paramagnetic measurement also indicated the octahedral geometry of the complexes (74).



Scheme 33. The synthetic route for bis-chelate Ni(II) complexes (74) with azo-Salen ligand (73)

In a report by A. S. Burlov and his coworkers, paramagnetic Ni(II) complexes (**76**) were synthesized using a similar method as diamagnetic Ni(II) complexes (**32**) incorporating azomethine ligands (**75**) containing azobenzene groups in the ortho positions of the amine fragment. Herein, the Ni(II) complexes give diverse structures due to the involvement of the azo-N atom of the phenylazo group in the ortho-position of the amine fragment. The central Ni-atom is surrounded by ligand N, N, and O atoms in a tridentate fashion, which results in an octahedral geometry, as shown in Scheme 14. Elemental analysis, X-ray, spectral analysis, and other physicochemical studies confirmed the geometrical structure of the paramagnetic Ni(II) complexes [62].



Scheme 34. The synthetic route for diamagnetic and paramagnetic Ni(II) complexes (76) with two different azo-Schiff base ligands (75)

In 2015, Khalid J. Al-Adilee et al. reported the synthesis of an industrially important new heterocyclic thiazolyl azo dye ligand (77) and its metal complex (78) with Ni(II) ion. In ethanol, the metal chelate was synthesized in a neutral buffer solution by refluxing with the ligand and nickel chloride (2:1). Various analytical, physical, and spectral data such as FT-IR,

UV-Vis, ¹H NMR, and mass spectra of the complex showed that the ligand behaves as a mono-basic N, N, O tridentate coordination motif. XRD studies revealed that the ligand binds to the metal centre with one of the azo-N, which is furthest from the thiazole ring, the N-atom of the thiazole ring, and the phenolic-O to form a five-membered metal ring with octahedral geometry (see Scheme 35). Magnetic measurements also confirmed the paramagnetic nature and regular geometry of the Ni(II) complex [78].

A current investigation by H. K. Dakheel et al. has synthesized a Ni(II) complex (80) with a ligand-tometal molar ratio of 2:1 by the addition of thiazolebased azo ligand (79) and nickel (II) hexahydrate chloride in absolute ethanol. Electron spectra and magnetometry of the metal complex suggested the octahedral geometry around the Ni(II) ion. In the bischelate complex (80), the azo-N atom, adjacent to the benzene ring, the imine-N atom of the thiazole ring, and the amino-N atoms of two ligands coordinated with the Ni(II) ion (see Scheme 36) [79].



Scheme 35. The synthetic route for Ni(II) complex (78) of thiazolyl-azo ligand (77)



Scheme 36. The synthetic route for bis-chelate Ni(II) complex (80) of thiazolyl-azo ligand (79)

In the current research, a new Ni(II) complex (82) was synthesized incorporating a heterocyclic tri-dentate azoimine ligand (81). Systematically, various spectral methods, molar conductance, magnetic moment measurements, and elemental analysis were used to explore the coordination mode of the azo ligand. The analytical and spectral studies depicted that azo-N, imino-N of the benzimidazole ring, and deprotonated-O atoms coordinated with the Ni(II) ion afford an octahedral geometry around the Ni(II) ion (see Scheme 37). The high magnetic moment and molar conductance value of the complex also suggested octahedral stereochemistry with a non-electrolyte nature [80].



Scheme 37. The synthetic route for octahedral Ni(II) complex (82) of benzimidazole-azo ligand (81)

Likewise, an imidazole-based azo dye ligand (83) and its divalent nickel complex (84) were synthesized in an alcoholic buffer medium and characterized by elemental analysis and physicochemical methods. The analytical data ascertained that the ligand coordinated to central Ni(II) ion via azo-N, which is the farthest of the imidazole ring, the imine-N atoms of the imidazole ring, and phenolic-O atoms, resulting in the octahedral geometry of the metal complex (see Scheme 38). The low molar conductance value suggested the non-electrolytic nature of the complex [81].

W. Chen et al. have synthesized a novel thiazolyl heterocyclic azo dye (85) and its Ni(II) complex (86) by the reaction of tetrahydrate nickel acetate, sodium acetate, and the azo-imine ligand in a THF/methanol solvent. The

(NNN) tridentate coordination mode of the ligand with the octahedral structure of the synthesized Ni(II) complex was confirmed by usual spectral methods and elemental analysis (see Scheme 39) [7].

In 2021, M. K. Mahdi et al. reported the preparation and identification of a new imidazole-based azo ligand (87) and its Ni(II) complex (88) by the reaction with NiCl₂.6H₂O in a hot ethanol-ammonium acetate buffer solution. The (NNO) tridentate coordination mode of the ligand in the bis-chelate complex was confirmed based on their analytical and spectral data (see Scheme 40). The observed electronic transition and magnetic moment value indicated the octahedral environment around the Ni(II) ion in the neutral complex [82].



Scheme 38. The synthetic route for bis-chelate Ni(II) complex (84) of imidazole-based (NNO) tridentate azo ligand (83)



Scheme 39. The synthetic route for bis-chelate Ni(II) complex (86) of (NNN) tridentate thiazolyl heterocyclic azo dye ligand (85)



Scheme 40. The synthetic route for bis-chelate Ni(II) complex (88) of imidazole-based azo ligand (87)

Another investigation described a synthetic route for a novel azo-Schiff base ligand (89) and its complex (90) of bivalent nickel ions based on triazole derivatives. The structure of this complex was confirmed through various spectroscopic techniques such as FTIR, UV-vis, ¹H/¹³C NMR, and TG-DTA. The metal ion in the complex was bonded to the ligand via the azomethine-N and thiol-S atoms, forming five-membered chelate rings [83]. The result indicated that the suggested structure of the complex had an octahedral geometry (see Scheme 41).

Another report provided the synthetic route of a new Ni(II) complex (92) by adding nickel chloride salt with double the quantity of the azo-imine ligand (91) in an ethanol-chloroform mixed solvent. The structure of metal chelate was studied with the help of ${}^{1}\text{H}/{}^{13}\text{C}$ NMR, MS, IR, magnetic susceptibility, and TGA. Magnetic susceptibility and electronic spectra proposed that the ligand behaves as tridentate, which coordinated with the Ni(II) ion through the azomethine-N, the azo N, and the carboxylate-O atoms and octahedral geometry around metal ions, as shown in Scheme 42. [41]



Scheme 41. The synthetic route for octahedral Ni(II) complex (90) of triazole based azo-Schiff base ligand (89)



Scheme 42. The synthetic route for paramagnetic Ni(II) complex (92) of pyrazole-based azo ligand (91)

In another report, S. S. Al-Muhanaa and his coworkers synthesized a new heterocyclic azo ligand (93) and its Ni(II) complex (94) and characterized all the compounds unequivocally. The ligand bound to metal ions through azo-N, imine-N, and carbonyl-O atoms and exhibited octahedral geometry around the Ni(II) centre [84]. The high value of molar conductivity for the complex referred to the electrolytic nature due to chloride ions outside the coordination sphere, as shown in Scheme 43.

A new ligand 2,2' -bis(diamino)azobenzene (**95**) was synthesized by oxidative coupling of ophenylenediamine with a strong base sodium hydroxide. After that, a crystalline Ni(II) complex (**96**) was prepared by the reaction of the ligand with Ni(ClO₄)₂. 6H₂O in methanol in the presence of PPh₃ with a high yield. Various spectral methods characterized the ligand and complex, and the X-ray structure of the complex indicated that the monoanionic ligand binds to the metal centre via N, N, N tri-dentate fashion producing two six-membered stable chelate rings. One PPh₃ ligand satisfied the fourth coordination site of the nearly square complex, and one perchlorate anion neutralized the charge of the complex, as shown in Scheme 44. Due to the delocalization of the negative charge through the sixmembered chelated ring of the complex, it recognized the imine (C=N) bond formation [30].



Scheme 43. The synthetic route for electrolyte bis-chelate Ni(II) complex (94) of heterocyclic azo ligand (93)



Scheme 44. The synthetic route for Ni(II) complex (96) of 2,2' -bis(diamino)azobenzene ligand (95)

A significant water-soluble azo-linked Schiff base ligands (97) and their corresponding Ni(II) complexes (98) were synthesized and characterized by elemental analyses, ¹H NMR, ¹³C NMR, DEPT (distortionless enhancement by polarization transfer), APT (attached proton test), IR spectra, UV-Vis, MS, spectroscopy, and magnetic susceptibility measurement. The spectral analysis revealed that Ligand coordinated to Ni(II) ion in N, O, and O tridentate fashion via the phenolic-O, the naphthalic-O, and the imino-N atom, as shown in Scheme 45. The measured magnetic moment at room temperature of the synthesized Ni(II) complexes (98) indicated the tetrahedral geometry of metal complexes [85]. The spectral analysis demonstrated that the ligand (97) showed keto-enamine tautomerism and stabilized through two six-membered H-bonds.

Subsequently, a tridentate-chelating azo-Schiff base ligand (99) substituted with salicylaldehyde derivatives with thiosemicarbazide and their Ni(II) complex (100) was prepared and characterized by elemental analysis, various spectral methods, and thermogravimetric analysis. The structure analysis indicated that the tridentate ligand (99) coordinated with the Ni(II) centre through thione-S, azomethine-N, and phenolic-O, and the fourth position was occupied by a water molecule. The Azo group acts as a spectator [86]. The molar conductivity values suggested the non-electrolyte nature of the complexes (100), as shown in Scheme 46.



Scheme 45. The synthetic route for tetrahedral Ni(II) complex (98) with azo-linked Schiff base ligands (97)



Scheme 46. The synthetic route for non-electrolyte (Ni(II) complex (100) with (NSO) tridentate azo-linked Schiff base ligand (99)

A similar type of Schiff base complexes (**102**) was synthesized by stirring NiSO₄.7H₂O and azo-based Schiff base ligands (**101**) in a hot ethanol-water solution. Elemental analyses, CHN, various spectral analyses, TG, and DTG analyses unequivocally confirmed the composition of the ligands and metal complexes, in which the ligand coordinated with the metal centre through azomethine-N and two protonated phenolic-O atoms in a tridentate fashion. Molar conductivity measurement of metal chelates indicated the electrolytic behavior and anion SO_4^{2-} present outside the coordination sphere of the complexes (see Scheme 47) [111].

Likewise, Ni(II) complexes (104), with modified heterocyclic azo dye ligands (103), were synthesized and characterized clearly by spectral data, X-ray powder diffraction, and molar conductivity measurement. The analytical data confirmed the stereochemical arrangement of (ONO) tridentate ligands around central metal ions (see Scheme 47). Unlike complexes (102), new complexes are nonelectrolyte in nature [42].



Scheme 47. The synthetic route for two Ni(II) complexes (102 & 103) with (ONO) tridentate azo-linked imine ligand (101 & 103)

A further set of azo-linked Schiff base ligands (105) and their corresponding Ni(II) complexes (106) were synthesized by the reaction of the ligands and CH₃COONa with NiCl₂.6H₂O salt in ethanol. All the compounds were purified by the usual methods and thin-layer chromatography. The elemental analyses, magnetic moment measurements, absorption spectra, infrared spectra, and thermogravimetric analysis authenticated the geometry of the complexes. The Ni(II) complexes (106) showed high magnetic moment values (2.99 - 3.02 BM), which confirmed the high-spin distorted octahedral structure [88]. The two units of the tridentate ligands interact with Ni(II) ions through the salicylic ring-O, the naphthalic-O, and the imino-N to form mononuclear, hexacoordinated metal complexes, as shown in Scheme 48.

C. Anitha et al. reported the synthetic route of a tetrahedral Ni(II) complex (108) from the new azo Schiff base ligand (107). Elemental analysis, UV-Vis, IR, ¹H-NMR, XRD, MS spectral analysis, magnetic,

SEM, and conductivity measurements have been utilized to determine the composition of a structure. Spectral analysis indicated that the Ni(II) centre bound with azomethine-N and two vicinal oxygen atoms of the ligand and afforded tetrahedral geometry around the metal ion. The azo group is free from coordination in this complex, as shown in Scheme 49. Low molar conductance values indicated their non-electrolytic nature [89].

Further, this group of researchers has synthesized a nickel complex (**110**) by the reaction of an equimolar mixture of a new azo azomethine ligand (**109**) based on pyrazole ring and nickel chloride salt in an alkaline ethanolic solution which was characterized by various physicochemical and spectral data and suggested the octahedral geometry around the metal ion of Ni(II) complex (**110**) (see Scheme 50). The molar conductance value implies the non-electrolytic nature of the complex [46].



Scheme 48. The synthetic route for mononuclear hexa-coordinated octahedral Ni(II) complex (106) with azo-linked Schiff base ligands (105)



Scheme 49. The synthetic route for tetrahedral Ni(II) complex (108) with tridentate (ONO) azo-imine ligand (107)



Scheme 50. The synthetic route for octahedral Ni(II) complex (110) with tridentate (ONO) azo-imine ligand (109)

A-N. M. A. Alaghaz et al. synthesized an asymmetrical tridentate Schiff base ligand (111), and a solid complex (112) of Ni(II) was also prepared with this ligand and characterized by various physicochemical techniques. The geometry of the complex (112) was characterized employing spectral,

magnetic, thermal studies, and DFT calculations and suggested that the Ni(II) complex (112) is paramagnetic and the NNO tridentate ligand affords an octahedral complex, as shown in Scheme 51. It is clear that the complex is non-electrolyte in nature, as indicated by the presence of chloride ions in coordination, as shown by the conductance measurements [90].



Scheme 51. The synthetic route for octahedral Ni(II) complex (112) with asymmetrical Schiff base ligand (111)

The new azo-imine complex of Ni(II) (114) in Scheme 52 was synthesized by the reaction of the newly designed pyrimidine-based azo-Schiff base ligand (113) and Ni(CH₃COO)₂.4H₂O in MeOH/CHCl₃ (1:1) mixed solvent The features of the ligand and complex were assigned based on various microanalytical data and spectroscopic data (magnetic, molar conductivity measurements, API-ES mass, ¹³C NMR, ¹H NMR, UV-Vis, IR, etc.). The Schiff base ligand operates as the monobasic tridentate ligand (**113**) that coordinates via an azomethine-N, an O-atom of one phenol-OH, and the pyrimidine-2 (1H)-one portion, and the mononuclear complex affords a high-spin octahedral arrangement around the central Ni(II) atom [91]. The azo (-N=N-) group lies in a pendant.



