European Journal of Chemistry 15 (4) (2024) 320-324

EurJChem An International Open Access Journal **European Journal of Chemistry** APH ATLANTA PUBLISHING HOUSE

Check for updates

View Journal Online
View Article Online

Synthesis, characterization, crystal structure and antioxidant activity of *N*-(3-chloropropionyl)-*N*'-(4-methoxyphenyl)thiourea

Hamza Milad Ahmed Abosadiya

Department of Chemistry, Faculty of Sciences, Bani Waleed University, Bani Waleed, PO Box 5338, Tripoli, Libya

* *Corresponding author at: Department of Chemistry, Faculty of Sciences, Bani Waleed University, Bani Waleed, PO Box 5338, Tripoli, Libya.*
e-mail: hamzamilad@bwu.edu.ly (H.M.A. Abosadiya).

RESEARCH ARTICLE

10.5155/eurjchem.15.4.320-324.2607

Received: 16 October 2024
Received in revised form: 28 October 2024
Accepted: 8 November 2024
Published online: 31 December 2024
Printed: 31 December 2024

KEYWORDS

Synthesis
DPPH method
Hydrogen bond
Thiourea derivative
Antioxidant activity
Single-crystal structure

ABSTRACT

In the present work, a new carbonoyl thiourea derivative, *N*-(3-chloropropionyl)-*N'*-(4-methoxyphenyl)thiourea, was synthesized by the reaction of 3-chloropropionyl isothiocyanate with 4-methoxyaniline in acetone solution. The newly synthesized compound was characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques. X-ray crystallographic studies indicate that the compound crystallized in the triclinic crystal system with space group P-1 and unit cell dimension are a = 10.2262(6) Å, b = 11.5007(7) Å, c = 12.6116(8) Å, α = 72.253(2)°, β = 66.348(2)°, γ = 88.099(2)°, Z = 4 and V = 1287.22 (14) Å^3. Strong intramolecular O-H···N hydrogen bonds are present that form a six-member pseudo-ring *S*(6). In the crystal structure, the molecules are linked by N-H···O, N-H···S, and C-H···O intermolecular hydrogen bonding interactions formed infinite one-dimensional chains with an $R_2^2(8)$ and $R_2^2(12)$ rings motif of molecules. The antioxidant test using the DPPH method showed that the compound exhibits a good antioxidant activity of about 80%.

Cite this: *Eur. J. Chem.* **2024**, *15(4)*, 320-324 **Journal website**: www.eurjchem.com

1. Introduction

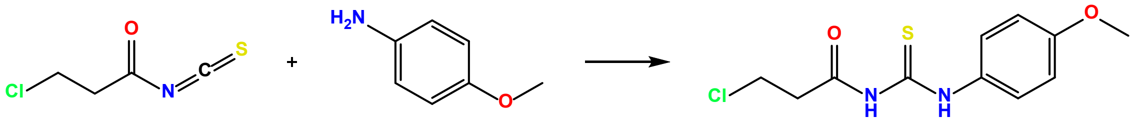
Thiourea and its derivatives are an important class of organosulfuric compounds with the general formula $(R^1R^2N)(R^3R^4N)C=S$ having N- and S-donor atoms. A great deal of research has been done on the synthesis and design of new carbonoylthiourea derivatives due to their applications in numerous fields such as organic synthesis and pharmaceutical industries, as well as coordination chemistry [1-13]. *N,N*-Diethyl, di-*n*-propyl-, di-*n*-butyl- and diphenyl-*N'*-(4-chloro benzoyl)thiourea and their Pt(II) complexes have been synthesized and structurally characterized and these complexes were also evaluated for both their *in-vitro* antibacterial and antifungal activity [14], and the results have been reported, explained, and compared with fluconazole and ampicillin, used as reference drugs. Over the past three decades, many derivatives of thiourea derivatives containing benzoyl groups have been reported [15-17], comparable to some structures which have been reported for halogeno-carbonyl thiourea derivatives [18,19]. The presence of C-halogen bonds in the structure of halogeno-carbonoylthiourea derivatives is a useful starting material for the synthesis of other derivatives such as 2-(4-fluoroanilino)-4,5-dimethyl-1,3-thiazole and 2-anilino-4,5-dimethyl-1,3-thiazole, in the synthesis process of thiourea derivatives from 3-chloro-2-butanone, 1,3-thiazole was instead obtained [20,21]. As part of our ongoing study of thiourea derivatives, *N*-(3-chloro propionyl)-*N'*-(4-methoxyphenyl)thiourea has been synthesized and fully characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopic techniques, and X-ray crystallographic studies. The antioxidant activity was also investigated using the DPPH method.

