ACADEMIA ONE
PEER REVIEWED JOURNALS
Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6

Synthesis and spectroscopic characterization of the new ligand 2-phenyl-5-[(2E)-2-(thiophen-2-ylmethylidene)hydrazinyl]-1,3,4-oxadiazole and its complexes with cobalt[II] and nickel[II]

Ali Hussein Mohammed Alwan
General Directorate of Education of Thi- Qar governorate - Specialist Supervision Department
al.hu_ch@utq.edu.iq

Abstract
The present work included a series of steps that can be sequenced into four steps: the first is the conversion of the ester to hydrazide by replacing the O-R group of the ester with the NH-NH2 group. The second and most important is the cyclization reaction to form thiol oxadiazole. The third step is the preparation step for Schiff-Biss reactions by replacing the S-H group with the NH-NH2 group. The fourth and final step is the reaction of hydrazide oxadiazole with aldehyde to form an important functional group in the complexation processes, which is the azomethine group N=CH. The synthesized ligand and the metals nickel (II) and cobalt (II) underwent complexation reactions. Melting point readings and thin layer chromatography(TLC) were used to track the produced compounds' purity . The suggested chemical structural formulas were validated using mass spectra, 1H-NMR, 13C-NMR, and FT-IR.
Keywords; 1,3,4- oxadiazole, coordination, Schiff-base

Introduction:
A flexible heterocyclic molecule, 1,3,4-Oxadiazole reveals a lot of chemical characteristics. As evidenced by using the synthesis and characterization of binary answers comprising 1, three,4-oxadiazole derivatives in diverse solvents, which includes DMF and DMSO, where thermodynamics became examined, it's miles distinguished by means of its capability for structural alteration [1]. Furthermore, the compound's ability as a precursor to novel biomaterials has been highlighted [2]. Derivatives of one,3,4-oxadiazole are useful in medicinal chemistry for the remedy of plenty of illnesses because of their strong binding skills to distinct enzymes and receptors and their extremely good healing potential [3]. Additionally, depending at the polarity of their quit companies, they show terrific thermal balance and varied liquid crystalline behaviors [4]. Generally talking, 1,3,4-oxa diazole and its derivatives have a wide variety of chemical traits that permit for their utility in several industries [5].

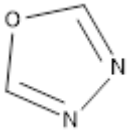


Figure 1: 1,3,4-oxadiazole

Because of its wonderful structural traits, 1,3,4-Oxadiazole has a huge variety of biological capabilities that allow effective binding to enzymes and receptors, resulting in quite a few bioactivities [6]. Derivatives of 1,3,4-Oxadiazole had been instrumental inside the development of healing retailers with anti-inflammatory, antibacterial, antifungal, antiviral, anticancer, and antioxidant residences [7], which makes them beneficial for protecting plants [8] and for human and animal fitness. In order to enhance their effectiveness and pharmacological efficacy, those compounds have so drawn a variety of take a look at interest [9]. The promise of 1,3,4-oxadiazole derivatives in remedy development and research has been showed by way of studies in their interactions with different.

Synthesis of Benzo hydrazide (A)

ACADEMIA ONE
PEER REVIEWED JOURNALS
Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6

In a round-bottom container, (25 mL, 0.2 mole) of methyl benzoate and (10 mL, 0.2 mole) of hydrazine monohydrate were refluxed in 80 mL of an absolute ethanol for six hours. The solution was then put into freezing water, forming a white precipitate that was filtered and crystallized in 100% ethanol (Eq.1). TLC analysis revealed that the solid (A) had a 95% yield, a white hue, and a melting point of 121 °C [16].

