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Nickel(II)-dithiocarbamate Mixed ligand Complexes: Synthesis, Characterization and Anti-bacterial Properties

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ABSTRACT

Six homoleptic (1 and 2) and heteroleptic (3-6) nickel(II) chelates comprising dithiocarbamate and triphenylphosphine ligands were prepared and elucidated by various spectroscopic analysis. The dithiocarbamate ligand was bonded in a bidentate chelation manner via the sulfur atoms to furnish a square planar geometry. The antibacterial activity of mixed Ni(II) dithiocarbamate and triphenylphosphine ligand chelates was obtained against three bacterial strains. Among the complexes, the heteroleptic nickel(II) chelates comprising mixed dithiocarbamate and triphenylphosphine ligands (6) manifested the highest antibacterial activity against all tested bacteria. Our study demonstrated that the heteroleptic nickel(II) chelates might be further elaborated and improved for enhanced antimicrobial applications.

Keywords: Nickel, dithiocarbamate, biphenyl, ligand, biological activity.

INTRODUCTION

Dithiocarbamates ($R_2NCSS–$) are unique amide compounds structurally characterised by a functional C=S bond and their ability to design stable chelates with a variety of cations, particularly transition metals[1-3]. They have also emerged as a versatile class of ligands often employed to anchor metals in a variety of applications in materials chemistry[3-7]. Since their discovery early in the 19th century, a vast number of $R_2NCSS–$ligands and complexes as diverse as the metals and nonmetals constituting their core structure have fascinated chemists[8,9]. A general perception of $R_2NCSS–$ complexes is that they act solely as precursors for the formation of metal chalcogenides[8]. In view of the rapid advances in chemistry and applications of $R_2NCSS–$, there is a rising interest in obtaining high-purity $R_2NCSS–$, as well as the additional need for enhanced facile synthetic routes. These research efforts have been directed mainly at

new ligand design, improved preparation methods, and better structures towards better performance as stabilisers[1-14].

R_2NCSS- are considered valuable auxiliary ligands due to their strong σ-donating thiolate group(s) accompanied by a moderate π-back-bonding ability[1-3]. These unique properties often lead to the formation of unconventional homoleptic and heteroleptic complexes[16-32], many of which are of size or shape well suited for a variety of applications. This, together with the increasing academic and industrial interest in R_2NCSS-complexes, warrants a deeper understanding of the coordination character and nature of the R2NCSS-metal bond[1-7]. Another wide range of applications can be seen including, but not limited to, in the fields of agriculture (as biocides such as the diethyldithiocarbamates), material science, medicine (as antabuse), photo-sensor-based polymers, and organic synthesis[9-14]. Critically, the produced insight could present new tactics in the rational design of these unconventional stress manifolds and, thus, their more efficacious applicability. There has consequently been a concerted effort to probe the nature of this coordination unit, in particular focusing on the detail of the metal–sulfur bonding interaction[1,2,32,33].

This work continues previous work on the synthesis of mixed ligand chelates comprising R_2NCSS-ligands and other ligands such as phosphines, amines, etc[16-26]. Herein, we utilised the $R_2NCSS-Ni(II)$ complex of [1,1'-biphenyl]-4-amine or 4-(4-methylphenyl)aniline as a foundation to synthesize various mixed ligand complexes that include triphenylphosphine and additional ligands. Furthermore, evaluate the antibacterial activity of the prepared chelates against three bacterial pathogens.

EXPERIMENTAL

Complexes $[Ni(L^1)_2]$ (1) or $[Ni(L^2)_2]$(2)

These complexes were achieved according to the one-pot producer as follows:

A synthetic pathway involving three components for dithiocarbamates[34] was utilised to synthesis the ligand. In brief, [1,1'-biphenyl]-4-amine (0.196 g, 1.000 mmol) (for ligand L^1H) or 4-(4-methylphenyl)aniline (0.183 g, 1.000 mmol) (for ligand L^2H) reacted with CS_2 (0.076 g, 1.000 mmol) at 0-5°C for 0.5 hours. Next, KOH (0.056 g, 1.000 mmol) was introduced, and the solution is lifted to stir for three hours to provide a yellowish-white solution. Then, $NiCl_2•6H_2O$ (0.119 g, 0.500 mmol) in (15 mL) H_2O was introduced with stirring for three h to give a light green ppt formed. The produced solid was isolated, rinsed with H_2O and then with $(C_2H_5)_2O$ ether.