2. Experimental

2.1. Instrumentation

The microelemental analysis for CHNS-O was performed using a Carlo Erba 1108 elemental analyzer (Milan, Italy). The infrared spectrum (IR) of the product (KBr pellets) was recorded using a Perkin Elmer GX spectrophotometer (Perkin Elmer, Waltham, MA, USA) in the range 400-4000 cm^{-1} with resolution 4 cm^{-1}. Electronic UV/vis spectra were recorded using the 1800-PC Shimadzu spectrophotometer in the range of 200-800 nm with the highest resolution. The experiments of multinuclear (^{1}H and ^{13}C) NMR were performed on a Bruker 600 MHz instrument in deuterated DMSO solvent. The X-ray single crystal diffraction measurement was performed on a Bruker D-QUEST diffractometer at 296(2) K.

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
https://dx.doi.org/10.5155/eurjchem.15.4.320-324.2607



Scheme 1. Synthesis of the title compound, *N*-(3-chloropropionyl)-*N'*-(4-methoxyphenyl)thiourea.

The intensity data were collected using graphite monochromated with λ = 0.71073 Å. The structure was solved by direction method and refined by full matrix least-squares against F^2 for all data using SHELXTL-97 program. The carbon and hydrogen atoms were positioned geometrically (C-H = 0.93-0.97 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydrogen atoms on the nitrogen were located in the difference Fourier map and refined freely using SHELXL [22] instruction 'DFIX 0.87 0.01.

2.2. Synthesis of N-(3-chloropropionyl)-N'-(4-methoxy phenyl)thiourea

The chemical materials and solvents used in this project were available from Sigma-Aldrich and used without further purification. An acetone solution (40 mL) of *p*-anisidine (0.01 mol, 1.23 g) was added dropwise into a two-necked round-bottomed flask containing an equimolar amount of 3-chloropropionyl-isothiocyanate (0.01 mol, 1.49 g) which produced by the reaction of 3-chloropropionyl chloride with ammonium thiocyanate. The mixture was refluxed for approximately 3 h and filtered into a beaker and left to evaporate at room temperature. The filtrate gave a precipitate after 7 days of evaporation. The yield is 85% and the melting point of the crystal obtained by recrystallization from ethanol is 448.3-449.1 K.

N-(3-Chloropropionyl)-N'-(4-methoxyphenyl)thiourea: Color: Colorless. Yield: 85%. M.p.: 175.15-175.95 °C. FT-IR (KBr, ν, cm^{-1}): 3215 (N-H), 3150 (C-$H_{aromatic}$), 2980 (C-$H_{aliphatic}$), 1698 (C=O), 1348 (C-N), 828 (C=S), 657 (C-Cl). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 3.86 (t, 2H, *J* = 6.0 Hz, ClC*H*$_2$C*H*$_2$), 3.77 (s, 3H, OCH_3), 3.00 (t, 2H, *J* = 6.6 and 6.0 Hz, ClC*H*$_2$C*H*$_2$), 7.49 (d, 2H, *J* = 5.4 Hz, Ar-H), 6.95 (d, 2H, *J* = 4.8 Hz, Ar-H), 11.56 (s, 1H, N*H*), 12.22 (s, 1H, N*H*). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 39.2 (CH_2), 40.4 (CH_2), 55.8 (OCH_3), 114.3 (Ar-C*)*,126.4 (Ar-C), 131.0 (Ar-C-NH), 158.0 (Ar-C-OCH_3), 173.0 (C=O), 179.0 (C=S). Anal. calcd. for $C_{11}H_{13}ClN_2O_2S$: C, 48.44; H, 4.80; N, 10.27; S, 11.75 %. Found: C, 48.30; H, 4.11; N, 10.09; S, 11.34%.