Scheme 52. The synthetic route for mononuclear Ni(II) complex (114) with pyrimidine-based azo-Schiff base ligand (113)

Later on, another group synthesized a novel heterocyclic azo-Schiff base ligand (115) and corresponding Ni(II) chelate complex (116) in ethanol, mixing metal and ligand in a (1:2) molar ratio. The spectral analyses revealed the composition of the complex. The high magnetic moment value indicated the regular octahedral geometry of the complex with sp^3d^2 hybridization. In the Ni(II) complex (see Scheme 53), the azo-imine (N, N, O) tridentate ligand binds to the metal centre through the azo-N atom nearest to the phenol ring, the phenolic-O atom, and the benzimidazole-N atom to give a two-five-membered chelate ring [92].

Recently, a new class of chelating ligands (117) and incorporating this (arylazo)pyrazole-based nickel complexes (118) have been synthesized and characterized by physicochemical, all spectral analyses. Single crystal X-ray crystallography data authenticated the (NNN) tridentate coordination mode of the ligands in the Ni(II) complexes as shown in Scheme 54. The two arylazo groups lie in a pendant [48].



Scheme 53. The synthetic route for Ni(II) complex (116) with heterocyclic azo-Schiff base ligand (115)



Scheme 54. The synthetic route for (arylazo)pyrazole-based Ni(II) complexes (118) with (NNN) tridentate azo-imine ligand

(117)

In 2019, G. Krishnamurthy and his co-workers synthesized a novel tridentate azo-azomethine ligand (**119**), and its Ni(II) complex (**120**) was structurally characterized by various analytical and spectroscopic techniques. The analytical data revealed that the metal reacts with the ligand and forms a two-five-membered bis-chelate complex. The molar conductance data indicated that the complex is non-electrolytic in

nature. The electronic spectra and magnetic moment measurement reported that the ligand coordinated with Ni(II) ion with carbonyl-O, deprotonated phenolic-O, and azomethine-N atoms having an octahedral geometry [93]. The spectral study clearly showed the non-participation of the azo group in complex formation (see Scheme 55).



Scheme 55. The synthetic route for bioactive Ni(II) complexes (120) with azo-azomethine ligand (119)

Remarkably, the reaction of a newly synthesized pyrimidine-based azo-linked Schiff base ligand (**121**) and Ni(OAc)₂.4H₂O in a mixture of MeOH-CHCl₃ as solvent at room temperature yielded a deep bluecolored Ni(II) complex (**122**). The synthesized compounds were defined by using ¹H-NMR, ¹³C-NMR, elemental analysis, FT-IR, MS, UV-vis, molar conductance, magnetic susceptibility, and thermal analysis techniques. The physicochemical and spectroscopic results indicated that the Ni(II) ion is bonded to the azo-azomethine ligand through the phenolic-O and carbonyl-O of the pyrimidine ring, the imino-N atoms, and the octahedral geometry around the Ni(II) ion in the mononuclear complex (see Scheme 56) [94]. The azo chromogen group is a pendant in the metal complex (122).



Scheme 56. The synthetic route for octahedral Ni(II) complex (122) with azo-azomethine ligand (121)

2.3. Nickel complexes with tetra-dentate azoazomethine ligands

Daniela Pucci and his coworkers have synthesized and fully characterized a tetradentate and a bidentate multifunctional Schiff base ligand (**123 & 124**) with a flexible azo spacer between the pyridine moiety and the salicylidene fragment. After refluxing separately, these two ligands and Ni(CH₃COO)₂.4H₂O in ethanol afforded two solid complexes with a high yield. Analyses showed that in the first case, the ligand coordinated with the Ni(II) centre through (ONNO) tetradentate fashion, resulting in a mononuclear complex (**125**). In the latter case, nickel formed a bischelate complex (**126**), and two ligands bound through N and O atoms satisfied the tetra-coordination of nickel. Furthermore, when both Ni(II) complexes (125 & 126) were dissolved in a pyridine solvent, complexes exhibited hexa-coordination, which was confirmed by X-ray molecular structure determination. The molecular structure revealed that the central Ni atom (127) is pseudo-octahedrally coordinated by two Schiff base ligands and two pyridine ligands in cis positions. The Schiff base ligands form a six-membered chelate ring with the metal ion (see Scheme 57). [95]



Scheme 57. The synthetic route for Ni(II) complexes (125, 126 & 127) with multifunctional Schiff base (123 & 124)

Likewise, C. Anitha and her co-workers have synthesized the Ni(II) complex (129), incorporating a newly characterized azo-azomethine ligand (128). The complex (129) was characterized by various analytical and physicochemical techniques. Electronic spectral and magnetic susceptibility studies indicate the octahedral stereochemistry around the d^8 Ni(II) ion, where the ligand binds to the Ni(II) centre in a (N, N, O, O) tetradentate fashion, as seen in Scheme 58. The molar conductance values of mononuclear complexes

in DMSO $(1 \times 10^{-3} \text{M})$ suggest the absence of ionic character [96].

In another report [97], a new Ni(II) complex (131) with the tetradentate Schiff base N_2O_2 dibasic chelating ligand (130) and Ni(CH₃-COO)₂.4H₂O in ethanol have synthesized, and its structure was

elucidated by elemental, spectroscopic, and thermal analyses as well as conductivity and magnetic susceptibility measurements. Magnetic susceptibility and electronic spectra measurements confirmed the tetrahedral geometry of the metal complex, as shown in Scheme 59.



Scheme 58. The synthetic route for Ni(II) complex (129) of azo-methine ligand (128)



Scheme 59. The synthetic route for Ni(II) complex (131) with N_2O_2 Schiff base chelating ligand (130)

Subsequently, novel azo-Schiff base ligands (132) with NNOS coordination sphere and their corresponding Ni(II) complexes (133)were synthesized by Saied Menati et al. (2013). Elemental analysis, ¹H-NMR, IR, and UV-Vis have been used to determine the structures of ligands and complexes. The X-ray results confirmed that the Ni(II) ions coordinate to two imine-N atoms from the imine moiety of the ligands, a S-atom from the methyl dithiocarboxylate moiety, and a phenolic-O atom, resulting in tetragonal distortion relative to the square planar geometry in Ni(II) complexes (**133**) (see Scheme 60) [98].

Continuing this work, the above group of researchers have synthesized and characterized unambiguously likewise asymmetric tetradentate ligands (134) and their corresponding Ni(II) complexes (135). The X-ray study showed that the Ni(II) ion is coordinated through the nitrogen atom soft hydrogen group, the oxygen atom of the phenolic

group, and sulfur of the C=S group for Ni(II) complexes, affords distorted square planar geometry (see Scheme 61) [99].



Scheme 60. The synthetic route for Ni(II) complex (133) with tetradentate (NNOS) Schiff base chelating ligand (132)



Scheme 61. The synthetic route for Ni(II) complex (135) with tetradentate (NNOS) Schiff base chelating ligand (134)

In a report by M. Kurtoglu et al. a new Salen-type azo-azomethine ligand (136) and its Ni(II) complex (137) were synthesized and characterized by spectroscopic and analytical methods. The spectral investigation revealed that in the Ni(II) complex, the metal ion is coordinated to two phenolate-O atoms and two imine-N atoms of the bis-azo Schiff base ligand in ONNO tetradentate fashion to give an approximate square planar geometry [100], as shown in Scheme 62.

In an article, a new organometallic Ni(II) complex (139) was synthesized by mixing an azo-azomethine ligand (138) with nickel chloride salts in a hot CHCl₃/MeOH-mixed solvent. The structure of the complex was elucidated by elemental analyses and different analytical methods. The tetradentate bis-azo Schiff base ligand is coordinated through two

phenolic-O and two imine-N atoms with the Ni(II) centre in an almost square planar shape [101] (see Scheme 63).

Likewise, Z. Shaghaghi et al., another Ni(II) complex (141) was synthesized by the reaction of nickel acetate salts and a new tetradentate N_2O_2 donor azo-azomethine-type ligand (140). The ligand and complex were characterized by different spectroscopic methods, molar conductivity measurements, and elemental composition analysis. It showed that the central metal ion is surrounded in a tetra-dentate fashion with ONNO donor atoms, as shown in Scheme 63. The low value of molar conductivity indicated the nonelectrolyte behavior of the complex [102].



Scheme 62. The synthetic route for Ni(II) complex (137) with tetradentate (ONNO) Schiff base chelating ligand (136)



Scheme 63. The synthetic route for Ni(II) complexes (139 & 141) with tetradentate (ONNO) azo-Schiff base chelating ligands (138 & 140)

Similarly, another novel tetradentate azo-imine ligand (142) was synthesized by the condensation process of an azo-aldehyde and ethylenediamine. The nickel complex (143) in Scheme 64 was also prepared in a hot MeOH-CHCl₃ mixed solvent, mixing this

ligand, and its structure was confirmed by elemental analysis, molar conductivity measurement, and other spectral methods. The Ni (II) is coordinated with the ONNO dibasic tetradentate ligand, resulting in approximately square planar geometry [103].



Scheme 64. The synthetic route for Ni(II) complex (143) with tetradentate (ONNO) azo-Schiff base chelating ligand (142)

M. Almáši et al. have prepared a novel tetracarboxylic Schiff base ligand (144) by condensation reaction in anhydrous ethanol. This ligand formed a stable chelate complex (145) when it was treated with Ni(NO₃)₂.6H₂O in a mixture of solvents (DMF, EtOH, and H₂O). The ligand and complex were characterized by elemental analyses, ¹H

and ¹³C NMR, powder X-ray diffraction, thermal analysis, UV-Vis, IR, spectroscopy, and ICP-MS analyses. The Ni(II)ion is coordinated with the ligands two imine-N and two phenolate-O atoms (see Scheme 65). Here, the azo group acts as a spectator, and all carboxylic groups are free [104].



Scheme 65. The synthetic route for Ni(II) complex (145) with novel tetracarboxylic azo-azomethine ligand (144)

In the present study, a new azo-Schiff base ligand (146) and its Ni(II) complex (147) were synthesized and characterized by elemental and spectral analyses. (UV-Vis, IR, ¹H NMR, and natural bonding orbital analysis) (NBO). Quantum chemical calculations have been performed to provide the geometrical and

electronic structures of the Ni(II) complex. The spectral analysis indicated the ONNO tetracoordination mode of the ligand and suggested squareplanar or distorted square-planar geometry of the complex (see Scheme 66). The Ni(II))complex is diamagnetic [105].



Scheme 66. The synthetic route for Ni(II) complex (147) with an azo-azomethine ligand (146)

In a report by S. Chattopadhyay et al., a novel azoaldimine hybrid ligand (**148**) was prepared by refluxing 2-(arylazo)aniline with salicylaldehyde in diethyl ether. The reaction of this ligand with Ni(CH₃COO)₂·4H₂O in refluxing methanol precipitated the ortho-nickelated green complex (**149**). Furthermore, the reaction of the complex (C) in CH₂Cl₂ with aqueous H₂O₂ or m-chloroperbenzoic acid (m-CPBA) or *tert*-butyl hydroperoxide (TBHP) affords a new metalloazosalophens (**150**) (see Scheme 67) as a result of oxygen insertion into the Ni-C bond. All the ligands and complexes were characterized by elemental and spectral analyses. The X-ray structure authenticated the structure of the complexes (149 & 150) unequivocally. In the complex (149), the dianionic ligands bind to the metal centre through the azo-N, imine-N, phenolic-O, and ortho-C atoms of the benzene ring nearer to the azo group and furnished distorted square planar geometry. In complex (150), the di-anionic ligands bind Ni(II) in tetradentate (ONNO) fashion in distorted square planar geometry. The Ni(II) azosalophens (150) are diamagnetic and neutral [106].



Scheme 67. The synthetic route for tetradentate Ni(II) complex (149) metalloazosalophens (150) with an azo-aldimine ligand (148)

Subsequently, in another report, stable Ni(II) chelate complexes (152) were synthesized upon reaction with Ni(OAc)₂.4H₂O and newly designed

azo-Schiff base ligands (151) in methanol. The structure features of the synthesized complexes were examined by elemental analysis, UV-vis, IR-

spectroscopy, and ¹H NMR spectral data [43]. The Xray structure asserted that the di-anionic ligand (**151**) is coordinated through imine nitrogen-N, azo nitrogen-N, amido-N, and phenolate-O atoms, affording square planar geometry, as shown in Scheme 68.



Scheme 68. The synthetic route for (NNNO) tetradentate Ni(II) complex (152) with azo-Schiff base ligand (151)

In a research work, a group of researchers have explored the synthesis and coordination chemistry of a nickel metal complex (154) obtained from the reaction of the newly designed tetra dentate heterocyclic ligand (153) with nickel chloride salt in hot ethanol. The prepared compounds were characterized by different micro-analytical techniques and elemental analysis. The spectral analysis indicated that the metal ion is coordinated with the ligand through thioamido-S, azomethine-N of pyrazole and imidazole rings and azo-N atoms in (SNNN) tetradentate fashion and suggested a diamagnetic square-planar geometry of the metal complex (see Scheme 69). The high molar conductance value indicates the electrolytic nature of the metal complex [107].



Scheme 69. The synthetic route for Ni(II) complex (154) with tetradentate (SNNN) azo-Schiff base ligand (153)

Another noteworthy tetradentate azo-Schiff base ligands (155), as well as their Ni(II) complexes (156), were synthesized by refluxing Ni(OAc)₂.4H₂O and these ligands in an ethanol/chloroform mixed solvent. Elemental analysis, infrared, UV-Vis, mass spectra, and ¹H NMR spectroscopy were used to characterize

the composition and geometrical arrangement of all compounds [108]. The Ni(II) complexes are diamagnetic and square-planar, which was confirmed by the magnetic moment measurement value. In the complexes, the metal atom is surrounded by ONNO tetradentate fashion, as shown in Scheme 70.



Scheme 70. The synthetic route for Ni(II) complex (156) with tetradentate (ONNO) azo-Schiff base ligand (155)

Likewise [109], a new non-electrolyte Ni(II) complex (158) embedded in N_2O_2 donor azo-Schiff base ligand (157) was synthesized and characterized by elemental analysis, various spectral analysis, as well as molar conductivity and magnetic susceptibility

measurement. The spectral data suggested that the central Ni(II) ion is coordinated through two azomethine-N and two deprotonated-O atoms, which bestow octahedral geometry with sp^3d^2 hybridization (see Scheme 71).