Synthesis of complexes (3-6)

These complexes were prepared according to the one-pot producer as follows:

A mixture of complexes $[Ni(L^1)_2]$(1) (0.50 mmol) or $[Ni(L^2)_2]$(2) (0.001 mol), $NiCl_2•6H_2O$ (0.50 mol), triphenylphosphine (PPh_3) (1.00 mmol) and potassium thiocyanate (KSCN) (1.0 mol) was heated at 69°C for three h in MeOH (50 mL). The produced material was isolated, washed with distilled water and then with $(C_2H_5)_2O$ ether. The physical properties, yield percentage, conductivity and elemental analysis are listed in Table 1.

Biological activity studies

The antibacterial efficacy of nickel(II) complexes with dithiocarbamate and other ligands was assessed toward three bacterial species: *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Escherichia coli*. The efficacy of the Ni(II)-dithiocarbamate complexes was evaluated using the agar disc diffusion method established by Biemer[35], with data compared to streptomycin as the typical antibiotic.

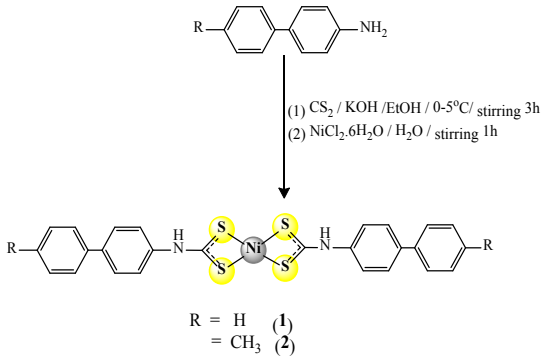
RESULTS AND DISCUSSION

Chemistry and the synthesis protocols

Complexes (1) and (2) were prepared by one-pot method as follows:

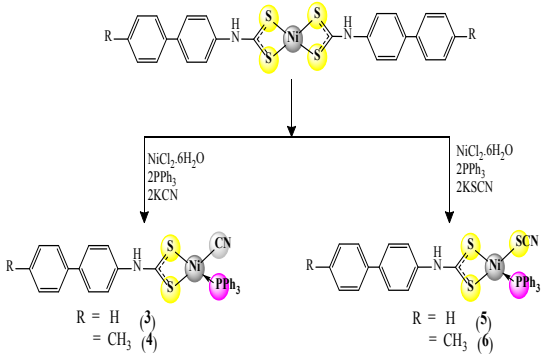
First step: The solution of [1,1'-biphenyl]-4-amine dithiocarbamate (L^1Na) or 4-(4-methylphenyl) aniline dithiocarbamate (L^2Na) was prepared by the reaction of [1,1'-biphenyl]-4-amine or 4-(4-methylphenyl)aniline with CS_2 in presence NaOH as a base below 5°C.

Second step: Nickel chloride hexahydrate was introduced to the fresh solution of [1,1'-biphenyl]-4-amine dithiocarbamate (L^1Na) or 4-(4-methylphenyl)aniline dithiocarbamate (L^2Na) in (1:2) molar ratio to afford complexes (1) and (2) as a product in good yield 81% and 87%, respectively (for more details and information see Scheme 1).



Scheme 1. The route for the preparations of complexes (1) and (2)

Refluxed a mixture of equivalent moles of complex (1) or complex (2) and nickel chloride hexahydrate with two equivalent moles of triphenylphosphine and potassium thiocyanate or potassium cyanide afforded complexes of the type $[Ni(SCN)(L)(PPh_3)]$ (3,4) and $[Ni(CN)(L)_2(PPh_3)]$ (5,6) (Scheme 2) in good yields (75- 90%). The products are soluble in DMSO and DMF, warm $CHCl_3$ or warm CH_2Cl_2 and partially soluble in THF. We endeavored to obtain a single crystal for X-ray analysis but were unsuccessful. Consequently, it was impossible to investigate this kind of material by crystallography.