2.3. Antioxidant activity studies

The sample solution of *N*-(3-chloropropionyl)-*N'*-(4-methoxyphenyl)thiourea was prepared in dimethyl sulfoxide solvent (*C* = 15 mg/5 mL). The free radical stock solution of diphenylpicrylhydrazyl (DPPH, 97% purity) was also prepared daily at a concentration of 0.4 g in 1000 mL in methanol solvent and protected from light (A_{DPPH} = 1.012). 1 mL DPPH solution was mixed with 100 µL from the stock solution of the new synthesized carbonoylthiourea compound. The mixture was shaken well and kept in the dark at room temperature for 2 hours. The absorbance of the mixture was recorded at 517 nm using a spectrophotometer (A_{Sample} = 0.191) [23,24]. The percentage reduction of the DPPH was calculated using Equation 1:

$$\text{DPPH Scavenging activity (\%)} = [(A_{DPPH} - A_{Sample})/(A_{DPPH})] \times 100 \quad (1)$$

where A_{DPPH} is the absorbance of 2,2-diphenyl-1-picrylhydrazyl (DPPH) and A_{Sample} is the absorbance of the mixture (DPPH and the synthesized compound).

3. Results and discussion

3.1. Synthesis

The synthesis of halogenoalkoyl thiourea derivatives including functional groups of alkyl halides (C-X, where X = Cl, Br, and I) is quite important and interesting for the preparation of a variety of derivatives by catalyzed substitution and elimination reactions [25,26]. Therefore, the solution mixture of 3-chloropropionyl-isothiocyanate with 4-methoxyaniline in acetone gave a homogeneous colorless solution after refluxing for about three hours (Scheme 1).

The microelemental analysis data of the precipitate are in agreement with the expected formula of *N*-(3-chloro propionyl)-*N'*-(4-methoxyphenyl)thiourea. The infrared spectrum of the compound showed the stretching frequencies of C-H (*sp*^{2} and *sp*^{3}) stretching of the aromatic ring and alkyl chain at approximately 3150 and 2980 cm^{-1}, respectively. The N-H stretching bond of the compound appeared at 3215 cm^{-1}, this hydrogen atom of the thioamide group H-N-C=S displays an intramolecular hydrogen bond with the oxygen atom of the carbonyl group, leading to a decrease in the stretching value than that in the normal secondary amines and amides absorption (3300-3500 cm^{-1}). The characteristic frequency of ν(C=O) stretching appeared at 1698 cm^{-1}, this vibrational frequency is in agreement with other thiourea derivatives [1,2]. The stretching vibration at 828 cm^{-1} for the compound is assigned to the C=S functional group. The vibration mode observed at 657 cm^{-1} in the spectrum corresponding to ν(C-Cl) stretching vibration. ^{1}H NMR spectrum shows the chemical shifts of the methylene protons (-C*H*$_2$-) as a distinctive multiplet in the range of δ 3.00-3.86 ppm, these protons are more deshielded than those in alkyl-thiourea derivatives due to the electron withdrawing effect of chlorine atom [1]. The aromatic protons appeared in the normal range of δ 6.95-7.49 ppm. The chemical shifts of the amide and thiomide protons of compound are quite similar to the other thiourea derivatives [1,15,27] and appeared as a singlet at δ 12.22 and 11.56 ppm, respectively. The downfield of amide protons is mainly due to the formation of intramolecular hydrogen bonding between the amino proton N-H and the oxygen atom of the carbonyl group, as well as to the anisotropic effect. In the ^{13}C NMR spectrum, the chemical shift of the methoxy group is found at δ 55.8 ppm, whereas the carbon chemical shifts of the methylene groups -*C*H_2- appear at lower chemical shifts at δ *39.2 and* 40.4 ppm. Similarly, the carbon chemical shifts of *C*=O and *C*=S are found at δ 173.0 and 179.0 ppm, respectively, for the compound. The aromatic carbon chemical shifts appeared in the range of δ 114.3-158.0 ppm.