Synthesis: [of 5-phenyl-1,3,4-oxadiazole-2-thiol] (B)

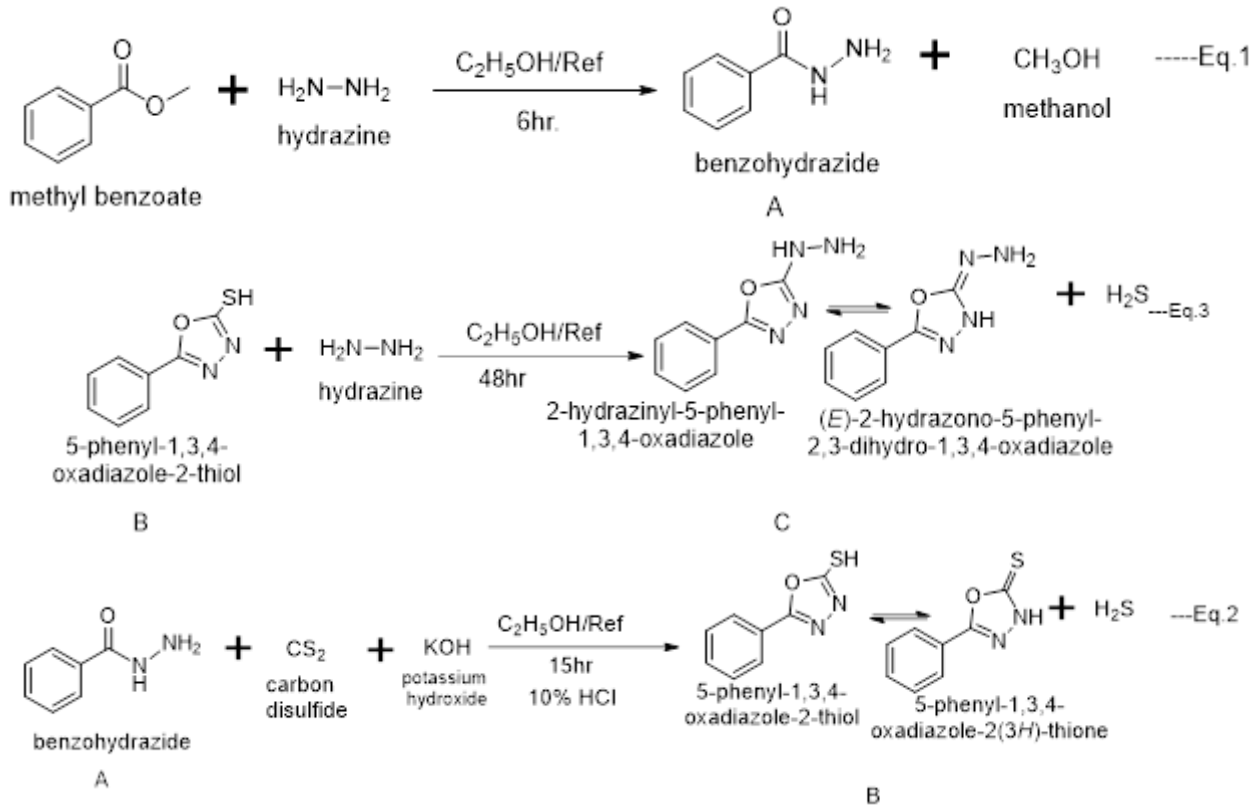
(7.8 g, 0.05 mol) of Benzo hydrazide (A), (2.8 g, 0.05 mole) of KOH and (3 mL, 0.05 mole) of carbon disulfide (CS_2) were mixed and refluxed in (70 mL) of an absolute ethanol (Eq.2), The precipitate was filtered, the solid product was recrystallized from 100% ethanol, and the solvent was evaporated and acidified with 10% hydrochloric acid. TLC was used to analyze the yellowish white solid (B), which had a yield of 92.3% and a melting point of 220 °C [17].

Synthesis: [of 2-hydrazinyl-5-phenyl-1,3,4-oxadiazole] (C)