Scheme 71. The synthetic route for non-electrolyte octahedral Ni(II) complex (158) with N_2O_2 -donor azo-Schiff base ligand (157)

Benjamin J. Coe and his coworkers [110] have synthesized a series of tetradentate (N_2O_2) -chelated Ni(II) complexes (160, 162 & 164) incorporating new alkyl esterfunctionalized pro-ligands (159) /biphenyl-based pro-azo ligands (161) or Salen-like pro-azo ligands (163) with various substituents close to and remote from the metal centre. These compounds were characterized using different physical techniques, including ¹H NMR and matrix-assisted laser desorption/ionization mass spectroscopy. Single crystal X-ray structure confirmed the coordination geometry around the Ni(II) is strictly square-planar geometry for the bis-chelate Ni(II) complexes (**160 & 162**) and distorted square-planar geometry for the Ni(II) complexes (**164**) for Salen-like ligands (**163**) (see Scheme 72).



Scheme 72. The synthetic route for Ni(II) complex (160, 162 & 164) with tetradentate alkyl functionalized, biphenyl-based, and Salen like Pro azo ligand (159, 161 & 163)

At present, Eman A. Bakr and his groups have synthesized a novel azo-Schiff base ligand (165) based on heterocyclic benzoxazole and pyridine moieties and its Ni(II) complex (166) with a metal-to-ligand 2:1 ratio. The investigated compounds were structurally characterized experimentally using various analytical and spectroscopic tools and theoretically using the DFT method. The spectral analyses indicated that the multidentate ligand coordinated with the Ni(II) ions in two centres and formed a binuclear complex. In the first centre, Ni(II) is coordinated through azo-N and azomethine-N atoms of the benzoxazole ring. Another Ni(II) ion is coordinated with azomethine-N and carbonyl-O atoms, as shown in Scheme 73. Moreover, the electronic transition, as well as the high magnetic moment value of the complex, suggested the paramagnetic with tetrahedral geometry. Nonetheless, the 3D molecular structure of the Ni(II) complex is in concordance with the geometrical structures proposed experimentally [111].



Scheme 73. The synthetic route for bi-nuclear Ni(II) complex (166) with azo-azomethine benzoxazole based ligand (165)

2.4. Nickel complexes with denticity $(\kappa)>4$ azoazomethine ligands

In another article, Eman M. Abdel-Satar and his coworkers reported a bi-nuclear Ni(II) complex (168) with pentadentate azo-Schiff base ligand (167). The Ni(II) chelate complex was synthesized by the mixture of NiCl₂.6H₂O and ligand with continuous stirring at 70 °C. The proposed structures of the ligand and it chelates were characterized by employing several Spectro-analytical techniques and elemental analysis. The ligand shows a pentacoordinate binding mode in metal chelate and coordinates via carbonyl-O, azomethine-N atoms, and phenolic-OH group on one side, along with azo-N atom and phenolic-OH group on the other side. The spectral data proposed that the Ni(II) chelate has square-pyramidal and square planar geometry around two metal ion centres, as shown in Scheme 74. According to the measured molar conductance values, the Ni(II) chelate is ionic due to the presence of two chloride ions in the outer sphere of the complex [112].

In a report, new bis-iminated azo-azomethine ligands (169) and their Ni(II) complexes (170 & 171) were synthesized and characterized unequivocally by H. Khanmohammadi et al. The single crystal X-ray structure of the Ni(II) complex (170) suggested that the coordination sphere of Ni(II) is surrounded by $N_2S_2O_2$ donor atoms, resulting in a slightly distorted octahedral geometry. On the other hand, spectral analyses revealed that in complexes (171), Ni(II) ions are coordinated with two-S, one phenolic-O, and an azomethine-N atom, and one perchlorate anion is also coordinated with the metal centre, resulting in different geometry as shown in Scheme 75. In both complexes, the azo (-N=N-) groups are free for coordination [113].



Scheme 74. The synthetic route for bi-nuclear Ni(II) complex (168) with pentadentate azo-Schiff base ligand (167)



Scheme 75. The synthetic route for Ni(II) complexes (170 & 171) with hexa- and penta- coordinated azo-azomethine dye ligands (169)

In another investigation by L. K. Abdul Karem et al., they reported the synthetic procedure of a novel Ni(II) complex (**173**) of a newly designed and synthesized azo-Schiff base ligand (**172**). The composition elemental composition and structural environment of the prepared metal complexes were confirmed by FT-IR, ¹H, ¹³C NMR, and CHN elemental analysis. The spectral data revealed that the

ligand coordinated with the metal centre through two azo-N atoms, two azomethine-N atoms, and two phenolate-O atoms to build an octahedral environment around the Ni(II) ion (see Scheme 76). The magnetic susceptibility data and molar conductivity values indicated the paramagnetic and non-electrolytic nature of the Ni(II) complex [114].



Scheme 76. The synthetic route for Ni(II) complex (173) with hexa-coordinated azo-imine ligand (172)

Synthesized compounds	Geometry	Color	% Yield	Characterization techniques	Characteristics	Reference
$C_{11}H_{12}N_4(1)$	 Distanta d	Orange	45	UV–Vis, IR, thermal		[33]
$C_{13}H_{16}I_{16}I_{10}O_2S_2,$	Distorted	D 11	<i>с</i> 4	and magnetic studies,		
$2(C_3H_7NO)(2)$	octahedral	Dark brown	54	X-ray		
$RC_{13}H_9N_4$ (3) $R_2C_{26}H_{18}N_{10}NiS_2$ (4)	 Distorted	Orange	54	UV–Vis, IR, thermal and magnetic studies,		[50]
2 20 10 10 2 ()	octahedral	Dark brown	50-70	cyclic voltammetry,		
		Dal	60	A-ray		[61]
$C_{30}H_{25}N_5(5)$		Rea	08	UV = VIS, FI = IR,		[31]
$C_{60}H_{50}N_{10}N_{10}N_{1}C_{12}$ (b)	Octanedral	Brown				[[]]
$C_{20}H_{16}N_4O_4(7)$		Bloody red	70	UV–V1s, FT-IR, H		[52]
$C_{20}H_{17}N_4 O_5NiCl(8)$	Square	Deep orange	82	NMR, magnetic		
	planar			studies and molar		
				conductivity		
$C_{19}H_{15}N_{3}O(9)$			84	UV–Vis, FT-IR,		[53]
C ₃₈ H ₂₈ N ₆ O ₂ Ni (10)	Square			$^{1}\text{H}/^{13}\text{C}$ NMR, mass,		
	planar			magnetic studies and		
$C_{38}H_{27}N_6O_2$ (11)	-			TG, DTA		
$C_{76}H_{52}N_6O_2N_1$ (12)	Tetrahedral					
$C_{26}H_{21}N_4O_{4.5}$ (13)		Orange	77	UV–Vis, FT-IR, ¹ H	Genotoxic	[54]
$C_{52}H_{48}$ Ni N_8O_{13} (14)	Octahedral	Orange	70	NMR,cyclicvoltammetryand X-raypowder		
				diffraction		
$C_{20}H_{22}N_4O_4\ ({\bf 15})$			70	UV–Vis, FT-IR, ¹ H	Catalytic,	[55]

$C_{40}H_{42}Ni N_8O_2$ (16)	Square planar		72	NMR, mass, cyclic voltammetry and	antimicrobial	
$C_{39}H_{55}N_{3}O_{3},$ $C_{43}H_{63}N_{3}O_{3},$ $C_{47}H_{71}N_{3}O_{3},$ (17)		Yellow	85-87	UV–Vis, FT-IR, ¹ H NMR, DSC measurement and X-	Glass-forming properties	[56]
$C_{78}H_{108}N_6O_6Ni,$ $C_{86}H_{124}N_6O_6Ni,$ $C_{94}H_{140}N_6O_6Ni$ (18)	Square planar	Yellow green	80	ray powder diffraction		
$\begin{array}{l} C_{16}H_{14}N_4O~({\color{black}19})\\ C_{32}H_{20}N_8O_4Ni~({\color{black}20}) \end{array}$	 Square planar	Green Light green	70 72	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, magnetic studies and	DNA cleavage/ Anti-bacterial	[57]
$C_{34}H_{27}N_5O_4S$ (21)		Light orange Brown	70	Powder XRD UV–Vis, FT-IR, ¹ H NMR, mass, thermal,	Anti-microbial	[58]
$\begin{array}{l} C_{68}H_{52}N_{10}O_8S_2Ni\\ \textbf{(22)}\end{array}$	Square planar		60-70	molar conductance, thermal, magnetic susceptibility and Powder XRD		
$\begin{array}{l} C_{13}H_{14}N_4O_2S~({\color{black}{23}})\\ C_{10}H_7N_3O_2S~({\color{black}{24}}) \end{array}$		Dark brown Reddish	86 79	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, mass,	Anti-microbial	[59]
$\begin{array}{c} C_{26}H_{26}N_8O_4S_2Ni~(\textbf{25})\\ C_{32}H_{28}N_6O_4Cl_4Ni\\ \textbf{(26)}\end{array}$	Square planar	brown Orange Dark brown	70 63	thermal, molar conductance, magnetic moment, TGA/DTA		
$C_{19}H_{13}N_{3}O_{2}Cl_{2}\left(\textbf{27}\right)$		Light orange Brown	70	UV–Vis, FT-IR, ¹ H NMR. mass. molar	Anti-bacterial	[60]
$C_{38}H_{54}N_6O_4Cl_4Ni$ (28)	Square planar		60-70	conductance, thermal, magnetic moment, VSM, TGA, DSC		
$\begin{array}{llllllllllllllllllllllllllllllllllll$		Orange Orange	79/75	UV–Vis, FT- IR ¹ H/ ¹³ C NMR, X- ray, mass, molar		[61]
$\begin{array}{ll} C_{38}H_{26} & Br_2N_6O_2Ni / \\ C_{42}H_{34} & Br_2N_6O_2Ni \\ \textbf{(30)} \end{array}$	Square planar		79/87	conductance, thermal, magnetic moment, TG/DTA		
$\begin{array}{c} C_{22}H_{19}N_{3}O \\ C_{20}H_{17}N_{3}O_{2}\left(\textbf{31}\right) \end{array} /$		Orange	86/75	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, X-ray,		[62]
$\begin{array}{l} C_{44}H_{36}NiN_6O_{2/} \\ C_{40}H_{32}NiN_6O_4 \ (\textbf{32}) \end{array}$	Square planar	Brown/Red- brown	70/81	mass, molar conductance, thermal, magnetic moment, TG/DTA		
$\begin{array}{ccc} C_{14}H_{13}N_3O_3 & / \\ C_{14}H_{12}N_4O_5 / \\ C_{14}H_{12}N_3O_3Cl~(\textbf{33}) \end{array}$		Yellow/Brown /Yellow	72 /79 /74	UV–Vis, FT-IR, ¹ H NMR, X-ray, mass, molar conductance, ESR spectra, TGA	Anti-bacterial	[63]
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Square planar	Green/ Brown/ Yellow	78 /85 /81	List special, 1011		
$C_{13}H_{15}N_5O_2S$ (35)		Orange	68	UV–Vis, FT-IR, ¹ H NMR, LCMS, TGA,	Anti-bacterial /antioxidant/ DNA	[45]
C ₂₆ H ₂₈ NiN ₁₀ O ₄ S (36)	Square planar	Color	-	magnetic susceptibility, DFT, powdered XRD	cleavage/ molecular docking	
C ₁₆ H ₁₁ N ₄ OSBr (37)		Brown	80	UV–Vis, FT-IR, ¹ H NMR, LCMS, TGA,	Anti-bacterial	[64]

C ₃₂ H ₂₀ NiN ₈ O ₂ S ₂ Br ₂ . 2H ₂ O (38)	Octahedral	Dark-orange	76	magnetic susceptibility,		
C ₁₄ H ₁₈ N ₆ O ₄ S /		Red/ Reddish	71 /74	UV–Vis, FT-IR,	antimicrobial,	[65]
$C_{15}H_{10}N_6O_4S$ /		brown /	/ 62	$^{1}\text{H}/^{13}\text{C}$ NMR, TG-	antitubercular,	
$C_{16}H_{12}N_6O_4S$ (39)		Orange- yellow		DTA, magnetic susceptibility,	anti-inflammatory,	
$C_{28}H_{18}NiN_{12}O_{10}S_2$ /	Octahedral	Brown-solid /	71/78	conductivity,		
$C_{30}H_{22}NiN_{12}O_{10}S_2$ /		Brick-red /	/75	powdered XRD		
$C_{32}H_{26}NiN_{12}O_{10}S_2$ (40)		Red-solid				
$C_9H_8N_6O_2S$ (41)		Brown	76	$UV-Vis$, FT-IR, ${}^{1}H/{}^{13}C$ NMR,		[66]
$C_{18}H_{18}NiN_{12}O_5S_2Cl_2.$	Octahedral	Purple	77	magnetic		
(42)				susceptibility, molar conductivity		
$C_{17}H_{11}N_{3}O_{2}$ (43)		Dark-grey	80	UV–Vis, FT-IR, ¹ H	Anti-oxidant	[67]
1, 11 5 2 ()		6,		NMR, magnetic	Anti-cancer	
$C_{34}H_{20}NiN_6O_4.2H_2O$ (44)	Octahedral	Black	93	susceptibility, molar conductivity, CV	activity	
$C_{11}H_9N_5O_3$ /		Orange	68	UV–Vis, FT-IR, ¹ H		[68]
$C_{11}H_8N_5O_3Cl(45)$		-		NMR, ESI-Mass,		
C33H27NiN9O8Cl2	Octahedral		-	magnetic		
(46)		Dark-green		susceptibility, DFT,		
$C_{23}H_{20}N_6Cl_2Ni$ (47)	Octahedral			X-ray, CV		
$C_{22}H_{18}N_6Ni$ (48)	Distorted	Green				
	tetrahedral	Brown	86-90	. 1		
$C_{23}H_{23}N_7$ (49)		Light red	76	UV–Vis, FT-IR, ¹ H NMR, TGA, X-ray,	antibacterial, antifungal and	[69]
$\begin{array}{c} C_{46}H_{48}N_{14}Cl_2ONi\\ \textbf{(50)}\end{array}$	Octahedral	Purple	68	SEM magnetic susceptibility, molar	anti-cancer	
				conductivity, thermal analyses		
$C_{21}H_{50}N_3$ (51)		Yellow	70-90	UV–Vis, FT-IR, ¹ H		[70]
				NMR, mass, X-ray,		
$C_{42}H_{52}N_6O_4Ni$ (52)	Distorted tetrahedral	Green	68	thermal analyses		
C ₃₀ H ₂₄ N ₄ O/		Yellow	79	UV–Vis, FT-IR, ¹ H	Anti-tumour	[71]
C ₃₀ H ₂₃ N ₄ OCl (53)				NMR, mass, X-ray,	activity	
C ₃₀ H ₂₃ N ₄ ONi/		Yellow/ Green	80/58	thermal analyses		
$C_{30}H_{22}N_4OCl_3Ni(\textbf{54})$						
$C_{25}H_{19}N_{3}O_{4}\left(\textbf{55}\right)$		Yellow	81	UV–Vis, FT-IR,		[72]
C ₅₀ H ₃₆ N ₆ O ₈ Ni (56)	Octahedral			$^{1}\text{H}/^{13}\text{C}$ NMR		
$C_{21}H_{26}N_3O_2$ (57)				UV–Vis, FT-IR, CD	Photochromism	[73]
$C_{42}H_{48}N_6O_2N_1$ (58)	Square planar	Brown	71	spectra		
$C_{17}H_{14}N_4 / C_{17}H_{16}N_4$ (59)		Yellow	60	UV–Vis, FT-IR, ¹ H NMR, ESI-Mass,		[74]
$C_{34}H_{26}N_8Ni/C_{34}H_{30}N_8Ni/60)$	Octahedral	Green	85	magnetic susceptibility. DFT.		
2. 00 0 /				X-ray, CV		
$C_{16}H_{13}N_{5}(61)$		Orange-	70	UV–Vis, FT-IR, ¹ H		[49]
$C_{32}H_{26}N_{10}$ Cl_2ONi_2		yellow		NMR, ESI-Mass,		
62)	Distorted-		80	magnetic		
	Octahedral	Bright-blue		susceptibility, DFT, X-ray, CV		
$C_{17}H_{14}N_4O_2S$ (63)		Light-brown	76	UV–Vis, FT-IR, ESR		[75]