3.2. X-ray structure of N-(3-chloropropionyl)- N'-(4-methoxyphenyl)thiourea

The synthesized compound *N*-(3-chloropropionyl)-*N'*-(4-methoxyphenyl)thiourea has been obtained in the crystalline form by recrystallization from an ethanol solvent. X-ray single crystal investigation showed that the compound crystallized in a triclinic system with space group *P*-1. The crystallographic data are summarized in Table 1.

Table 1. Crystal data and structure refinement of *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea.

Crystal parameters	Data/values
Empirical formula	$C_{11}H_{13}ClN_2O_2S$
Formula weight (g/mol)	272.74
Temperature (K)	296(2)
Crystal system	triclinic
Space group	P-1
a, (Å)	10.2262(6)
b, (Å)	11.5007(7)
c, (Å)	12.6116(8)
α (°)	72.253(2)
β (°)	66.348(2)
γ (°)	88.099(2)
Volume (Å^3)	1287.22(14)
Z	4
ρ_{calc} (g/cm^3)	1.407
μ (mm^{-1})	0.450
F(000)	568.0
Crystal size (mm^3)	0.5 × 0.32 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	6.04 to 56.8
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	33072
Independent reflections	6434 [R_{int} = 0.0360, R_{sigma} = 0.0275]
Data/restraints/parameters	6434/4/325
Goodness-of-fit on F^2	1.069
Final R indexes [I≥2σ (I)]	R_1 = 0.0572, wR_2 = 0.1281
Final R indexes [all data]	R_1 = 0.0837, wR_2 = 0.1508
Largest diff. peak/hole (e.Å^{-3})	0.46/-0.37
CCDC deposition number	2388367

Table 2. Selected bond lengths of *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
C1	Cl1	1.771(3)	C12	Cl2	1.769(3)
C2	C3	1.511(3)	C13	C14	1.507(3)
C3	N1	1.374(3)	C14	N3	1.365(3)
C3	O1	1.209(3)	C14	O3	1.221(3)
C4	N1	1.388(3)	C15	N3	1.389(3)
C4	N2	1.324(3)	C15	N4	1.321(3)
C4	S1	1.669(3)	C15	S2	1.671(2)
C5	N2	1.431(3)	C16	N4	1.431(3)
C8	O2	1.368(4)	C19	O4	1.363(3)
C11	O2	1.381(6)	C22	O4	1.421(4)

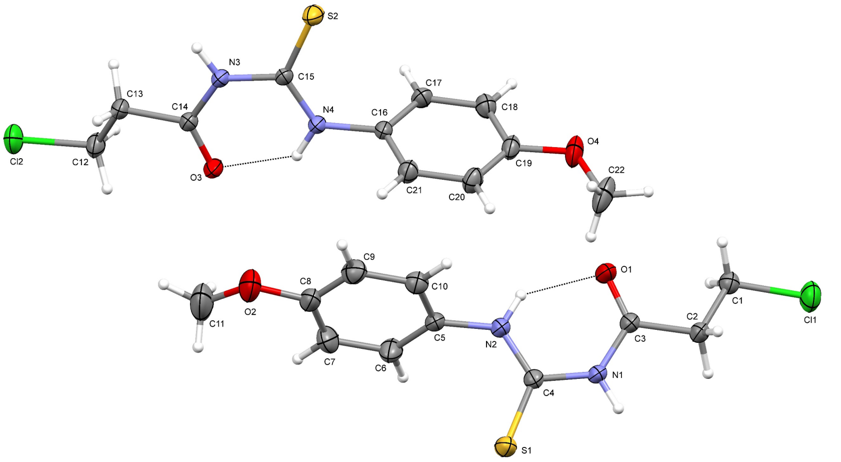


Figure 1. The molecular structure of *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea with 50% probability displacement ellipsoids. The dashed line indicates an intramolecular hydrogen bond.