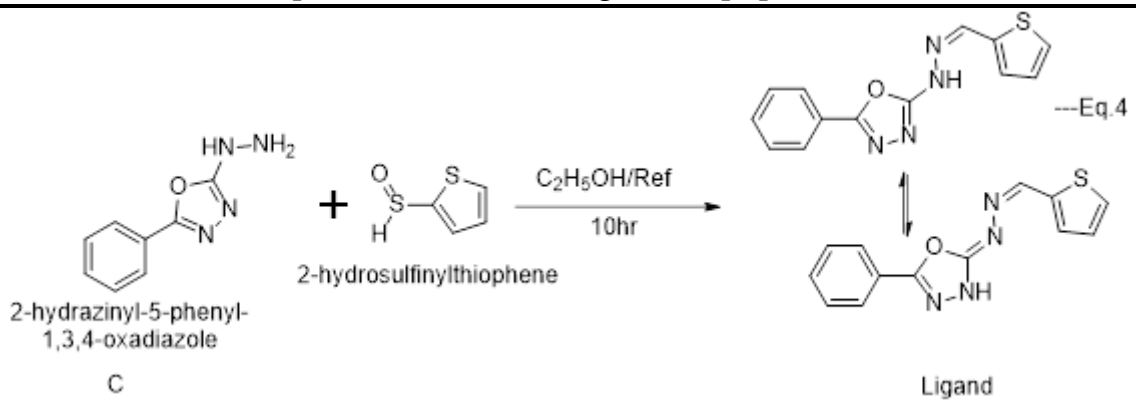
In the round bottom, (4.5 g, 0.25 mole) of 5-phenyl-1,3,4-oxadiazole-2-thiol (b) and (2.5 mL, 0.05 mole) of hydrazine monohydrate were refluxed in (30 mL) of an absolute ethanol as solvent for 48 h(Eq.3). A white solid of product appeared. After filtering and recrystallizing the precipitate from 100% ethanol, which has a melting point of 226 °C and a yield of 72%, it was subjected to TLC analysis [17].

Synthesis: [of 2-phenyl-5- [(2E) -2 -(thiophen-2- ylmethylidene) hydrazinyl] -1,3,4-oxadiazole] (Ligand)

Using 30 mL of pure ethanol, 2.5 g 0.014 mol of 2-hydrazinyl-5-phenyl-1,3,4-oxazadiazole (C) and 1.6 mL 0.014 mol of thiophene-2-carbaldehyde were condensed to create the ligand. The combination was then refluxed for 10 hours (Eq.4) while being observed by TLC. After the ligand was precipitated, filtered, and recrystallized from 100% ethanol, a light brown ligand with a 68% yield that melted at 242 °C was obtained and subjected to TLC analysis.



Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6



Preparation of complexes:

The complexes were created by mixing 0.001 mol of the ligand with salts (COCl2.6H2O, NiCl2.6H2O) in 40 milliliters of 100% ethanol, then refluxing the mixture for two hours. To get rid of any unreacted salts or ligand, the precipitate was filtered and repeatedly washed with aqueous ethanol. The resulting complexes were then dried and examined by TLC. Table 1.

Results and discussion

Table1. physical poetries

no	Compound	Formula	M.Wt	Mp °C	Color	Yield %
1	Ligand	C13H10N4OS	270	242	Light-brown	68%
2	[CoLCl2]	NiC13H10Cl2N4OS	399	236-238	Bale-brown	72%
3	[NiLCl2]	CoC13H10Cl2N4OS	400	>300	Dark-brown	80%

[FT-IR] spectral

The synthesized ligand and its complexes were subjected to FT-IR employing CsI for complexes and KBr disc for ligands. As a result of (υNH) (3119) cm-1, (υCH-Aromatic) (3039) cm-1, (υC=N) (1558) cm-1, (υC=C) (1446) cm-1, (υC-O-C) sym (1253) cm-1, and (υ C-O-C) asy (1292) cm-1, respectively, the loose ligand (L) displayed prominent bands.There are now new bands in existence. assigned to the coordinated (M-N) and (M-Cl) bonds, and are located in the corresponding regions of (690-686) cm-1 and (312-239) cm-1. This suggested that the (N) and (Cl) atoms were responsible for the coordinate. As depicted in figures (2-4),