				magnetic		
C ₃₄ H ₂₆ N ₈ Cl ₂ O ₄ S ₂ Ni ₂	Tetrahedral	Light-red		susceptibility,		
64)		-		thermogravimetry		
$C_{17}H_{13}N_5$ (65)		Dark-red	30	UV–Vis, FT-IR, ¹ H		[76, 77]
C H N CLOCN	D'	Due s'al	02	NMR, ESI-Mass,		
$C_{34}H_{26}N_8 Cl_2O_4S_2N_12$	Distorted-	Brownish-	82	magnetic		
00)	octaneurai	green		X-ray CV		
$C_{17}H_{12}N_5$ (65)		Dark-red	30	UV-Vis, FT-IR. ¹ H		[76, 77]
		2 4111 100	20	NMR, ESI-Mass,		[, 0, , ,]
C ₃₄ H ₂₆ N ₈ Cl ₂ O ₄ S ₂ Ni ₂	Distorted-	Brownish-	82	magnetic		
66)	octahedral	green		susceptibility, DFT,		
		_		X-ray, CV		
$C_{18}H_{10}N_4Cl_2$ (67)		Brown	90	UV–Vis, FT-IR, ⁴ H	Catalytic activity	[34]
$C_{36}H_{20}N_8CI_6N1$ /	Distorted	Dad	00	NMR, ESI-Mass,		
$C_{36}H_{22}N_8Cl_4N100)$	octahedral	Red	90	susceptibility DFT		
$C_{54}H_{30}N_{8}C_{12}N_{10}$	octuneeru	iteu	85	X-ray, CV		
(69)						
C ₃₆ H ₂₄ N ₈ Ni /			95/90			
$C_{36}H_{22}N_8Cl_2Ni$ (70)				1		
$C_{18}H_{14}N_4O(71)$		Orange-	64	UV–Vis, FT-IR, ¹ H		[31]
C II N O N: (73)	Distantal	yellow	72	NMR, ESI-Mass,		
$C_{36}H_{26}N_8O_2N_1(72)$	Distorted-	Black	/3	magnetic susceptibility DFT		
	octaneurai	DIACK		X-ray, CV		
RC ₂₀ H ₁₅ N ₃ OX (73)		Orange	60/85	UV–Vis, FT-IR, ¹ H	Photoluminescence	[32]
$R = H, CH_3, Cl$		/brown	/95	NMR, ESI-Mass,		
X = O,				DFT, X-ray		
$NC(C)(CO_2Et)$						
$C_{36}H_{26}N_8O_2Ni_2$ (74)	Octahedral	Deep-brown	50-60			[(2]
$C_{24}H_{23}N_{3}O$ /		Red	/5	UV-VIS, FI-IK, H		[62]
$C_{22}H_{21}N_{3}O_{2}(75)$				magnetic		
$C_{44}H_{40}N_6O_4Ni$ (76)	Octahedral	Dark-brown	88/89	susceptibility, DFT,		
				X-ray, CV		
C ₁₃ H ₁₅ N ₃ OS (77)		Reddish-	82	UV–Vis, FT-IR, ¹ H	Thermal stability	[78]
		orange		NMR, XRD, SEM,		
$C_{26}H_{30}N_6O_5SNi$ (78)	Octahedral	Green-bluish	64	molar conductivity,		
				susceptibility		
C11H12N5S (79)		Orange	68	UV–Vis. FT-IR. ¹ H		[79]
0111131(30 (77)		orunge	00	NMR, mass, molar		[, >]
$C_{22}H_{26}N_{10}S_2Cl_2Ni$	Octahedral	Blue	78	conductivity,		
(80)				magnetic		
				susceptibility		
$C_{13}H_8N_4OBrCl~(\textbf{81})$		Orange-red	83	UV–Vis, FT-IR, ¹ H	Cytotoxicity	[80]
C II N O D ₂ Cl N	O at a h a d mal	Calarlaga	70	NMR, molar	activity	
(82)	Octanedral	Coloness	78	magnetic		
(02)				susceptibility		
C ₉ H ₇ N ₄ OCl (83)		Dark-brown	78	UV–Vis, FT-IR, ¹ H	Thermal properties	[81]
				NMR, Mass, XRD,		
$C_{18}H_{12}N_8O_2Cl_2Ni$	Octahedral	Purple	64	SEM, molar		
(84)				conductivity,		
				magnetic		
				susceptionity,		

$C_{12}H_{10}N_{1}O_{2}S_{2}F_{2}(85)$				TG/DSC-DTG UV-Vis FT-IR ¹ H	Ontical & Thermal	[7]
C1611191 (402021 3(00)				NMR, Mass, DSC-	properties	[,]
$C_{32}H_{36}N_8O_4S_4F_6N_1$ (86)	Octahedral			TGA		
$C_{11}H_9N_4O_2Cl~(87)$		Dark-red	76	UV–Vis, FT-IR, ¹ H NMR, Mass,	Cytotoxicity activity	[82]
$C_{22}H_{16}N_8O_4Cl_2O_4Ni$ (88)	Octahedral	Greenish-olive	61	FESEM, XRD		
$C_{22}H_{17}N_7O_4S_2$ (89)			76	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, TGA,		[83]
C ₂₂ H ₂₁ N ₇ O ₇ S ₂ Ni. 2CH ₃ COOH (90)	Octahedral		61	DTG		
$C_{28}H_{26}N_6O_3$ (91)		Red-brown	64	$UV-Vis, FT-IR, {}^{1}H/{}^{13}C NMR,$		[41]
C ₂₈ H ₂₉ N ₆ O ₅ ClNi (92)	Octahedral		68	magnetic susceptibility, TGA		
$C_{33}H_{28}N_6O_3$ (93)		Orange	72	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, Mass,	Anti-bacterial and anti-fungal activity	[84]
$\begin{array}{l} C_{56}H_{60}N_{12}O_4Cl_2Ni\\ \textbf{(94)} \end{array}$	Octahedral	Reddish- purple	80	magnetic susceptibility, molar conductance		
$C_{12}H_{12}N_4$ (95)		Orange	10	UV–Vis, FT-IR, ¹ H NMR, X-ray		[30]
C ₃₀ H ₂₆ N ₄ O ₄ ClPNi (96)	Distorted square- planar	Deep-orange	80			
$C_{24}H_{15}N_3Cl_2Na_2O_9S_2$ (97)			58	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR (APT,		[85]
$\begin{array}{l} C_{24}H_{21}N_{3}Na_{2}O_{13}S_{2}\\ Cl_{2}Ni \ (\textbf{98}) \end{array}$	Octahedral		71	DEPT), Mass, magnetic susceptibility, molar conductance		
C ₁₄ H ₁₃ N ₅ OS (99) C ₁₄ H ₁₈ N ₅ O ₄ SNi	 Square-	Red	78	UV–Vis, FT-IR, ¹ H NMR, Mass,	Biological activity	[86]
(100)	planar	Brown	80	thermogravimetry molar conductance,		
$\begin{array}{l} RC_{19}H_{14}N_{3}O_{2}\ (\textbf{101})\\ RC_{19}H_{19}N_{3}O_{8}SNi\\ \textbf{(102)}\\ \end{array}$	 Square-	Red Reddish- brown	94 91 71-73	UV–Vis, FT-IR, ¹ H NMR, Mass, SEM, X-ray, magnetic	Anti-bacterial activity	[87, 42]
$RC_{19}H_{14}N_{3}O_{3} (103)$ $RC_{19}H_{19}N_{3}O_{4}Ni$ (104) R = H Me Cl	planar	Yellow	62	susceptibility, molar conductance, thermogravimetry		
$\begin{array}{l} C_{23}H_{17}N_{3}O_{5}S/\\ C_{25}H_{21}N_{3}O_{5}S/\\ C_{23}H_{16}N_{4}O_{7}S \ (\textbf{105})\\ C_{46}H_{30}N_{6}O_{10}S_{2}NiNa_{2} \end{array}$		Brown/dark- pink/light- pink	56/45/ 62	UV–Vis, FT-IR, ¹ H NMR, Mass, thermogravimetry molar conductance,		[88]
$\begin{array}{c} C_{50}H_{38}N_6O_{10}S_2NiNa_2\\ C_{46}H_{28}N_8O_{14}S_2NiNa_2\\ \textbf{(106)} \end{array}$	Octahedral	Brown/claret- red/black	50/48/ 52	magnetic susceptibility		
$C_{20}H_{15}N_4O_3Cl(107)$	 Distorted		92	UV–Vis, FT-IR, ¹ H NMR, Mass, SEM,	Anti-microbial activity, NLO	[89]
C ₂₀ H ₁₆ N ₄ O ₄ Ni (108)	Square- planar		80	X-ray powder, magnetic susceptibility, molar conductance	property	

$C_{24}H_{20}N_5O_2Cl$ (109)			89	UV–Vis, FT-IR, ¹ H NMR, ESR and EI	NLO property	[46]
$\begin{array}{l} C_{24}H_{23}N_5O_4NiCl_2\\ \textbf{(110)} \end{array}$	Octahedral		88	Mass, SEM, X-ray, magnetic susceptibility, molar conductance		
$C_{28}H_{26}N_8O_5S_2(111)$		Yellow		UV–Vis, FT-IR, ¹ H/ ¹³ H NMR, Mass,	Antimicrobial activity	[90]
C ₂₈ H ₃₃ N ₈ O ₉ NiS ₂ Cl (112)	Octahedral	Dark-red		SEM, TEM, EDX, XRD, molar conductance, magnetic susceptibility, thermal		
$C_{30}H_{21}N_5O_3$ (113)		Yellow	68	UV–Vis, FT-IR, ¹ H/ ¹³ H NMR, API-	Antioxidant, Anti- microbial activity	[91]
C ₆₀ H ₄₆ N ₁₀ O ₉ Ni (114)	Octahedral	Claret-red	40	ES mass, TGA, molar conductance, magnetic susceptibility		
$C_{22}H_{20}N_6O$ (115)		Reddish- orange	78	UV–Vis, FT-IR, ¹ H NMR, mass, molar	Antibacterial & Anti-fungal	[92]
C ₄₄ H ₄₀ N ₁₂ O ₃ Ni (116)	Square- planar	Dark-brown	69	conductance, magnetic susceptibility	activity	
$\begin{array}{llllllllllllllllllllllllllllllllllll$		Yellow/ Orange	60/65	UV–Vis, FT-IR, ¹ H/ ¹³ H NMR, X-ray,	Photo-switching behavior	[48]
$C_{26}H_{33}N_9Cl_2Ni/$	` TBP	Light green	90	HRMS, DFT		
$C_{20}H_{17}N_5O_3$ (119)		Orange	77	UV–Vis, FT-IR, ¹ H/ ¹³ H NMR, LCMS,	Cytotoxic activity Thermal property	[93]
$C_{40}H_{36}N_{10}O_8Ni$ (120)	Octahedral	Dark-brown	69	ESR, Powdered XRD, molar conductance, magnetic susceptibility		
$C_{31}H_{23}N_5O_4$ (121)		Yellow	79	UV–Vis, FT-IR, ¹ H/ ¹³ H NMR, MS,	DNA cleavage Antioxidant/	[94]
$C_{62}H_{46}N_{10}O_9Ni$ (122)	Octahedral	Dark-blue	56	molar conductance, magnetic susceptibility	antibacterial property	
$\begin{array}{c} C_{27}H_{24}N_8O_2 ({\bf 123}) \\ C_{24}H_{34}N_4O \ ({\bf 124}) \end{array}$		Orange	73/71	UV–Vis, FT-IR, ¹ H NMR, MS, DSC,	Supramolecular network	[95]
$\begin{array}{l} C_{27}H_{22}N_8O_2Ni~(\textbf{125})\\ C_{48}H_{66}N_8O_2Ni~(\textbf{126})\\ C_{58}H_{76}N_{10}O_2Ni~(\textbf{127}) \end{array}$	 Octahedral	Reddish Orange 	80 88 	powder X-ray		
$\begin{array}{c} C_{30}H_{18}N_8O_2Cl_2\ ({\bf 128})\\ C_{30}H_{20}N_8O_4NiCl_2 \end{array}$		Brown	60-70	UV–Vis, FT-IR, ¹ H NMR, MS, EPR,	NLO property Fluorescence	[96]
(129)	Octahedral	Colored	60-77	SEM, molar conductance, magnetic susceptibility	property	
$\begin{array}{l} C_{28}H_{26}N_8O_6S_2\ (\textbf{130})\\ C_{28}H_{32}N_8O_{10}NiS_2 \end{array}$		Yellow	85	UV–Vis, FT-IR, ¹ H NMR, MS, EPR,	Thermal properties	[97]
(131)	Tetrahedral	Dark-red		SEM, molar conductance, magnetic		