Scheme 2. Synthesis of complexes (3) to (6)

The novel chelates were analysed through conductivity measurements, chemical analysis (CHN), infrared spectroscopy, UV-visible spectra, magnetic susceptibility, and NMR (1H and ^{31}P) spectra. The molar conductivity of each complex has been studied in solution of DMSO (10^{-3} M). The low molar conductivity measurements, between 5.9 and 17.6 $ohm^{-1}•cm^2•mol^{-1}$, indicate that all complexes behave as non-electrolytes. The CHN analysis supported the proposed geometries of the synthesised chelates. The data for characterisation can be found in Table (1).

Table 1: Spectral data of Ni(II) complexes

Seq.	Complexes	Colour	m.p.(C°)	Yield%	Λ (ohm^{-1}. cm^2. mol^{-1}) in DMSO	C	H	N
1	$[Ni(L^1)_2]$	Light green	167-168	81	11.2	57.05 (57.23)	3.68 (3.89)	5.12 (5.32)
2	$[Ni(L^2)_2]$	Greenish yellow	136-139	87	5.9	58.44 (58.38)	4.20 (4.43)	4.87 (4.94)
3	$[Ni(SCN)(L^1)_2(PPh_3)]$	Brownish-yellow	278-280	79	7.8	61.65 (61.80)	4.04 (4.30)	4.49 (4.78)
4	$[Ni(SCN)(L^2)_2(PPh_3)]$	Green	290-291	84	10.1	62.18 (62.29)	4.27 (4.20)	4.39 (4.53)
5	$[Ni(CN)(L^1)_2(PPh_3)]$	Brownish-yellow	213-214	75	8.9	62.18 (62.29)	4.27 (4.20)	4.39 (4.53)
6	$[Ni(CN)(L^2)_2(PPh_3)]$	Green	193-195	90	12.9	65.47 (62.29)	4.50 (4.20)	4.63 (4.53)

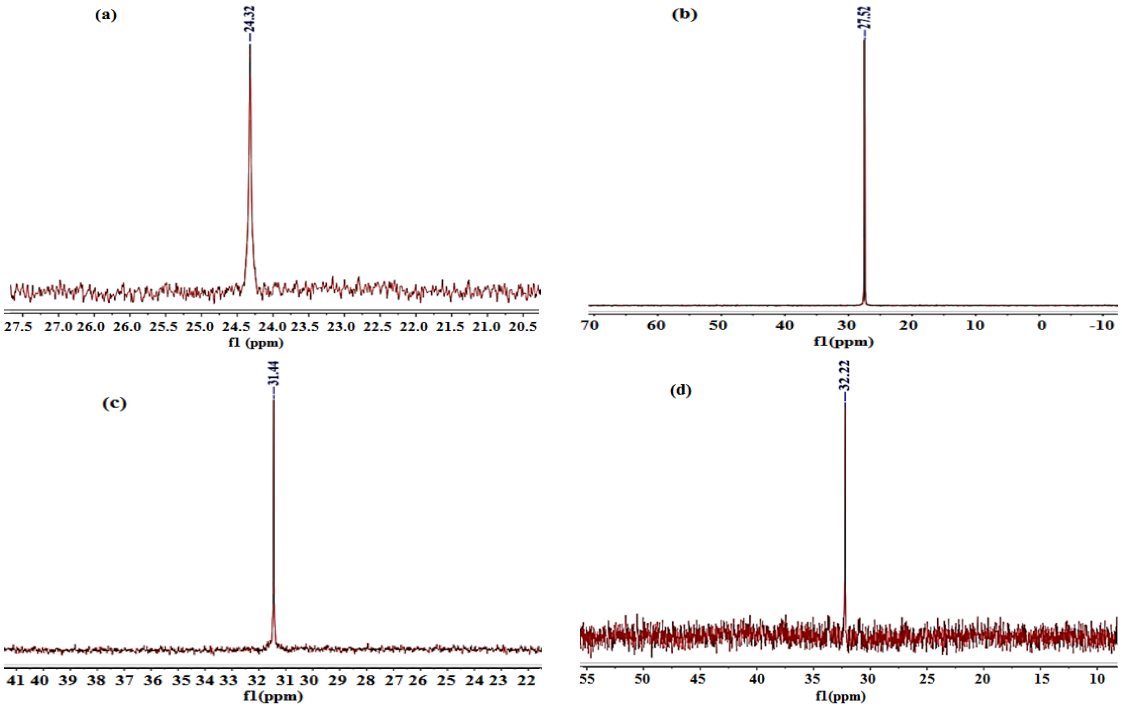


Fig. 1. 31P NMR spectra of the (a) [Ni(SCN)(L^1)$_2$(PPh$_3$)] (3); (b) [Ni(SCN)(L^2)$_2$(PPh$_3$)] (4); (c) [Ni(CN)(L^1)$_2$(PPh$_3$)] (5) and (d) [Ni(CN)(L^2)$_2$(PPh$_3$)] (6)