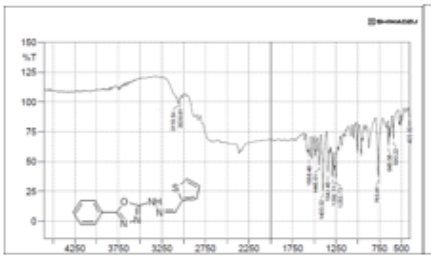


Fig 2;FT-IR of Ligand

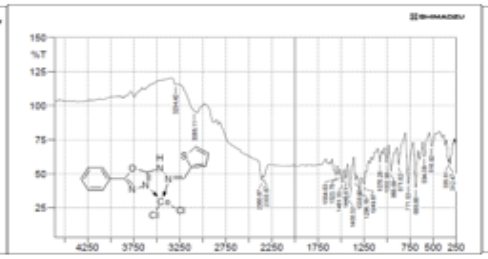


Fig 3;FT-IR of Co(II) complex

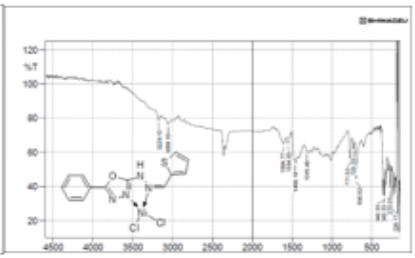


Fig 4;FT-IR of Ni(II) complex

^{1}H-NMR spectrum

ACADEMIA ONE
PEER REVIEWED JOURNALS
Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6

As seen in the figure below [fig.5], the ligand's 1H-NMR spectrum revealed signals at (13.95 ppm, H) NH proton and [(7.30-8.04) ppm, 8H] due to chemical shifts of aromatic ring protons connecting the oxadiazole ring and proton of the azomethen group.