				susceptibility		
$RC_{22}H_{23}N_4OS_2$ (132)		Coloured	68-93	UV–Vis, FT-IR, ¹ H		[98]
$RC_{22}H_{21}N_4ONiS_2$				NMR, X-ray, CV		
(133)	Distorted		75-88			
$\hat{R} = H$, Me, Et, Cl,	square-					
NO ₂	planar					
$R_1R_2C_{22}H_{25}N_4OS_2$		Coloured	68-93	UV–Vis, FT-IR, ¹ H		[99]
(134)				NMR, X-ray, CV		
$R_1R_2C_{22}H_{23}N_4OS_2$	Distorted	Coloured	57-80			
$(135) R_1 = H, NO_2$	square-					
$R_2 = Cl$	planar					
$C_{32}H_{32}N_6O_2$ (136)		Orange	38	UV–Vis, FT-IR,	Photoluminescence	[100]
$C_{32}H_{34}N_6O_4Ni(137)$	Square-	Coloured	74	¹ H/ ¹³ H NMR, X-ray	property	
G H N O (120)	planar	0	50			[101 100]
$C_{32}H_{24}N_6O_2$ (138)		Orange	59	UV-V1S, FT-IR,		[101, 102]
$C_{32}H_{22}N_6O_2Ni(139)$	Square-	Coloured	74	¹ H/ ¹³ H NMR, CV,		
	planar			SEM, XRD		
$C_{32}H_{23}N_6O_2CI(140)$	a					
$C_{32}H_{21}N_6O_2N_1Cl$	Square-	Red powdered	80			
(141)	planar	0	0.4		Q	[100]
$C_{30}H_{28}N_6O_4(142)$		Orange	84	UV-V1S, FT-IR,	Cytotoxicity	[103]
$C_{30}H_{28}N_6O_5N_1(143)$	Square-	Khaki	11	'H/"H NMR, X-ray,		
	planar	0	52	molar conductance		[104]
$C_{34}H_{24}N_6O_{10}(144)$		Orange	53	UV-V1S, FI-IR,	Thermal stability	[104]
$C_{34}H_{22}N_7O_{10}N_1(145)$	Square-	Orange	57	'H/"H NMR, PXRD,		
	planar			ICP-MIS, thermal		
			50	analysis		[10]
$C_{30}H_{26}N_6O_2(140)$			38 50	UV = V1S, $F1 = IK$, H	Catalytic activity	[105]
$C_{30}\Pi_{24}\Pi_{6}O_{2}\Pi_{1}(147)$	square-		39	NWIK, PAKD, DF I		
$\mathbf{PC} \mathbf{H} \mathbf{N} \mathbf{O} (148)$	pianai	Colourad	05			[106]
$RC_{19}\Pi_{14}N_{3}O(140)$	 Distorted	Green	95 60 70	$UV = VIS, \Gamma I = IK, \Pi$ NMP V rov CV		[100]
PC = N O N;	Square	Olive green	60.65	NIVIR, A-lay, CV		
(150)	Square-	Onve-green	00-05			
(130) R – H Me Cl	planai					
$C_{10}H_{10}N_{10}O/$		Red	95/95	UV_Vis FT_IR ¹ H		[43]
$C_{20}H_{18}N_{4}O$ (151)		Rea)51)5	NMR X-ray CV		[-5]
$C_{21}H_{20}N_4O(151)$	Square-	Dark-green	75/72	Tunik, A Tuy, C V		
$C_{20}H_{10}N_4ONi$ (152)	planar	Durk green	13112			
$C_{15}H_{17}N_0S(153)$		Red	80	UV–Vis FT-IR ¹ H	Antimicrobial	[107]
$C_{15}H_{17}N_0SNiCl_2$		100	00	NMR. MS. X-ray.	activity	[10,]
(154)	Square-	Brown	60	molar conductance.		
	planar			magnetic		
	L			susceptibility		
C ₃₀ H ₂₉ N ₇ O ₂ /		Yellow	80/87	UV–Vis, FT-IR, ¹ H	Thermal property	[108]
$C_{32}H_{33}N_7O_4(155)$				NMR, MS, molar		
$C_{30}H_{27}N_7O_2N_1$ /	Square-	Green	80/80	conductance,		
$C_{32}H_{31}N_7O_4Ni$ (156)	planar			magnetic		
	-			susceptibility		
$C_{36}H_{40}N_8O_2(157)$		Deep-green	81	UV–Vis, FT-IR,		[109]
				$^{1}\text{H}/^{13}\text{C}$ NMR, MS,		
C ₃₆ H ₄₂ N ₈ O ₄ Ni (158)	Octahedral	Green	80/80	molar conductance,		
				magnetic		
				susceptibility		
$C_{24}H_{31}N_3O_3$ /		Orange/grey	39-76	UV–Vis, FT-IR, ¹ H	Dichroism	[110]
$C_{22}H_{19}N_3O_3$				NMR, MALDI, TD-	property	
$C_{24}H_{31}N_3O_3$			80/80	DFT, MS, X-ray,		

(159/161/163)		Square-					
C48H60N6O6Ni	/	planar	Light-brown	67/53/			
C66H88N6O4Ni		Distorted	Red/brown	49			
C38H38N6O6Ni		square-					
(160/162/164)		planar					
$C_{19}H_{12}N_5O_3Cl(165)$			Faint-brown	81	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, MS,	Antimicrobial activity	[111]
$\begin{array}{c} C_{21}H_{19}N_5Cl_4Ni_2O_5\\ \textbf{(166)}\end{array}$		Tetrahedral	Greyish- brown	80/80	XRD, TGA, molar conductance, magnetic susceptibility	Cytotoxicity	
$C_{19}H_{21}N_5O_6(167)$			Light-brown	88	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, MS,	Anti-oxidant property	[112]
$\begin{array}{c} C_{19}H_{24.5}N_5Cl_4Ni_2O_{7.7}\\ \textbf{(168)}\end{array}$	75	Tetrahedral	Olive-green	81	XRD, TGA, molar conductance, magnetic susceptibility		
C40H30N6O2Cl2S2/				72-78	UV–Vis, FT-IR,	Fluorescence	[113]
C42H36N6O4S2/			Brown		$^{1}\text{H}/^{13}\text{C}$ NMR, MS, X-	property	
$C_{42}H_{36}N_6O_2S_2/(169)$)			71-83	ray, TGA-DTA	Thermal property	
$\begin{array}{l} C_{40}H_{29}N_6Cl_2Ni_2O_{2.5}S\\ C_{44}H_{39}N_6ClNi_2O_9S_2\\ C_{44}H_{39}N_6ClNi_2O_9S_2\\ \textbf{(170/171)}\end{array}$	S ₂	Distorted octahedral TBP	Brown				
$C_{40}H_{40}N_{10}O_4({\bf 172})$			Yellow	71	UV–Vis, FT-IR, ¹ H/ ¹³ C NMR, Mass,	antimicrobial activity	[114]
$C_{40}H_{40}N_{10}$ O ₇ N (173)	Ni	Octahedral	Green	62	molar conductance, magnetic susceptibility		

3. Notable features of azo-azomethine ligands and their Ni(II) complexes

3.1a. Genotoxicity

Dose-dependent *mutagenic activity* of ligand (13) and Ni(II) complex (14) were tested, and the compounds exhibited significant mutagenic activity on S. Typhimurium TA98 than that on S. Typhimurium TA100 in the absence or presence of the S9 mix [54]. *3.1b. Antimicrobial activity*

The antimicrobial activity [55] of the synthesized ligand (15) and complex (16) was tested against a few microorganisms using the minimum inhibitory concentration (MIC). The complex (16) exhibited higher reactivity than the ligand (15). The antibacterial activity of the ligand (19) and its Ni(II) complex was also examined by the Well diffusion method, and it was noticed that the complex (20) has more antibacterial activity than the ligand (19) against pathogenic organisms such as gram-positive Bacillus subtilis and gram-negative Klebsiella pneumonia [57]. Similarly, antibacterial activity was performed using the azoazomethine ligand (21) and its Ni(II) chelated complex (22) against E. coli, K. pneumonia, and B. subtilis. Due to the higher lipophilic character of the chelate complex (22) than the ligand (21), the metal chelated complex (22) showed enhanced antibacterial activity [58]. Further, azo-azomethine ligands (23 and 24) and their Ni(II) chelates (25 and 26) were tested for their antimicrobial activity against the Gram-negative bacteria (Escherichia coli), the Gram-positive bacteria (Staphylococcus aureus) and the fungus (Candida albicans) using Kirby-Bauer and MIC/MBC methods [59]. The result showed that the mononuclear Ni(II) complexes (25 and 26) have enhanced antibacterial activity than the ligands (23 and 24). The antibacterial properties of the azo-Schiff base ligand (27) and its bischelate nickel(II) chelate complex (28) were investigated in vitro on standard bacteria as well as on bacteria isolated from clinical specimens (urine). The results revealed that the ligand (27) and its metal complex (28) showed very high antibacterial activity against Staphylococcus aureus but were ineffective against other studied bacteria [60].

In another investigation, an antibacterial study using MIC against gram-positive (S. aureus & B. subtilis) and gram-negative (E. coli & S. typhi) bacteria revealed that the ligands (**33**) showed good antibacterial potency over

the standard broad-spectrum antibiotic chloramphenicol. Furthermore, the metal Ni(II) complexes (**34**) showed low antibacterial sensitivity against all isolates compared to their parent ligands but were better than chloramphenicol [63].

The antimicrobial studies for the ligand (**37**) and its complex (**38**) were performed against S. aureus and P. aeruginosa using the well-diffusion method. The enhanced antibacterial activity of the Ni(II) chelate (**38**) compared to the ligand has been observed due to the lipophilic nature of metal ions in the complex ^[64]. The pharmacological studies of the newly synthesized azo dyes (**39**) and their Ni(II) complexes (**40**) were carried out against various species. It was reported that the Ni(II) complexes (**40**) exhibited increased antimicrobial and antitubercular activity, and the Ni(II) chelates (**40**) have the ability to act as an inflammatory agent in the future. The Ni(II) complexes (**40**) can cleave supercoiled plasmid pBR322 DNA [65].

The free ligand (**35**) and its bivalent nickel complex (**36**) were tested against Gram-negative bacteria (E. coli), Gram-positive bacteria (B. subtilis), and two strains of fungi. In contrast with the ligand, all the complexes showed enhanced activity and can act as a potent antimicrobial agent against selective pathogens. Furthermore, in silico docking studies have also indicated that the Ni(II) complex (**36**) showed more negative relative binding energy, had a strong binding affinity with the target receptor GlcN-6-P synthase, and acted as an excellent inhibitor [45].

Similarly, the octahedral Ni(II) complex (172) exhibited higher antimicrobial activity compared to the free ligand (171) against microorganisms such as E. Streptococcus Klebsiella pneumonia, coli, spp., Streptococcus Staphylococcus spp., aureus, Pseudomonas aeruginosa, and V. cholera [114]. In another report, the azo-azomethine ligand (165) exhibited higher microbial activity against E. coli, and the Ni(II) complex (166) showed higher activity against C. albicans. Moreover, the Ni (II) complex (166) has the highest cytotoxic effect on HCT-116 cells (IC50 = 11.45µM). Another biological study reported that the square planar Ni(II) complex (154) displayed more toxicity against the gram-positive (S. aureus) and gram-negative (E. coli, K. pneumonia) than the fungi (A. niger, R. bataicola, and A. flavus). It was also noticed that the enhanced antimicrobial activity of the complex (154) than the tetradentate azo-Schiff base ligand (153) was attributed to the chelation effect [107]. 3.1c. Antioxidant activity

The antioxidant activity of the heterocyclic azoimine ligand (**35**) and its Ni(II) complex (**36**) was carried out by using DPPH (2,2-diphenyl—1picrylhydrazyl) assay, and the Ni(II) complex (**36**) displayed significant antioxidant activity by scavenging DPPH compared to the free ligand (**35**) [45]. In another investigation based on ferrous chelating activity, DPPH scavenging activity and reducing power of the Ni(II) complex (**122**) suggested that the complex showed significant antioxidant property [94].

3.1d. DNA binding property

The DNA binding studies of the complex (20) were examined by viscosity measurements, electronic absorption, and thermal denaturation methods. It was evident that Ni(II) complex interacted with CT-DNA through an intercalation mode. DNA cleavage studies were carried out by Gel electrophoresis techniques and revealed that the Ni(II) complex (20) effectively cleaved supercoiled pUC-19 DNA in the presence of UV light and metalation, believed to be the prime factors for cleaved DNA [54]. Likewise, the DNA cleavage activity of the synthesized Ni(II) complex (22) was investigated against CT-DNA, and the complex entirely cleaved the DNA [58].

The DNA binding strength of the synthesized tridentate azo-Schiff base Ni(II) complex (**36**) was ascertained with calf thymus DNA using electronic absorption titrations and fluorescence spectroscopy. The results revealed that the metal chelate bound with CT DNA through intercalation, and the complex (**36**) efficiently cleaved supercoiled DNA in the absence of an external reagent [45]. Another tridentate azo-imine Ni(II) complex (**121**) showed two-strand DNA cleaving properties [94].

3.1e. Cytotoxic activity

The anticancer activity of the synthesized nonchlorinated azo-Schiff base ligand (53) was tested against a single-dose concentration (100 $\mu g/ml$) of MCF-7 and WRL68 cell lines. The invitro screening result indicated that the ligand (53) had significant antibreast cancer activity [71]. The cytotoxic property of the Ni(II) chelate complex (82) was investigated by MTT test toward breast cancer cell (MCF7). The result indicated that the Ni(II) complex (82) has the capability to cure human cancers [80].