Spectroscopic data

The ^{31}P-{^{1}H} NMR spectra of products of the reaction of [Ni(L)$_2$] (1 and 2) with triphenylphosphine in presence nickel chloride and KSCN or KCN (Fig. 1a-d) displayed a single peak at δP = 24.32 ppm, 27.52ppm, 41.44ppm and 32.22ppm, for the complexes (3-6), correspondingly. This indicates the presence of a singular isomer each.

The ^{1}H NMR spectrum of the dithiocarbamate chelate (1) displayed the protons of the Ph rings as three separated peaks, the first peak as a multiplet peak at δH 7.32ppm (6H), the second as a doublet peak δH 7.50ppm ($^3J_{HH}$ 8:00Hz, 2H), and the third peak also as doublet peak δH 7.72ppm ($^3J_{HH}$ 8:00Hz, 2H), whereas the proton of NH group displayed as a singlet peak at δH 12.88 ppm. Complex (2) (Fig. 2) displayed the distinct four separated doublet peaks for the Ph rings, the first peak as at δH 7.67ppm ($^3J_{HH}$ 8:00Hz, 2H), the second at δH 7.41ppm ($^3J_{HH}$ 8:00Hz, 2H), the third at δH 7.24ppm ($^3J_{HH}$ 8:00Hz, 2H), and the fourth at δH 7.04ppm ($^3J_{HH}$ 8:00Hz, 2H), whereas the proton of the NH and methyl groups displayed as a singlet peak at H 1.93 ppm and H 12.41 ppm, respectively.

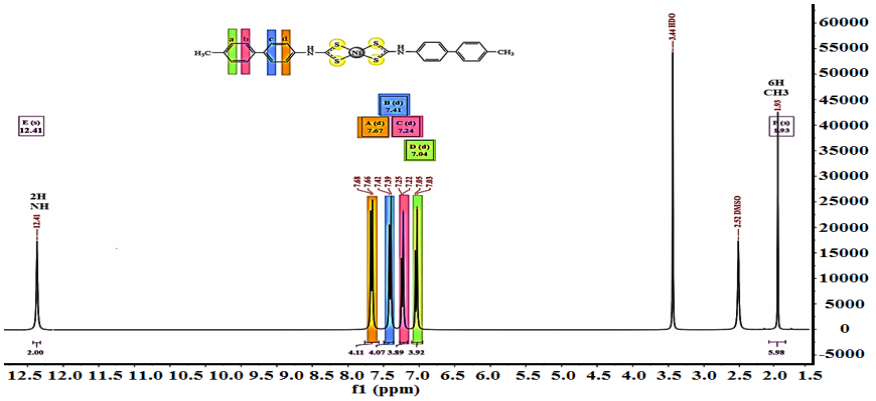


Fig. 2. ^{1}H NMR spectrum of the [Ni(L^2)$_2$] (2) complex

In the case of the dithiocarbamate complexes (3-6)(Fig. 3) displayed the protons of the

Ph in the dithiocarbamate and triphenylphosphine ligands as multiplet peaks at δH 7.56ppm, δH 7.64ppm, δH 7.49ppm, and δH 7.61ppm, whereas the proton of the NH group displayed as a singlet peak at δH 12.71ppm, δH 12.39ppm, δH 12.43ppm and δH 12.28ppm, for the four complexes, respectively. At the same time, the methyl group displayed a singlet peak at δH 2.09 ppm and δH 2.01 ppm, respectively.