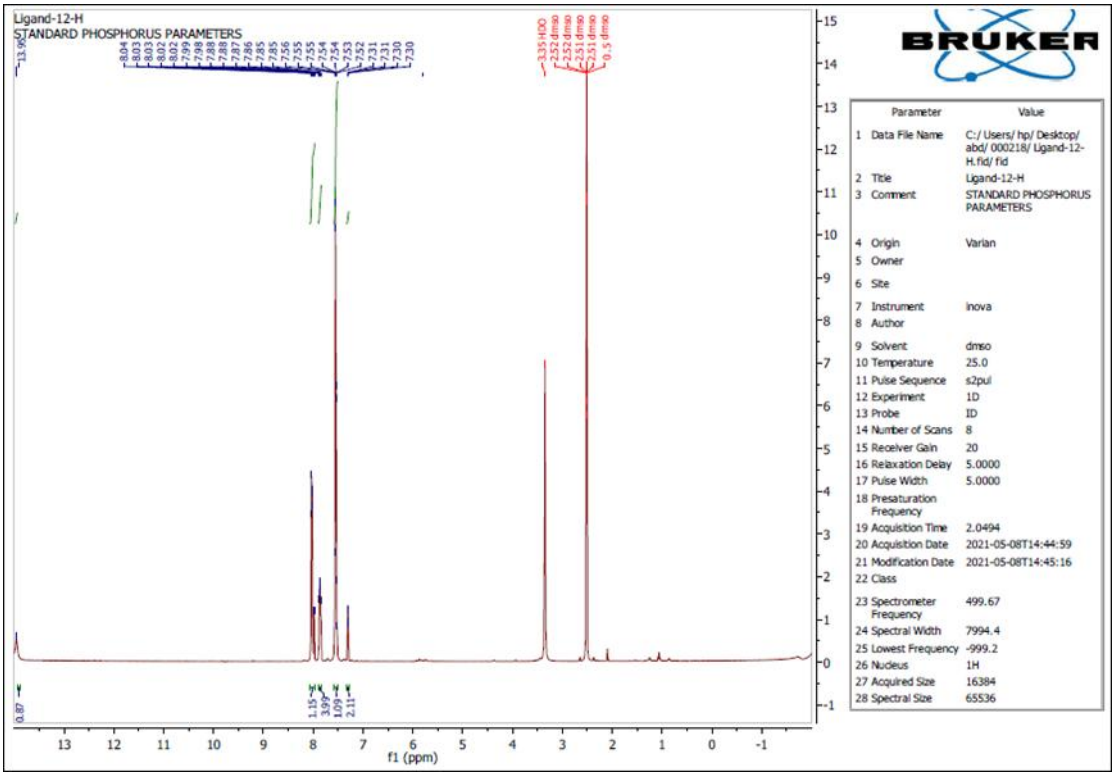


Fig 5;1H-NMR of Ligand

Mass spectra :
The molecular ion peak at 270 m/z in the ligand's mass spectrum aligned with the chemical formulation C13H10N4OS. Pase peak at 174 m/z [C8H6N4O]• .Other peaks ware because of the following fragments like [C8H5N2O]• =a hundred forty five m /z , [C8H6N3O]• =160 m /z , [C4H3S]• =83 m/z , [C5H5S]• =ninety six m/z , [C5H4NS]• =one hundred ten m/z , [C5H5N2S]• =a hundred twenty five m/z , [C7H5N4OS]• =193 m/z , [C7H5O]• =a hundred and five m/z, [C6H6]• =seventy seven m/z,[C4H3]• =fifty one m/z .

The Co (II) complexes' mass spectrum revealed molecular ion peaks at 399 m/z that resembled [Co(L) Cl2]• stoichiometry. Given that one and two chlorine atoms were lost, respectively, this complex verified the existence of any additional fragmentation peaks at 364 m/z and 329 m/z.

The Ni(II) complexes' mass spectrum revealed molecular ion peaks at 400 m/z that resembled the [Ni(L)Cl2]• stoichiometry. The loss of one and two chlorine atoms, respectively, caused this complex to display every other fragmentation peak at 364 m/z and 329 m/z.

ACADEMIA ONE
PEER REVIEWED JOURNALS
Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6