The ORTEP diagram of the compound is shown in Figure 1 with the numbering scheme and the asymmetric unit contains two crystallographically independent molecules with different conformations. Both molecules maintain the *trans-cis* configuration with respect to the positions of the 3-chloropropionyl and 4-methoxyphenyl groups, respectively, against the thiono C=S bond across their C-N bonds.

The structure molecules are analogous to the previously reported *N*-(3-chloropropionyl)-*N′*-phenylthiourea [28] except that they have a methoxy group at position 4 of the phenyl ring. The carbonoyl thiourea fragments (S1/N1/N2/O1/C3/C4/C5 (A) and S2/N3/N4/O3/C13/C14/C15 (B)) and benzene rings (C5-C10 and C16-C21) in both molecules are planar with a maximum deviation of 0.057(2) Å for atom N3. In each independent molecule, the benzene rings are vertical to the thiourea fragments A and B with dihedral angles of 67.61(13) and 77.65(12)°, respectively, for the first and second molecules. A small reduction compared to the analog, *N*-(3-chloropropanoyl)-*N′*-phenylthiourea of 82.62(10)° [28]. Bond lengths and angles (Tables 2 and 3) are in normal ranges and comparable to those found in 1-(4-bromophenyl)-3-(3-chloropropanoyl)thiourea [18].

Table 3. Selected bond angles of *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C2	C1	Cl1	110.29(18)	O3	C14	C13	121.6(2)
C1	C2	C3	111.0(2)	O3	C14	N3	122.8(2)
N1	C3	C2	114.4(2)	N3	C15	S2	118.78(17)
O1	C3	C2	121.9(2)	N4	C15	N3	116.7(2)
O1	C3	N1	123.7(2)	N4	C15	S2	124.56(17)
N1	C4	S1	118.62(18)	C17	C16	N4	120.0(2)
N2	C4	N1	116.4(2)	C21	C16	C17	120.3(2)
N2	C4	S1	124.91(19)	C21	C16	N4	119.5(2)
C5	C10	C9	120.3(3)	C14	N3	C15	127.5(2)
N3	C14	C13	115.5(2)	C19	O4	C22	118.2(3)

Table 4. Geometric parameters of hydrogen bonds of *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (°)
N2—H2···O1	0.87(3)	1.94(2)	2.655(3)	138(3)
N4—H4···O3	0.87(3)	1.93(3)	2.627(3)	136(3)
N1—H1···S2 i	0.87(2)	2.58(2)	3.439(2)	170(2)
N2—H2···O3 ii	0.87(3)	2.37(3)	3.048(3)	134(2)
N3—H3···S1 iii	0.87(2)	2.55(2)	3.424(2)	177(3)
N4—H4···O1 iv	0.87(3)	2.42(3)	3.132(3)	139(3)
C18—H18···O3 v	0.93	2.56	3.316(4)	138

Symmetry codes: i 1+*x*, 1+*y*, *z*; ii *x*, 1+*y*, *z*; iii -1+*x*, -1+*y*, *z*; iv *x*, -1+*y*, *z*; v 1-*x*, -*y*, -*z*.

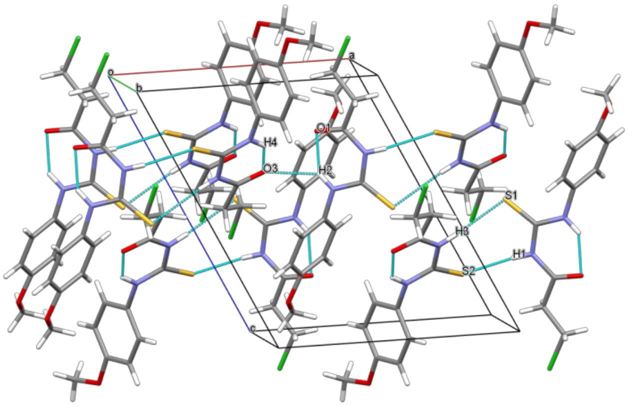


Figure 2. Molecular packing of *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea, viewed down the b axis. The dashed lines denote N-H···O, N-H···S, and C-H···O hydrogen bonds.