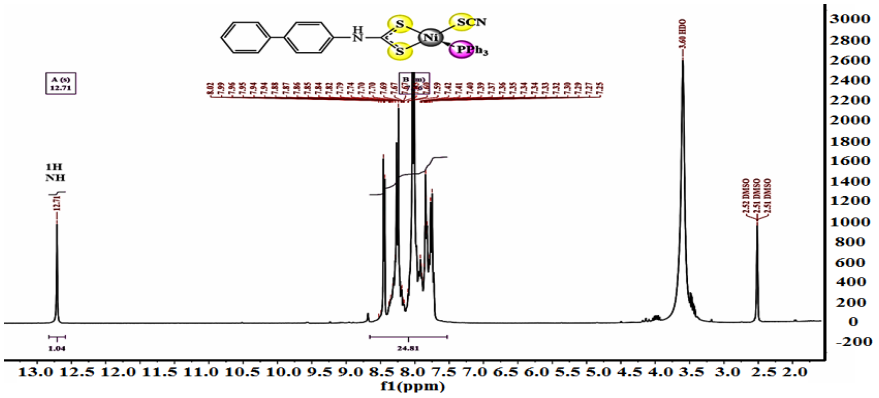


Fig. 3. ^{1}H NMR spectrum of the [Ni(SCN)(L^1)$_2$(PPh3)] (3) complex

The IR spectra of the dithiocarbamate chelates (1) and (2) displayed a strong band at position 1504 cm^{-1} and 1512 cm^{-1} referred to the stretching frequency of the υ(C=C) group of the Ph system in the two complexes, respectively, further, the spectra displayed band at 3254 cm^{-1} and 3210 cm^{-1} as medium to broadband due to the stretching frequency of the υ(N-H) group. Also, t, the spectra displayed bands 1464 cm^{-1} and 1451 cm^{-1} due to the stretching frequency of the υ(C-N) group[17-19].

In the spectra of the complexes (3-6), three bands were observed that were not present in the spectra of (1) and (2) complexes, located in the ranges of (1429-1442) cm^{-1}, (1109-1130) cm^{-1}, and (493-513) cm^{-1}, attributed to the υ(P-Ph), υ(P-C) stretching, and bending of the υ(P-C) band, respectively[22-25]. The CSS thiocarbonyl stretching showed as a strong to medium band within (1043-1078) cm^{-1} range for complexes (3-6)[20-30]. Our data indicates that the dithiocarbamate ligands were chelated in a bidentate chelating manner via the sulfur atoms with nickel(II) ions[28-31,34]. Additional groups are documented in Table 2.

Table 2: IR data in (cm^{-1})

Compounds	ν(N-H)	ν(C-H)		Phosphine ligands			ν(C=C) ν(C-N)	ν(CSS)	ν(M-P) or ν(M-S)
		Aliph.	Arom.	ν(P-Ph)	ν(P-C)	ν(P-C)			
1	3254m	3062w	-	-	-	-	1504s1464m	1076m	-431w
2	3210m	3038w	2962w	-	-	-	1512s1451m	1069m	-414w
3	3255m	3078w	-	1430s	1109s	498s	1512s1451m	1078m	451w423w
4	3210w	3023w	2897w	1434s	1123s	503s	1512s1451m	1059s	467w410w
5	3189w	3087w	-	1442s	1130s	513s	1554m1429s	1070m	478w437w
6	3209w	3051w	2913w	1429s	1116s	493s	1560s1476s	1043m	459w420w

Anti-bacterial activity

The antibacterial properties of the mixed ligand chelates of nickel(II) dithiocarbamate and triphenylphosphine ligands. The outcomes were attained against three bacterial strains (see Table 3) usingt. The standard agar disc diffusion method. The diameter of the inhibition zone (DIZ) was compared to that of streptomycin as the positive control. The relative activity index (%) was calculated as shown below:

$$\%\ activity\ index = \frac{\text{Inhibition zone of the test compounds}}{\text{Inhibition zone of the standard drug}} * 100$$

Table 3: DIZ (mm) and activity index (%) of synthetic compounds (3-6)

Compounds	DIZ (mm)			Activity index (%)		
	P. aeruginosa	*B. subtitles*	*E. coli*	*P. aeruginosa*	*B. subtitles*	*E. coli*
3	16	14	20	59	50	67
4	18	19	24	67	68	80
5	17	17	22	63	61	73
6	22	20	26	81	71	87
Streptomycin	27	28	30	100	100	100

*DMSO is used as a negative control.

The mixed ligand complexes of nickel(II) of dithiocarbamate and triphenylphosphine showed moderate to effective activity towards the examined pathogenic bacterial species. The results achieved may be described as follows:

1- The synthetic nickel(II) compounds showed good activity towards the *E. coli* species, whilst the minimal activity was observed against *B. subtills*.