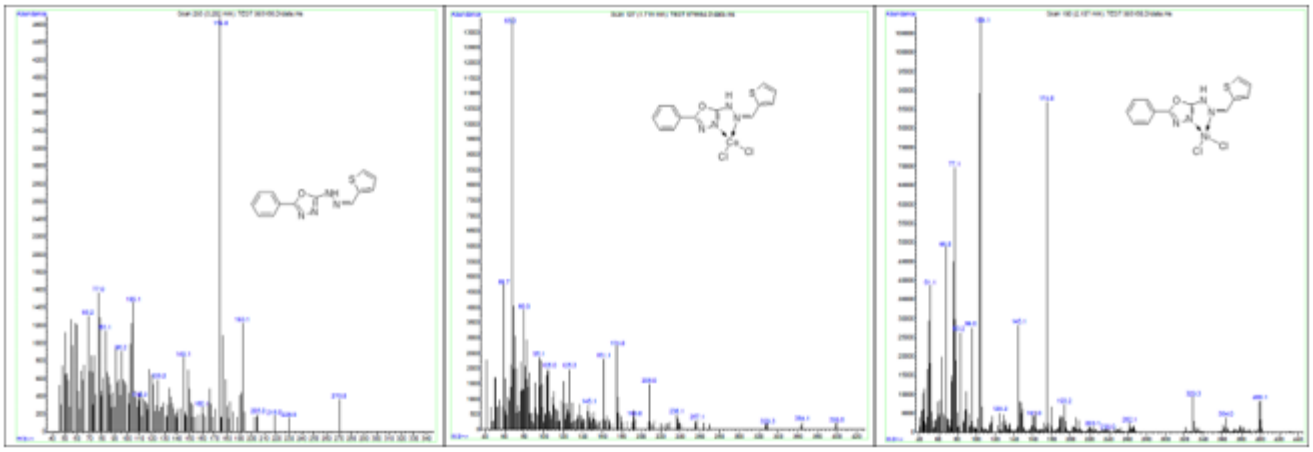


Fig 6;Mass of Ligand Fig7;Mass of Co(II) complex Fig8;Mass of Ni(II) complex

Theoretical study

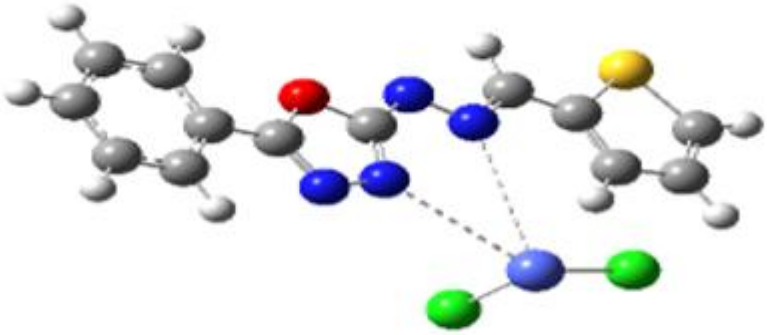
At the B3LYP level of their ground country, as depicted in Figure 8, full geometry optimization of the ligand and its complexes with co(II) and Ni(II) ions was performed using density functional theory (DFT). Figure 2 also provides the ligand and its complexes' HOMO and LUMO border orbitals. Direct access to every parameter pertaining to the molecular geometry is made possible by the optimized systems. The following equations [18-21] in table (2) were used to predict the gap energies ΔE, the electronic chemical potentials μ, the chemical hardness η, electronegativities (χ), absolute softness (σ), international electrophilicity (ω), and international softness (S) for the ligand and its complexes.

Table (2). Quantum chemical parameters.

Parameters	L1	$Co(L)Cl_2$	$Ni(L)Cl_2$	Equations
E_{HOMO} (eV)	-7.2805	-6.4807	-5.6644	$\Delta E = E_{LUMO} - E_{HOMO}$
E_{LUMO} (eV)	-5.3185	-5.0399	-4.1209	$\chi = -\frac{(EHOMO + ELUMO)}{2}$
Δ E (eV)	1.9619	1.4408	1.5435	$\eta = \frac{(ELUMO - EHOMO)}{2}$
χ (eV)	6.2995	5.7603	4.8927	$\sigma = \frac{1}{\eta}$
η (eV)	0.98095	0.7204	0.7728	$S = \frac{1}{2\eta}$
σ $(eV)^{-1}$	1,0194	1.3881	1.2957	$\mu = -\chi$
μ (eV)	-6.2995	-5.7603	-4.8927	$\omega = \frac{\mu}{2\eta}$
S $(eV)^{-1}$	0.5097	0.6941	0.6469	
ω (eV)	-4.5722	-3.9979	-3.1656	

Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6

Ligand

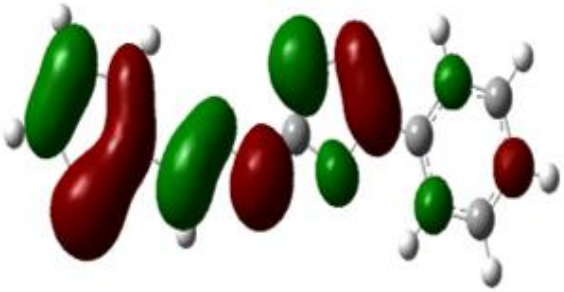


$[Co(L)Cl_2]$

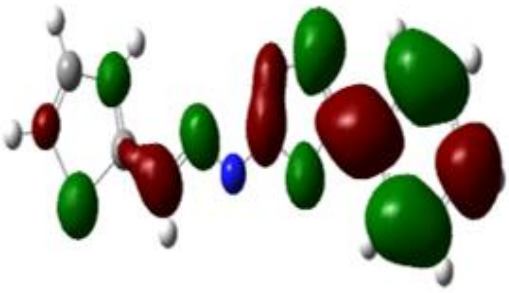
$[Ni(L)Cl_2]$

Fig9. Geometric optimization of the ligand and its complexes

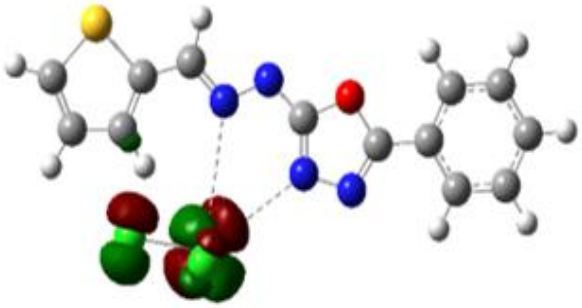
Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6