Likewise, the anticancer activity of the azo Schiff base ligand (142) and its mononuclear Ni(II) complex (143) were studied using MCF7 and L929 cell lines. The result exhibited that the Ni(II) complex (143) had the slightly better cytotoxicity than the ligand (142) against MCF7 than the L929 cell line [103].

3.2. Catalytic activity

The catalytic activity of the Ni(II) complex (16) was examined towards the oxidation of cyclohexene and styrene under a microwave-assisted system, and the result showed that the azo-Schiff base complex (16) has good catalytic activity over styrene oxidation ^[55]. In another investigation, the catalytic potential of the square planar tetradentate azo-Schiff base Ni(II) complex (147) was carried out under optimized conditions in CH₃CN. The result indicated that the complex (147) showed significant catalytic activity towards the oxidation of various alkenes to the corresponding epoxide, alcohol, aldehyde, and acids with higher TON and TOF in contrast with other familiar catalysts [105].

3.3. Glass-forming property

The glass-forming properties of the Schiff base ligands (17) and the related Ni(II) complexes (18) were studied by differential scanning calorimetry, polarizing optical microscopy (POM), and X-ray diffraction (XRD). The result disclosed that the Schiff base ligands (17) did not show any tendency toward glass formation and go to a crystalline phase. Even the related Ni(II) complexes (18) have a great propensity for glassforming and, after several days, change to an anisotropic glassy state due to different conformers of the complexes [56].

3.4. Photoluminescence properties

Photoluminescence properties of the azo-imine ligands (73) and Thetheir metal complexes (74) were examined and the result showed that the ligands (73) exhibited significant photoluminescence properties near 505 and 585 nm upon excitation at 400 nm in CH₃CN is attributed to the keto form of the ligands (73). Besides the complexes (74) are non-emissive and the addition of CN⁻, the complexes shown enhanced emissive intensity. Likewise, the tetradentate azo-Schiff base ligand (136) in DMF solvent displayed strong photoluminescence at 441 nm, while it Ni(II) chelate (137) revealed unlike luminescence intensity and quantum efficiency and shifting from 441 to 425 nm [100]. The Fluorescence properties of azo-imine ligands (169) and their Ni(II) chelate complexes (170) were examined in DMF at room temperature and the ligands show different emissive behavior. After chelation with Ni(II) ions, ligands exhibited quenched fluorescence attributed to the delocalization of electrons to the chelate ring [113]. In another investigation Ni(II) complex (129) showed strong fluorescence with moderate quantum yield than the azo-Schiff base ligand (128) in DMSO at room temperature [96].

3.5. Thermal stability

The thermal properties of tridentate azo-Schiff base ligand (78) and its chelated complex (78) of nickel metal were examined from ambient temperature up to 700 ^oC by thermogravimetric (TG) and deferential thermogravimetric (DTG) in argon atmosphere at a heating temperature of 11 °C min⁻¹. The thermogram showed that the ligand (77) is stable up to 275 °C, then it decomposes into a mixture of compounds up to 439 °C, and then a mixture of gases is produced up to 700 °C. Besides, the Ni (II) complex was stable up to 337 °C, then the complex (78) decomposed to yield NiS until reaching a temperature of 413 °C, and then NiO was produced up to 700 °C [78]. Likewise, in other thermogravimetric analyses in an oxygen atmosphere in the temperature range of 30-800 ^oC, the thermogram revealed that the azo-azomethine ligand (83) and its bivalent nickel complex (84) show four stages of decomposition. The TGA curve of the complex (84) indicated the final decomposition temperature in the range of 593-800 °C, leaving carbon atoms and NiO residue as a final product. ^[81] Another thermogram of azo-azomethine-based Ni(II) complex showed high thermal stability and decomposed in four stages in the temperature range between 26 to 510 °C, and another Ni(II) chelate complex (114) decomposed in the air ended at > $600 \,^{\circ}$ C with NiO formation [93, 91].

Another thermogravimetric analysis indicated that the decomposition of the Ni(II) complex (131) proceeds in five steps. Water molecules were lost between 50 to 300 °C, and NiO was formed up to 737 to 800 °C [97]. The tetradentate Ni(II) complex (145) started to decompose after heating at 160 °C. [104] In an investigation, the TGA curves indicated that the tetradentate ligands (155) began to lose weight at 230 and 245 °C, respectively. The thermogram displayed that the Ni(II) complex started to decay at about 245 °C due to the loss of ligand molecules [108]. The thermal decomposition studies of the hexadentate azoazomethine ligands (169) and their Ni(II) chelates (170 & 171) were carried out using TGA techniques. The TGA curves of the ligands (169) did not display any mass loss up to 290 °C. The thermogram showed that the complex (170) decomposition occurs in the temperature range of 100-270 °C and suddenly decomposes after 345 °C; besides, the complexes (171) initiate to disintegration in the temperature range of 30-190 $^{\circ}$ C [113].

3.6. Non-linear optical (NLO) property

Total hyperpolarizability of the azo-Schiff base ligand (107) was studied and showed higher second harmonic generation (SHG) conversion efficiency than urea and KDP [89]. Likewise, donor-acceptor the azo-Schiff base ligand (109) showed 2.1 times more SHG efficiency than urea and KDP [46]. In another report, the tetradentate azo-Schiff base ligand (128) showed SHG efficiency one fourth of the activity of urea and 0.5 times more activity than KDP. It was also reported that the presence of electron-withdrawing chlorine groups on both sides of the ligand (128) reduces the second-order nonlinearity [96].

4. Conclusion

In this review article, we have portrayed the synthetic strategies of various notable bivalent nickel chelate complexes incorporating azo-azomethine ligands in which the azo (-N=N-) and azomethine (-C=N-) groups are present in a conjugated or non-conjugated way in the ligand backbone. The synthesized Ni(II) complexes with azo-azomethine ligands noticeably coordinated to the Ni(II) centre in a bidentate, tridentate, and tetradentate fashion. The Ni(II) complexes embedded with ligands that have denticity (κ) > 4 are scarce. The study revealed that the Ni(II) complexes bestowed structural diversity, offering square planar, octahedral, and a few have tetrahedral geometries. The Ni(II) chelate complexes with heterocyclic (N, O, S) azo-imine ligands are redox-active. The azo-azomethine ligands containing heteroatoms (N, O, S) possessed significant biological activity against different microbial stains, and their activity has drastically increased after chelation due to reduced polarity of Ni(II) ions, lipophilicity, and the presence of heteroatoms (N, O, S) in ligands and Ni(II) complexes, which facilitates ease of strong binding with active binding sites of biological molecules. Most of the Ni(II) chelate complexes exhibited higher thermal stability, which may help their use in high-density optical recording media in the near future.

We are optimistic that this review work will inspire the researchers to synthesize various multidentate heterocyclic azo-azomethine ligands and their metal complexes with structural diversity. Moreover, this study will help the researchers design, synthesize, and develop new environmentally benign catalysts that are more effective, less toxic, and have higher efficacy for deadly biological diseases, which is the most challenging task for the future.

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References

- [1] E. Mitscherlich, Ueber das Stickstoffbenzid. *Ann. Pharm.*, 12 (1834), 311–314.
- [2] S.C. Catino, E. Farris, Concise Encyclopaedia of Chemical Technology, John Wiley & Sons, New York, 1985.
- [3] R. Egli, in: A.P. Peter, H.S. Freeman (Eds.), Colour Chemistry: The Design and Synthesis of Organic Dyes and Pigments, Elsevier, London, 1991 (Chapter VII).
- [4] H. Khanmohammadi, K. Rezaeian, Thermally stable water insoluble azo-azomethine dyes: Synthesis, characterization and solvatochromic properties. *Spectrochim. Acta A.*, 97 (2012) 652-658.
- [5] M. Ghasemian, A. Kakanejadifard, F. Azarbani, A. Zabardasti, S. Shirali, Z. Saki, S. Kakanejadifard, The triazine-based azo-azomethine dyes; synthesis, characterization, spectroscopy, solvatochromism and biological properties of 2,2'-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1phenylene)) bis(azanylylidene) bis(methanylylid ene)) bis(4-(phenyldiazenyl)phenol). Spectrochim. Acta A., 138 (2015) 643-647.
- [6] M. Odabasoglu, C. Albayrak, R. Zkanca, F.Z. Aykan, P. Lonecke, Some polyhydroxy azo–azomethine derivatives of salicylaldehyde: Synthesis, characterization, spectroscopic, molecular structure and antimicrobial activity studies. J. Mol. Struct. 840 (2007) 71-89.
- [7] W. Chen, Y.Q. Wu, D.H. Gu, F.X. Gan, Synthesis, optical and thermal characterization of novel thiazolyl heterocyclic azo dye. *Mater. Lett.*, 61 (2007) 4181–4184.
- [8] D. Sardar, P. Datta, R. Saha, P. Raghavaiah, C. Sinha, The C–H activation of pendant naphthyl group of 1-alkyl-2-(naphthyl-α-azo)imidazole by rhodium(III). Spectral, structural characterization and, DFT computation. *J. Organomet. Chem.*, 732 (2013) 109-115.
- [9] N. Biswas, D. N. Neogi, P. Das, A. Choudhury, P. Bandyopadhyay, Regioselective and regiospecific C(naphthyl)–H bond activation: Isolation, characterization, crystal structure and TDDFT study of isomeric cyclopalladates. *J. Organomet. Chem.*, 761 (2014) 147-155.
- [10] J. L. Pratihar, N. Maiti, P. Pattanayak, S. Chattopadhyay, 'A strategy of Pd(II) assisted C–H activation in 2-alkylamino azobenzene ligands: Syntheses, characterization and structure of a new family of

orthopalladated complexes, *Polyhedron*. 24 (2005,) 1953-1960.

- [11] P. Gupta, R. J. Butcher, S. Bhattacharya, Chemically Induced Cyclometalation of 2-(Arylazo)phenols. Synthesis, Characterization, and Redox Properties of a Family of Organoosmium Complexes, *Inorg. Chem.* 42 (2003) 5405-5411.
- [12] S. Kannan, R. Ramesh, Y. Liu, Ruthenium(III) mediated C-H activation of azonaphthol: Synthesis, structural characterization and transfer hydrogenation of ketones. J. Organomet. Chem., 692 (2007) 3380-3391.
- [13] S. Saha (Halder), P. Mitra, C. Sinha, Synthesis, structure and photochromism of zinc(II) complexes of alkylthioarylazoimidazoles. *Polyhedron.* 67 (2014) 321-328.
- [14] E. Ispir, M. Ikiz, A. Inan, A.B. Sünbül, M. Elmastaş, Synthesis, structural characterization, electrochemical, photoluminescence, antiproliferative and antioxidant properties of Co(II), Cu(II) and Zn(II) complexes bearing the azo-azomethine ligands. *J. Mol. Struc.*, 1182 (2019) 63-71.
- [15] C. Nandi, S. Sen, D. Roy, K. Mallick, R. Sinha, T. K. Mondal, C. Sinha, Synthesis, structure, photochromism, mesogenic property and DFT computations of silver(I) complexes of long chain alkyl group containing 1-alkyl-2-(arylazo)imidazoles. *Polyhedron*. 79 (2014) 186-196.
- [16] Z. Rezvani, B. Divband, A. R. Abbasi, K. Nejati, Liquid crystalline properties of copper(II) complexes derived from azo-containing salicylaldimine ligands. *Polyhedron.* 25 (2006) 1915-1920.
- [17] J. Arias, M. Bardaji, P. Espinet, C. L. Folcia, J. Ortega,
 J. Etxebarria, Azo Isocyanide Gold(I) Liquid Crystals,
 Highly Birefringent and Photosensitive in the Mesophase.
 J. Inorg. Chem., 48 (2009), 6205-6210.
- [18] A. Taylor, A. R. J. Lough, P. K. Poddutoori, M. T. Lemaire, Structural features and electronic properties of a cupric complex with redox active 1-(2-pyridylazo)-2phenanthrol (papl). *Polyhedron*. 108 (2015) 74-79.
- [19] A. Taylor, J. Lough, T. Seda, P. K. Poddutoori, M. T. Lemaire, Di- and trivalent iron complexes with redoxactive 1-(2-pyridylazo)-2-phenanthrol (papl). *Polyhedron*. 123 (2017) 462-469.
- [20] Sengupta, S. K. Rajput, Barman, R. Mukherjee, Lowspin $[M^{II}(L)_2]$ and $[M^{III}(L)_2]^+$ (M = Fe and Co) complexes of tridentate azo-containing pyridine/pyrazine amide ligands: structures, properties and redox potential correlations. *Dalton Trans.*, 46 (2017) 1129111305.
- [21] M. Mallikarjuna, J. Keshavayya, M. R. Maliyappa, R. A. Shoukat Ali, T. Venkatesh, Synthesis, characterization, thermal and biological evaluation of Cu (II), Co (II) and Ni (II) complexes of azo dye ligand containing sulfamethaxazole moiety. *J. Mol. Struc.*, 1165 (2018) 28-36.
- [22] N. M. Mallikarjuna, J. Keshavayya, B. N. Ravi, Synthesis, spectroscopic characterization, antimicrobial, antitubercular and DNA cleavage studies of 2-(1*H*-indol-

3-yldiazenyl)-4, 5, 6, 7-tetrahydro-1, 3-benzothiazole and its metal complexes. *J. Mol. Struc.*, 1173 (2018) 557-566.