2- $[Ni(CN)(L^2)_2(PPh_3)]$(6) compound exhibited a high activity towards examined bacteria matched with other tested compounds. Whereas the $[Ni(SCN)(L^1)_2(PPh_3)]$(3) exhibited the lowest activity.

3- Inhibition order against the *P. aeruginosa*, *B. subtilis*, and *E coli* bacteria species of the compound are as follows:

3 > 5 > 4 > 6

increase of inhibition zone→

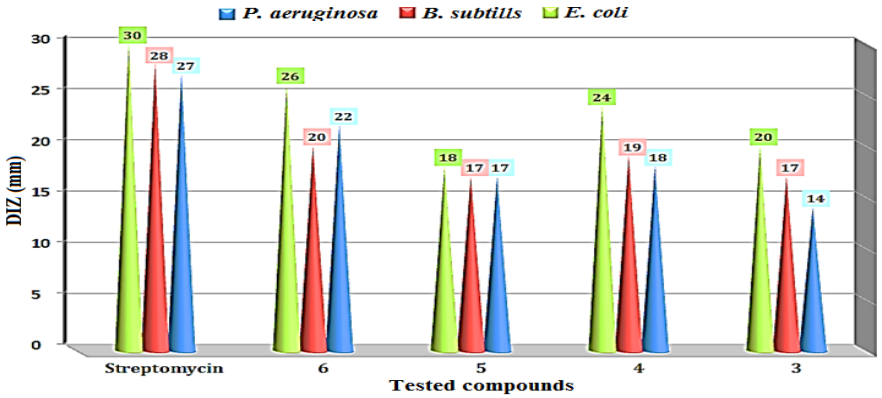


Fig. 4. The anti-bacterial activities

CONCLUSION

Mixed ligand Ni(II) complexes that involve the dithiocarbamate ligand, triphenylphosphine, thiocyanate, and cyanide ligand were synthesized. The complexes have been completely characterised through CHN analysis, molar conductivity measurements, as well as NMR (^{1}H and 31P) and IR methods. The spectroscopic findings indicated that the thione ligand coordinates bidentate via S atoms with Ni(II). The study of biological activity against *Escherichia coli*, *Pseudomonas aeruginosa*, and *Bacillus subtilis* was conducted, revealing that the $Ni(CN)(L^2)_2(PPh_3)]$(6) complex exhibited superior inhibition against all tested organisms to other chelates evaluated. In contrast, the $[Ni(SCN)(L^1)_2(PPh_3)]$(3) displayed the least activity.

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Conflict of interest

The author declare that we have no conflict of interest.

REFERENCES

1. Heard, P., *J. Prog. Inorg. Chem.*, **2005**, *53*, 1-69.
2. Hogarth, G., *Prog. Inorg. Chem.*, **2005**, *53*, 71-561.
3. Hogarth, G., *Mini-Rev. Med. Chem.*, **2012**, *12*(12), 1202-1215.
4. Magee, R. J.; Hill., *J. O. Rev. Anal. Chem.*, **1985**, *8*(1-2), 5-72.
5. Adeyemi, J. O.; Onwudiwe, D. C., *Molecules.*, **2018**, *23*(10), 2571.
6. Sarker, J. C.; Hogarth, G., *Chem. Rev., 2021*, *121*(10), 6057-6123.
7. Ajiboye, T. O.; Ajiboye, T. T.; Marzouki, R.; Onwudiwe, D. C., *Int. J. Mol. Sci.*, **2022**, *23*(3), 1317.
8. Odularu, A. T.; Ajibade, P. A., *Bioinorg. Chem. Appl.,* **2019**, *2019*(1), 8260496.
9. Hill, J. O.; Magee, R. J.; Liesegang., *J. Com. Inorg. Chem.*, **1985**, *5*(1), 1-27.