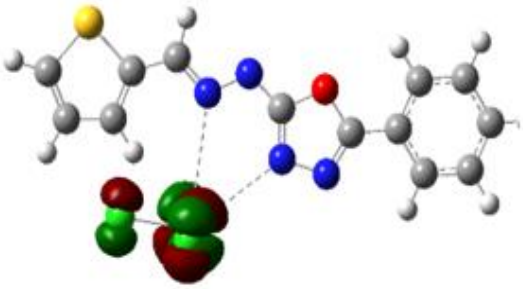
HOMO of Ligand



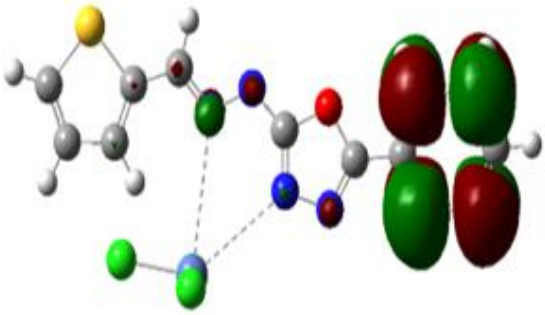
LUMO of Ligand



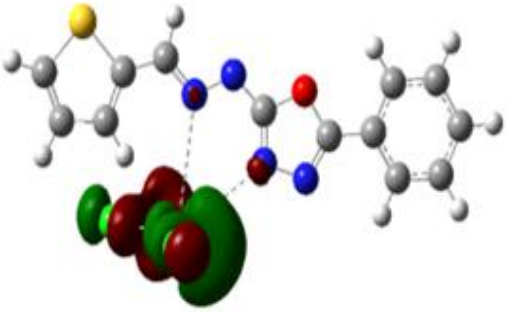
HOMO of $[Co(L)Cl_2]$



LUMO of $[Co(L)Cl_2]$



HOMO of $[Ni(L)Cl_2]$



LUMO of $[Ni(L)Cl_2]$

Fig.9 HOMO and LUMO orbital of the ligand and its complexes

References

1- Kizhnyaev, V.N., Pokatilov, F.A. and Vereshchagin, L.I., 2008. Carbochain polymers with oxadiazole, triazole, and tetrazole cycles. Polymer Science Series C, 50, pp.1-21 .
2- Pace, A., Buscemi, S., Piccionello, A.P. and Pibiri, I., 2015. Recent advances in the chemistry of 1, 2, 4-oxadiazoles. Advances in Heterocyclic chemistry, 116, pp.85-136 .
3- Verma, G., Khan, M.F., Akhtar, W., Alam, M.M., Akhter, M. and Shaquiquzzaman, M., 2019. A review exploring therapeutic worth of 1, 3, 4-oxadiazole tailored compounds. Mini Reviews in Medicinal Chemistry, 19(6), pp.477-509 .
4- Han, J., 2013. 1, 3, 4-Oxadiazole based liquid crystals. Journal of Materials Chemistry C, 1(47), pp.7779-7797 .
5- Pitasse-Santos, P., Sueth-Santiago, V. and Lima, M.E., 2018. 1, 2, 4-and 1, 3, 4-Oxadiazoles as Scaffolds in the Development of Antiparasitic Agents. Journal of the Brazilian Chemical Society, 29(3), pp.435-456.
6- Gupta, O., Chawla, G. and Pradhan, T., 2024. 1, 3, 4-Oxadiazole Scaffold in Antidiabetic Drug Discovery: An Overview. Mini Reviews in Medicinal Chemistry, 24(20), pp.1800-1821.
7- Kurup, S.S. and Jat, R.K., 2023. A Review Exploring Therapeutic Effect of 1, 3, 4-Oxadiazole Compounds. Journal of Drug Delivery and Therapeutics, 13(10), pp.147-148.
8- Rahul, K., Amarnath, D.P., Narayanan, H. and Das, A., 2017. The biological potential and synthetic diversity of 1, 3, 4-oxadiazole multiplexed with various heterocyclic compounds. Journal of the Turkish Chemical Society Section A: Chemistry, 10(2), pp.267-276.
9- Biernacki, K., Daśko, M., Ciupak, O., Kubiński, K., Rachon, J. and Demkowicz, S., 2020. Novel 1, 2, 4-oxadiazole derivatives in drug discovery. Pharmaceuticals, 13(6), p.111 .
10- de Freitas Filho, J.R., de Freitas, J.J.R., de Freitas, J.C.R., de Souza Ramos, C., de Souza, F.A.M., Ramos, J.F., Tavares, R. and de Oliveira, D.E.T.B., Synthesis, Biological Activity and Applications of 1, 2, 5-Oxadiazol: A Brief Review.
11- Wang, J.J., Sun, W., Jia, W.D., Bian, M. and Yu, L.J., 2022. Research progress on the synthesis and pharmacology of 1, 3, 4-oxadiazole and 1, 2, 4-oxadiazole derivatives: a mini review. Journal of Enzyme Inhibition and Medicinal Chemistry, 37(1), pp.2304-2319 .
12- Homocianu, M. and Airinei, A., 2016. 1, 3, 4-Oxadiazole derivatives. Optical properties in pure and mixed solvents. Journal of fluorescence, 26, pp.1617-1635 .