- [23] S. Das, P. Banerjee, S-M. Peng, G.-H. Lee, J. Kim, S. Goswami, Mononuclear to Polynuclear Transition Induced by Ligand Coordination: Synthesis, X-ray Structure, and Properties of Mono-, Di-, and Polynuclear Copper(II) Complexes of Pyridyl-Containing Azo Ligands. *Inorg. Chem.*, 45 (2006) 562–570.
- [24] S. Nag, S. Bhattacharya, P. Gupta, R. J. Butcher, Unprecedented Migration of a Methyl Group in 2-(2^{,6}-Dimethylphenylazo)-4-methylphenol Mediated by Ruthenium. *Inorg. Chem.* 43 (2004) 4814-4816.
- [25] E. Peker, S. Serin, Synthesis and Characterization of Some Cobalt(II), Copper(II), and Nickel(II) Complexes with New Schiff Bases from the Reaction of p-Aminoazobenzene with Salicylaldehyde. Synth. React. Inorg. Met-Org. Chem., 34 (2004) 859-872.
- [26] E. Ispir, The synthesis, characterization, electrochemical character, catalytic and antimicrobial activity of novel, azo-containing Schiff bases and their metal complexes. *Dyes. Pigm.*, 82 (2009) 13–19.
- [27] A-N. M.A. Alaghaz, Y. A. Ammar, H. A. Bayoumi, S. A. Aldhlmani, Synthesis, spectral characterization, thermal analysis, molecular modeling and antimicrobial activity of new potentially N₂O₂ azo-dye Schiff base complexes. *J. Mol. Struc.*, 1074 (2014) 359-375.
- [28] H. Velders, K. van der Schilden, A.C.G. Hotze, J. H. Reedijk, A. L. Spek, Dichlorobis(2phenylazopyridine)ruthenium(II) complexes: characterization, spectroscopic and structural properties of four isomers. *J. Chem. Soc., Dalton Trans.*, 2004 448-455.
- [29] S. Senapati, U. S. Ray, P. K. Santra, J. D. Woolins, A. M. Z. Slawin, C. Sinha, Osmium–azopyrimidine chemistry. Part VII: synthesis, structural characterisation and electrochemistry. *Polyhedron* 21 (2002) 753-762.
- [30] P. Mandal, Chia. H. Lin, P. Brandao, D. Mal, V. Felix, J. L. Pratihar, Synthesis, characterization, structure and catalytic activity of (NNN) tridentate azo-imine nickel (II), palladium (II) and platinum (II) complexes. *Polyhedron.* 106 (2016) 171-177.
- [31] K. Sharma, S. Biswas, S. K. Barman, R. Mukherjee, 'Azo-containing pyridine amide ligand. A six-coordinate nickel(II) complex and its one-electron oxidized species: Structure and properties. *Inorg. Chim. Acta.*, 363 (2010) 2720-2727.
- [32] S. P. Parua, P. Mondal, P. Pattanayak, S. Chattopadhyay, Synthesis, structure and photoluminescence properties of functionalized azoimine ligands and their nickel complexes. *Polyhedron.* 89 (2015) 142-148.
- [33] U. Ray, D. Banerjee, J. -C. Liou, C. -N. Lin, C. Sinha, Iron(II) and nickel(II)-thiocyanato complexes of 1-alkyl-2-(arylazo)imidazole: single crystal X-ray structure of [Fe(MeaaiEt)₂(NCS)₂] (MeaaiEt = 1-ethyl-2(*p*-tolylazo)imidazole) and [Ni(MeaaiMe)(NCS)₂(H₂O)₂] · 2DMF (MeaaiMe = 1-

methyl-2(*p*-tolylazo)imidazole). *Inorg. Chim. Acta.*, 358 (2005) 1019-1026.

- [34] S. Das, S. Sinha, U. Jash, R. Sikari, A. Saha, S. K. Barman, P. Brandão, N. D. Paul, 'Redox-Induced Interconversion and Ligand-Centreed Hemilability in Ni^{II} Complexes of Redox-Noninnocent Azo-Aromatic Pincers. *Inorg. Chem.*, 57 (2018) 5830-5841.
- [35] M.I. Islam Moustafa, H. Magda Abdellattif, Synthesis, Spectroscopic Studies and Biological Evaluation of Co(II), Ni(II), Cu(II) and Zr(IV) Complexes of Azo Dyes and Thiamine Hydrochloride as Antimicrobial Agents. *Mod. Chem. Appl.*, 5 (2017) 1–7.
- [36] S. Bal, J. D. Connolly, Synthesis, characterization, thermal and catalytic properties of a novel carbazole derived Azo ligand and its metal complexes. *ARAB J. Chem.*, 10 (2017) 761–768.
- [37] T. Eren, M. Kose, K. Sayin, V. McKee, M. Kurtoglu, A novel azo-aldehyde and its Ni(II) chelate; synthesis, characterization, crystal structure and computational studies of 2-hydroxy-5-{(E)-[4-(propan-2yl)phenyl]diazenyl}benzaldehyde. J. Mol. Struct., 1065 (2014) 191–198.
- [38] A.Z. El-Sonbati, M.A. Diab, S. M. Morgan, Thermal properties, antimicrobial activity and DNA binding of Ni(II) complexes of azo dye compounds. *J. Mol. Liquid.*, 225 (2017) 195-206.
- [39] V. Kumar, J. Keshavayya, M. Pandurangappa, B. N. Ravi, Synthesis, characterization and electrochemical investigations of azo dyes derived from 2-amino-6ethoxybenzothiazole. *CDC*. 17-18 (2018) 13–29.
- [40] J. A- A Khalid, K. A, Ahmed, M. T. A; li, Synthesis of some transition metal complexes with new heterocyclic thiazolyl azo dye and their uses as sensitizers in photo reactions. *J. Mol. Struc.*, 1108 (2016) 378-397.
- [41] W. Al Zoubi, A. A. S. Al-Hamdani, S. D. Ahmed, Y.G. Ko, A new azo-Schiff base: Synthesis, characterization, biological activity and theoretical studies of its complexes. *Appl. Organomet. Chem.*, 32 (2018) e3895–e3909.
- [42] M. S. Refat, I.M. El-Deen, H.K. Ibrahim, S. El-Ghool, Synthesis and spectroscopic studies of some transition metal complexes of a novel Schiff base ligand derived from 5-phenylazo-salicyladehyde and o-amino benzoic acid. *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 65 (2006) 1208–1220.
- [43] J. L. Pratihar, P. Mandal, C.K. Lai, S. Chattopadhyay, Tetradentate amido azo Schiff base Cu(II), Ni(II) and Pd(II) complexes: Synthesis, characterization, spectral properties, and applications to catalysis in C-C coupling and oxidation reaction. *Polyhedron.* 161 (2019) 317–324.
- [44] M. Lashanizadegan, H. A. Ashari, M. Sarkheil, M. Anafcheh, S. Jahangiry, New Cu(II), Co(II) and Ni(II) azo-Schiff base complexes: Synthesis, characterization, catalytic oxidation of alkenes and DFT study. *Polyhedron*. 200 (2021) 115148.

- [45] N. Venugopal, G. Krishnamurthy, H. S. Bhojya Naik, J. D. Manohara, DNA Binding, Molecular Docking and Antimicrobial Evaluation of Novel Azo Dye Ligand and Their Metal Complexes. J. Inorg. Organomet. Polym. Mat., 30 (2020) 2608–2625.
- [46] Anitha, C.D. Sheela, P. Tharmaraj, S. Sumathi, Spectroscopic studies and biological evaluation of some transition metal complexes of azo Schiff-base ligand derived from (1-phenyl-2,3-dimethyl-4-aminopyrazol-5one) and 5-((4-chlorophenyl)diazenyl)-2hydroxybenzaldehyde. Spectrochim. Acta-Part A Mol. Biomol. Spectrosc., 96 (2012) 493–500.
- [47] M. Khadem Sadigh, M. Hasani, J. Rahimpour, Media polarity and substituent effects on the photophysical properties of some nickel complexes with azoazomethine dyes. J. Mol. Struc., 1212 (2020) 128122.
- [48] Gupta, A. K. Gaur, D. Chauhan, S. K. Thakur, V. Jeyapalan, S. Singh, G. Rajaraman, S. Venkataramani, Solid-state photochromic arylazopyrazole based transition metal complexes. *Inorg. Chem. Front.*, 9 (2022) 2315-2327.
- [49] K. K. Kamar, S. Das, C-H. Hung, A. Castin[~] eiras, M. D. Kuz'min, C. Rillo, J. Bartolome[′], Sreebrata Goswami, Design and Synthesis of a New Binucleating Ligand via Cobalt-Promoted C-N Bond Fusion Reaction. Ligand Isolation and Its Coordination to Nickel, Palladium, and Platinum. *Inorg. Chem.*, 42 (2003) 5367-5375.
- [50] P. Bhunia, U.S. Ray, J. Cheng, T.-H. Lu, C. Sinha, Nickel(II)-azido/thiocyanato complexes of 1-alkyl-2-(naphthylazo)imidazole. *Polyhedron*. 27 (2008) 319-3196.
- [51] R.T. Mahdi, A.A.M. Ali, H.A. Noaman, Preparation and Characterization of Some Metal Complexes with New Heterocyclic Schiff-Azo Ligand. J. Sci., 17 (2014) 51-58.
- [52] S. M. Mahdi, A. K Ismail, Preparation and Identification of new azo-Schiff base ligand (NASAR) and its divalent transition metal Complexes. *J. Pharm. Sci. Res.*, 10 (2018) 2175-2178.
- [53] L. Peker, S. Serin, Syn. React. Synthesis and Characterization of Some Cobalt(II), Copper(II), and Nickel(II) Complexes with New Schiff Bases from the Reaction of p□Aminoazobenzene with Salicylaldehyde. *Inorg. metal-org. chem.*, 34 (2004) 859-872.
- [54] M. Bal, G. Ceyhan, B. Avar, M. Kose, A. Kayralidi, M. Kurtoglu, Synthesis and X-ray powder di_raction, electrochemical, and genotoxic properties of a new azo-Schiff-base and its metal complexes. *Turk J Chem.*, 38 (2014) 222-241.
- [55] S. BAL, A novel Azo-Schiff base ligand and its cobalt, copper, nickel complexes: synthesis, characterization, antimicrobial, catalytic and electrochemical features. J. Sci. Tech. A Appl. Sci. Eng., 17 (2016) 315-326.
- [56] Z. Rezvani, A. R. Abbasi, K. Nejati, M. Seyedahmadian, 'Syntheses, characterization and glassforming properties of new bis[5-((4-

ndode cyloxy phenyl) a zo)-N-(4-nalkoxy phenyl)

salicylaldiminato]nickel (II) complex homologues. *Polyhedron.* 24 (2005) 1461–1470.

- [57] B.R. Kirthan, M.C. Prabhakara, H.S. Bhojya Naik, P.H. Amith Nayak, E. Indrajith Naik, Synthesis, characterization, DNA interaction and anti-bacterial studies of Cu(II), Co(II) and Ni(II) metal complexes containing azo-dye ligand. *Chem. Data Collect.*, 29 (2020) 100056.
- [58] N.M. Mallikarjuna, J. Keshavayya, M.R. Maliyappa, R.A. Shoukat Ali, Talwara Venkatesh, Synthesis, characterization, thermal and biological evaluation of Cu (II), Co (II) and Ni (II) complexes of azo dye ligand containing sulfamethaxazole moiety. *J. Mol. Struc.*, 1165 (2018) 28-36.
- [59] M. Orojloo, P. Zolgharnein, M.Solimannejad, S. Amani, Synthesis and characterization of cobalt (II), nickel (II), copper (II) and zinc (II) complexes derived from two Schiff base ligands: spectroscopic, thermal, magnetic moment, electrochemical and antimicrobial studies. *Inorg. Chim. Acta.*, 467 (2017) 227-237.
- [60] S. Amani, F. Naderi, M. Orojloo, S. kamali, R. Jannesar, Synthesis, structural characterization, in vitro biological activity, and computational quantum chemical studies of new cobalt (II), nickel (II), and copper (II) complexes based on an azo-azomethine ligand. *Polycycl. Aromat. Compd.*, 43(2022) 1-17.
- [61] M. Ikiz, E. Espir, E. Aytar, S. Karabuğa, M. Aslantas, O. Celik, M. Ulusoy, Chemical fixation of CO₂ into Cyclic Carbonates by azo-containing Schiff Bases metal complexes. *New J. Chem.*, 39 (2015) 7786–7796.
- [62] S. Burlov, V. G. Vlasenko, S. I. Levchenkov, E. V. Korshunova, S. A. Mashchenk, Y. V. Zubavichusd, A. L. Trigubd, T. V. Lifintsevae, Copper, Cobalt, and Nickel Complexes of Azomethine Compounds Containing Phenylazo Group in the Amine Fragment: Syntheses, Structures, and Magnetic Properties. R. J. Coord. Chem., 43 (2017) 753-764.
- [63] M. S. Kasare, P. P. Dhavan, L. Jadhav, S. D. Pawar, Synthesis of Azo Schiff Base Ligands and Their Ni(II), Cu(II) and Zn(II) Metal Complexes as Highly-Active Antibacterial Agents. *Chem. Select.*, 4 (2019) 10792– 10797.
- [64] S. Mahdi, R. T. M. Al-Sa'edi, Preparation and Antibacterial Activity of New Azo- Schiff Thiazol Ligand and Some of its Metal Complexes. *Nano Biomed. Eng.*, 10(2018) 369-378.
- [65] B. N. Ravi, J. Keshavayya, N. M. Mallikarjuna, Synthesis, Spectral Characterization and Pharmacological Evaluation of Ni(II) Complexes of 6□Nitro□benzothiazole Incorporated Azo Dyes. J. Inorg. Organomet. Polym. Mater., 30 (2020) 3781–3796.
- [66] K. J. Al-Adilee, S. Adnan, Synthesis and Spectral Properties Studies of Novel Hetrocyclic Mono Azo dye Derived from Thiazole and Pyridine with Some Transition Complexes. *Orient. J. Chem.*, 33(2017) 1815-1827.