10. Fujii, S.; Yoshimura, T., *Coord. Chem. Rev*., **2000**, *198*(1), 89-99.
11. Bond, A. M.; Martin, R. L., *Coord. Chem. Rev*., **1984**, *54*, 23-98.
12. Adeyemi, J. O.; Onwudiwe, D. C., *Inorg. Chim. Acta*., **2020**, *511*, 119809.
13. Buac, D.; Schmitt, S.; Ventro, G.; Rani Kona, F.; Ping Dou, Q., *Mini-Rev. Med. Chem*., **2012**, *12*(12), 1193-1201.
14. Ahmed, A., *J. Asian J. Chem*., **2018**, *30*, 2595-2602.
15. Alshdoukhi, I. F.; Al-barwari, A. S.; Aziz, N. M.; Khalil, T.; Faihan, A. S.; Al-Jibori, S. A.; Al-Janabi, A. S., *Bull. Chem. Soc. Ethiop*., **2024**, *38*(4), 889-899.
16. Al-Jibori, S. A.; Al-Janabi, A. S.; Al-Sahan, S. W.; Wagner, C., *J. Mol. Struct*., **2021**, *1227*, 129524.
17. Al Janabi, A. S.; Kadhim, M. M.; Al Nassiry, A. I.; Yousef, T. A., *Appl. Organomet. Chem*., **35**(2), e6108.
18. Abdullah, T. B.; Behjatmanesh-Ardakani, R.; Faihan, A. S.; Jirjes, H. M.; Abou-Krisha, M. M.; Yousef, T. A.; Kenawy S. H. ; Al-Janabi, A. S., *Molecules*., **2023**, *28*(5), 2305.
19. Al Janabi, A. S.; Saleh, A. M.; Hatshan, M. R., *J. Chin. Chem. Soc.*, **2021**, *68*(6), 1104-1115.
20. Al Nassiry, A. I.; Al Janabi, A. S.; Thayee Al Janabi, O. Y.; Spearman, P.; Alheety, M. A., *J. Chin. Chem. Soc.*, **2020**, *67*(5), 775-781.
21. Salman, M. M.; Al-Dulaimi, A. A.; Al-Janabi, A. S.; Alheety, M. A., *Mater. Today Proc*., **2021**, *43*, 863-868.
22. Abdullah, K. T.; Al-Janabi, A. S.; Hussien, N. J.; Yousef, T. A., Shaaban, S.; Attia, M. I.; & Al Duaij, O. K., *Bull. Chem. Soc. Ethiop*., **2024**, 79-90.
23. Al-Janabi, E. M.; Alheety, M. A.; Al-Jibori, S. A.; Faihan, A. S.; Al-Janabi, A. S., *J Iran Chem. Soc*., **2023**, *20*(8), 1781-1790.
24. Al-Janabi, E. M.; Hatshan, M. R.; Adil, S. F.; Kadhum, W. R.; Al-Jibori, S. A., Faihan, A. S.; Al-Janabi, A. S., *J. Mol. Struct*., **2022**, *1252*, 132227.
25. Abdullah, T. B.; Jirjes, H. M.; Faihan, A. S.; Al-Janabi, A. S., *J. Mol. Struct*., **2023**, *1276*, 134730.
26. Kadhim, M. M.; Juber, L. A. A.; Al-Janabi, A. S., *Iraqi J. Sci*., **2021**, 3323-3335.
27. Pal, S. K.; Singh, B.; Yadav, J. K.; Yadav, C. L.;Drew, M. G.; Singh, N.; Kumar, K., *Dalton Trans*., **2022**, *51*(34), 13003-13014.
28. Bobinihi, F. F.; Osuntokun, J.; Onwudiwe, D. C., *J. Saudi Chem. Soc*., **2018**, *22*(4), 381-395.
29. Singh, S. K.; Kumar, V.; Drew, M. G.; Singh, N., *Inorg. Chem. Commun*., **2013**, *37*, 151-154.
30. Bobinihi, F. F.; Onwudiwe, D. C.; Hosten, E. C., *J. Mol. Struct.,* **2018**, *1164*, 475-485.
31. Rani, P. J.; Thirumaran, S.; Ciattini, S., *Phosphorus, Sulfur Relat. Elem*., **2013**, *188*(6), 778-789.
32. Kondo, T.; Mitsudo, T. A., *Chem. Rev*., **2000**, *100*(8), 3205-3220.
33. Abdalrazaq, E. A.; Abu-Yamin, A. A.; Taher, D., Hassan, A. E.; Elhenawy, A. A., *J. Sulf. Chem.,* **2024**, *45*(5), 714-739.
34. Bobinihi, F. F.; Onwudiwe, D. C.; Hosten, E. C., *J. Mol. Struct*., **2018**, *1164*, 475-485.
35. Biemer, J., *J. Ann. Clin. Lab. Sci*., **1973**, *3*(2), 135-140.