13- Chaudhary, T. and Upadhyay, P.K., 2023. Recent advancement in synthesis and bioactivities of 1, 3, 4-oxadiazole. Current Organic Synthesis, 20(6), pp.663-677.
14- Kumari, S., Kumar, R., Mazumder, A., Salahuddin, Saxena, S., Sharma, D., Joshi, S. and Abdullah, M.M., 2022. Recent updates on synthetic strategies and biological potential of 1, 3, 4-oxadiazole. Letters in Organic Chemistry, 19(9), pp.689-704.
15- Salassa, G. and Terenzi, A., 2019. Metal complexes of oxadiazole ligands: An overview. International journal of molecular sciences, 20(14), p.3483.
16- Hassoon, Z. M., Alkhayyat, I. A., Alsanafi, A. M. I. and Flifel, I. A. (2024) “Synthesis, Characterization & Biological Survey of Novel 1,2,4-Triazole Schiff Base Derivatives”, Central Asian Journal of Theoretical and Applied Science, 5(5), pp. 469-482. Available at: https://cajotas.centralasianstudies.org/index.php/CAJOTAS/article/view/1496 (Accessed: 20November2024).
17- Alsanafi, A.M. and Flifel, I.A., 2021. Syntheses, Characterization of a New Legend 2-Hydroxy-N'-(5-Phenyl-1, 3, 4-Oxadiazol-2-yl) Benzohydrazide with Some Transition Metal Complexes. Annals of the Romanian Society for Cell Biology, 25(6), pp.18167-18182 .
18- Hassan, M., El-Faham, A., Barakat, A., Haukka, M., Tatikonda, R., Abu-Youssef, M. A., Soliman, S. M., & Yousri, A. (2024). Synthesis, X-ray Structure, Cytotoxic, and Anti-Microbial Activities of Zn (II) Complexes with a Hydrazono s-Triazine Bearing Pyridyl Arm. Inorganics, 12(7), 176. https://doi.org/10.3390/inorganics12070176.
19- Khattab, S. M., Altowyan, M. S., El-Faham, A., Barakat, A., Haukka, M., Abu-Youssef, M. A., & Soliman, S. M. (2024). A New Bromo-Mn (II) Complex with 1, 3, 5-Triazine Derivative:

ACADEMIA ONE
PEER REVIEWED JOURNALS
Open Herald: Periodical of Methodical Research
Volume 3, Issue 3, March, 2025
ISSN (E): 2810-6385
Website: https://academiaone.org/index.php/6

Synthesis, Crystal Structure, DFT and Biological Studies. Inorganics, 12(11), 284. https://doi.org/10.3390/inorganics12110284

20- Boshra, M., Adly, O. M., Abdelrhman, E. M., Eid, M. F., & Samy, F. (2024). Novel Cu (II) and Zn (II) Nanocomplexes Based on 5, 6-Diphenyl-1, 2, 4-Triazine: Preparation, Spectroscopic, TD-DFT Calculations, Molecular Docking and Solvatochromic Studies. Applied Organometallic Chemistry, e7752. https://doi.org/10.1002/aoc.7752

21- Ali, S. H., Al-Redha, H. M. A., Sachit, B. A., Antibacterial activity of some Salen metal complexes. IOP Conference Series: Materials Science and Engineering, 2020, 5, p. 052016 https://doi.org/10.1088/1757-899x/928/5/052016.