- [67] V. G. Vidyaa, V. Sadasivana, Synthesis, spectroscopic characterization and biological activities of some metal complexes with new heterocyclic azodye ligand 2-(2-hydroxynaphthalen-1-yl azo)-pyridin-3-ol. *Curr. Chem. Lett.*, 12 (2023) 55–64.
- [68] D. Sengupta, P. Ghosh, T. Chatterjee, H. Datta, N. D. Paul, S. Goswami, Ligand-Centreed Redox in Nickel(II) Complexes of 2□(Arylazo)pyridine and Isolation of 2□Pyridyl-Substituted Triaryl Hydrazines via Catalytic N□Arylation of Azo-Function. *Inorg. Chem.*, 53 (2014) 12002–12013.
- [69] K. J. Al-Adilee, H. K. Dakheel, Synthesis, Spectral and Biological Studies of Ni(II), Pd(II), and Pt(IV) Complexes with New Heterocyclic ligand Derived from Azo- Schiff Bases Dye. *Eurasian J Anal Chem.*, 13(2018) 1-17.
- [70] A. A. Khandar, Z. Rezvani, K. Nejati, A. I. Yanovsky, J. M. Martinez, Syntheses and characterization of bis-[5-((4-Alkoxyphenyl-azo)-N- (n-salicyladiminato)]Nickel(II) complexes. *Acta Chim. Slov.*, 49 (2002) 733–741.
- [71] S. H. Abid, H. A. Mahdi, Synthesis, Characterization and Anticancer Activity Study of New Azo Schiff Base Derivatives and its Complexes with Copper (II) and Nickel (II) Ions. *CAJMNS*. 4 (2023) ISSN 2660-4159.
- [72] H. M. Alabidi, A. M. Farhan, N. S. Salh, A. A. J. Aljanaby, New Azo-Schiff Compounds and Metal Complexes Derived from 2-Naphthol Synthesis, Characterization, Spectrophotometric, and Study of Biological Activity. *Curr. Appl. Sci.*, 2023 23.
- [73] Y. Aritake, T. Akitsu, The role of chiral dopants in organic/inorganic hybrid materials containing chiral Schiff base Ni(II), Cu(II) and Zn(II) complexes. *Polyhedron.* 31 (2012) 278–284.
- [74] Saha, P. Majumdar, S.-M. Peng, S. Goswami, Transition-Metal-Promoted C-N Bond-Formation Processes-Low-Spin Fe^{III}, Fe^{II}, and Ni^{II} Complexes of 2-[(Arylamido)phenylazo]pyridine- X-ray Structure, Redoxand Spectroelectrochemistry. *Euro. J. Inorg. Chem.*, 12 (2000) 2631-2639.
- [75] P. P. Hankare, L. V. Gavali, B. M. Bhuse, S. D. Delekar, R. S. Rokade, Synthesis and characterization of tridentate Schiff's base derived from 5-(2'-thiazolylazo) salicylaldehyde and p-methoxy aniline and their Mn (II), Co (II), Ni (II), Cu (n), Zn (II), Cd (II) and Hg (II) complexes. *In. J. Chem.*, 43A (2004) 2578-2581.
- [76] D. Sengupta, R. Bhattacharjee, R. Pramanick, S. P. Rath, N. S. Chowdhury, A. Datta, S. Goswami, Exclusively Ligand-Mediated Catalytic Dehydrogenation of Alcohols. *Inorg. Chem.*, 55 (2016) 9602-9610.
- [77] M. Chakraborty, D. Sengupta, T. Saha, S. Goswami, Ligand Redox-Controlled Tandem Synthesis of Azines from Aromatic Alcohols and Hydrazine in Air: One-Pot Synthesis of Phthalazine. J. Orgomett. Chem., 83 (2018) 7771-7778.

- [78] K. J. AL-Adilee, A. K. Abass, A; li M. Taher, Synthesis of some transition metal complexes with new heterocyclic thiazolyl azo dye and their uses as sensitizers in photo reactions. *J. Mol. Struc.*, 1108 (2016) 378-397.
- [79] H. K. Dakheel, A. A. Habeeb, Synthesis and Characterization Studies of new Heterocyclic Azo Compound 2-[2⁻-(4,5-Dimethyl thaizolyl azo]-5-Amino Aniline with some Complexes Metal Ions. *MJPS*. 10(1) (2023).
- [80] N. Hasan, M. A. H. Shallal, H. A. Mubarak, M. M.Karhib, A. S Naje, Synthesis, Spectral, Cancer Inhibitory Activity and Antimicrobial Studies of Cobalt(II) and Nickel(II) Metal Complexes Containing Azo Derived from 2-Amino Benzimidazole. *Med. Chem. Sci.*, 6(2023) 1885-1896.
- [81] K. J. Al-Adilee, H. A.K. Kyhoiesh, Preparation and identification of some metal complexes with new heterocyclic azo dye ligand 2-[2⁻- (1- Hydroxy -4- Chloro phenyl) azo]- imidazole and their spectral and thermal studies', *J. Mol. Struc.*, 1137 (2017) 160-178.
- [82] M. A. Mahdi, L. S. Jasim, M. H. Mohamed, Synthesis, Spectral and Biological Studies of Co (III), Ni (II), and Cu (II) Complexes with New Heterocyclic Ligand Derived from Azo dye. *Sys Rev Pharm.*, 12(2021) 426-434.
- [83] N. A. R. Al-qasii1, A.T. Bader, Zaied Mosaa, Synthesis and Characterization of a Novel Azo-Dye Schiff Base and Its Metal Ion Complexes Based on 1,2,4-Triazole Derivatives. *Indones. J. Chem.*, 2023, xx (x), xx – xx.
- [84] S. S. Al-Muhanaa, A. H. Al-Khafagy, Preparation and Biological Activities of New Heterocyclic Azo Ligand and Some of Its Chelate Complexes. *Nano Biomed. Eng.*, 10(2018), 46-55.
- [85] M. Tunçel, S. Serin, Synthesis and Characterization of Copper(II), Nickel(II) and Cobalt(II) Complexes with Azo Linked Schiff Base Ligands. Inorg. *Metal-Organic, and Nano-Metal Chem.*, 35(2005), 203-212.
- [86] M. S. Refat, I. M. El-Deen, Z. M. Anwer, S. El-Ghol, Spectroscopic studies and biological evaluation of some transition metal complexes of Schiff-base ligands derived from 5-arylazo-salicylaldehyde and thiosemicarbazide. *J. Coord. Chem.*, 62 (2009) 1709–1718.
- [87] M. S. Refat, I M. El-Deen, R. R. Amin, S. El-Ghol, Spectroscopic studies and biological evaluation of some transition metal complexes of a novel Schiff base ligand derived from 5-arylazosalicyladehyde and o-amino phenol. *Toxicol. Environ. Chem.*, 92 (2010) 1093–1110.
- [88] Erdem, Eylem Y. Sari, R. Karslan, N. Kabay, Synthesis and characterization of azo-linked Schiff bases and their nickel(II), copper(II), and zinc(II) complexes. *Transition Met Chem.*, 34 (2009) 167-174.
- [89] C. Anitha, S. Sumathi, P. Tharmaraj, C. D. Sheela, Synthesis, Characterization, and Biological Activity of Some Transition Metal Complexes Derived from Novel

Hydrazone Azo Schiff Base Ligand' J. Inorg. Chem., 2011 (2011) 1-8.

- [90] A.-N. M.A. Alaghaz, M. E Zayed, S. A, Alharbi, Synthesis, spectral characterization, molecular modeling and antimicrobial studies of tridentate azo-dye Schiff base metal complexes. J. Mol. Struc., 1084 (2015) 36-45.
- [91] M. Gulcan, S. Özdemir, A. Dündar, E. I'spir, M. Kurtog'lu, , Mononuclear Complexes Based on Pyrimidine Ring Azo Schiff-Base Ligand: Synthesis, Characterization, Antioxidant, Antibacterial, and Thermal Investigations. Z. Anorg. Allg. Chem., 640 (2014) 1754-1762.
- [92] K. J. AL-Adilee, H. M. Hessoon, Synthesis, identification, structural, studies and biological activity of some transition metal complexes with novel heterocyclic azo-schiff base ligand derived from benzimidazole. J. Chem. Pharm. Res., 7(2015) 89-103.
- [93] N. Venugopal, G. Krishnamurthy, H. S. Bhojyanaik, M. Giridhar, Novel bioactive azo-azomethine based Cu (II), Co (II) and Ni(II) complexes, structural determination and biological activity. *J. Mol. Struc.*, 1191 (2019) 85-94.
- [94] Yeğiner, M. Gülcan, S. Işık, G. Ö. Ürüt, S. Özdemir, M. Kurtoğlu, Transition Metal (II) Complexes with a Novel Azo-azomethine Schiff Base Ligand: Synthesis, Structural and Spectroscopic Characterization, Thermal Properties and Biological Applications. J Fluoresc., J. Fluoresc., 27 (2017) 2239–2251.
- [95] D. Pucci, A. Bellusci, A. Crispini, M. Ghedini, M. La Deda, Synthesis and aggregation phenomena of multifunctional Schiff bases and Ni(II) complexes: an Xray investigation. *Inorg. Chimica Acta.*, 2004, 357, 495-504.
- [96] C. Anitha, C. D. Sheela,P. Tharmaraj,R. Shanmugakala, Studies on Synthesis and Spectral Characterization of Some Transition Metal Complexes of Azo-Azomethine Derivative of Diaminomaleonitrile. *International J. Inorg. Chem.*, 2013. <u>https://doi.org/10.1155/2013/436275</u>
- [97] A. Bayoumi1, A.-Nasser M.A. Alaghaz, Mutlak Sh. Aljahdali, Cu(II), Ni(II), Co(II) and Cr(III) Complexes with N₂O₂ Chelating Schiff's Base Ligand Incorporating Azo and Sulfonamide Moieties: Spectroscopic, Electrochemical Behavior and Thermal Decomposition Studies. *Int. J. Electrochem. Sci.*, 8 (2013) 9399-9413.
- [98] S. Menati, A. Azadbakht, R. Azadbakht, A. Taeb, A. Kakanejadifard Synthesis, characterization, and electrochemical study of some novel, azo-containing Schiff bases and their Ni(II) complexes. *Dyes and Pigment.*, 98 (2013) 499-506.
- [99] S. Menati, R. Azadbakht, H. A.Rudbari, G. Bruno, Synthesis and characterization of four new azo-Schiff base and their nickel(II) complexes. *Polyhedron*, 205 (2021) 115296.
- [100] M. Kurtoglu, G. Özkan, M. Köse, H. Zengin, V. McKee, A new Salen-type azo-azomethine ligand and its Ni(II), Cu(II) and Zn(II) com plexes: Synthesis, spectral

characterization, crystal structure and photolumines cence studies. *Spectrochim. Acta A.Mol and Biomol. Spectros.*, 150 (2015) 966-973.

- [101] Z. Salem, Synthesis and Study of an Azo-azomethine Dyes with N, O Donor Set of Atoms and Their Cu (II), Co (II) and Ni(II) Complexes. *Chemistry and Materials Research.*, 9(2017) ISSN 2224- 3224 (Print) ISSN 2225-0956. (Online)
- [102] Z. Shaghaghi, P. S. Kouhsangini, R, M-Rezaei, Water oxidation activity of azo-azomethine-based Ni (II), Co (II), and Cu (II) complexes. *Appl Organomet Chem.*, 35 (2021) e6103.
- [103] F. Sahan, M. Kose, C. Hepokur, D. Karakas, M. Kurtoglu, New azo azomethine based transition metal complexes: Synthesis, spectroscopy, solid state structure, density functional theory calculations and anticancer studies' *Appl Organometal Chem.*, 33(2019) e4954. https://doi.org/10.1002/aoc.4954
- [104] M. Almáši, M. Vilková, J. Bednarč ík, Synthesis, characterization and spectral properties of novel azoazomethine tetracarboxylic Schiff base ligand and its Co(II), Ni(II), Cu(II) and Pd(II) complexes. *Inorg. Chim. Acta.*, 515 (2021) 120064.
- [105] M. Lashanizadegan, H. A. Ashari, M. Sarkheil, M. Anafcheh, S. Jahangiry, New Cu(II), Co(II) and Ni(II) azo-Schiff base complexes: Synthesis, characterization, catalytic oxidation of alkenes and DFT study. *Polyhedron*. 200 (2021) 115148.
- [106] S. Chattopadhyay, P. Pattanayak, J. L. Pratihar, D. Patra, A.Burrows, M. Mohan, Regiospecific ortho-Aromatic Hydroxylation via Cyclonickelation Using Hydrogen Peroxide and Other Oxygen Donors: Synthesis of Metalloazosalophens. *Eur. J. Inorg. Chem.*, 27 (2007) 4263-4271.
- [107] L. A. Mohammed, N. I. Mahdi, R. A. B. Aldujaili Study of A New heterocyclic (Azo-Schiff base) Ligand and Their Complexation with {Co, Ni, Cu, Zn(II)}Ions. *Egypt. J. Chem.*, 63 (2020) 289- 300.
- [108] K. Nejatia, Z. Rezvanib, M. Seyedahmadian, The synthesis, characterization, thermal and optical properties of copper, nickel, and vanadyl complexes derived from azo dyes. *Dyes and Pigment.*, 83 (2009) 304–311.
- [109] S. A. A. Jawad, I. K. Kareem, Synthesis, Characterization of New Azo-Schiff Ligand Type N_2O_2 and Metal Complexes with Di Valance Nickel, Palladium and Tetra Valance Platinum. *Neuro Quantology*. 20 (2022) 62-70.
- [110] O. A. Blackburn, B. J. Coe, J. Fielden, M. Helliwell, J. J. W. McDouall, M. G. Hutchings, Nickel(II) and Palladium(II) Complexes of Azobenzene-Containing Ligands as Dichroic Dyes. *Inorg. Chem.*, 49 (2010) 9136– 9150.
- [111] E. A. Bakr, E. H. Atteya, G. B. Al-Hefnawy, H. G. El-Attar, M. M. El-Gamil, A novel azo-azomethine benzoxazole-based ligand and its transition metal (II), (III), (IV) complexes: Synthesis, characterization,

theoretical studies, biological evaluation, and catalytic application. *App. Organomet. Chem.*, 37(2023) 1-27.

- [112] S. A. Aboul-Enein, S. M. Emam, E. M. Abdel-Satar, Bivalent Metal Chelates with Pentadentate Azo-Schiff Base Derived from Nicotinic Hydrazide: Preparation, Structural Elucidation, and Pharmacological Activity. *Chem. Biodiversity*. e202201223 (2023) 1-16.
- [113] H. Khanmohammadi, K. Rezaeian, M. M. Amini, S. W. Ng, Azo-azomethine dyes with N, O, S donor set of atoms and their Ni(II) complexes: Synthesis, characterization and spectral properties *Dyes and Pigments.* 98(2013) 557-564.
- [114] L. K. Abdul Karem, F. H. Ganim, R. K. Rahem Al-Shemary, Synthesis, Characterization, Structural, Thermal, Pom studies, Antimicrobial DNA Cleavage activity of A New Schiff Base-Azo Ligand and its complexion with selected metal ions. *Biochem. Cell. Arch.*, 18(2018) 1437-1448.