There are intramolecular hydrogen bonds between the carbonyl oxygen atom and thioamide hydrogen, N2-H2···O1 and N4-H4···O3 in both molecules (Table 4) forming pseudo-six-membered rings. In the crystal packing, the molecules are linked by N-H···O, N-H···S, and C-H···O hydrogen bonds to form infinite one-dimensional chains along the *b* axis and the crystal structures showing $R_2^2(8)$ and $R_2^2(12)$ rings motifs.

3.3. Antioxidant evaluation

The DPPH scavenging activity of the synthesized carbonoylthiourea compound was 81.12%, which indicates good antioxidant properties compared to the scavenging activity of the 1,3-diphenyl-2-thiourea compound of approximately 60% at the higher concentration of C_m = 0.80 mM [24]. The antioxidant properties are due to the acceptance of an electron or the donation of a hydrogen atom from the thioamide H-N-C=S or amide groups to the free radical diphenylpicrylhydrazyl (DPPH) to form non-radical DPPH-H, and the color of the reaction mixture changes from purple to yellow when the DPPH radical is scavenged.

4. Conclusions

The new halogenocarbonyl thiourea compound, namely, *N*-(3-chloropropionyl)-*N′*-(4-methoxyphenyl)thiourea was successfully prepared by the reaction of an equimolar amount of 3-chloropropionylisothiocyanate with 4-methoxyaniline in an acetone solution. Its structure was confirmed by FT-IR, ^{1}H, and ^{13}C NMR spectroscopies. The molecular structure of the compound was also determined by using an X-ray crystallography technique. The antioxidant ability of the new synthesized compound was characterized based on the measurement of the color change of 2,2-diphenyl-1-picrylhydrazyl (DPPH·) from a purple to yellow color solution when it reacts with the synthesized thiourea compound and the compound showed a good antioxidant activity of about 80%.

Acknowledgements

The authors would like to thank the Ministry of Higher Education of Malaysia and Universiti Kebangsaan Malaysia for the facilities and financial support. I would also like to thank the Ministry of Education of Libya and Bani Waleed University for their support to carry out this work.

Supporting information S

CCDC-2388367 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement DS

Conflict of interest: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: A sample of the compound is available from the author.

ORCID and Email

Hamza Milad Ahmed Abosadiya
hamza_inorg@yahoo.com
hamzamilad@bwu.edu.ly
https://orcid.org/0000-0003-3847-0457

References

[1]. Abosadiya, H. M.; Anouar, E. H.; Hasbullah, S. A.; Yamin, B. M. Synthesis, X-ray, NMR, FT-IR, UV/vis, DFT and TD-DFT studies of N-(4-chlorobutanoyl)-N′-(2-, 3- and 4-methylphenyl)thiourea derivatives. *Spectrochim. Acta. A* **2015**, *144*, 115–124.

[2]. Abosadiya, H. M.; Anouar, E. H.; Abusaadiya, S. M.; Hasbullah, S. A.; Yamin, B. M. Synthesis, characterization, crystal structures and DFT studies of some new 1,2,4-triazole and triazolidin derivatives. *J. Mol. Struc.* **2018**, *1151*, 315–326.

[3]. Bai, W.; Ji, J.; Huang, Q.; Wei, W. Synthesis and evaluation of new thiourea derivatives as antitumor and antiangiogenic agents. *Tetrahedron Lett.*. **2020**, *61* (40), 152366.

[4]. Solmaz, U.; Gumus, I.; Binzet, G.; Celik, O.; Balci, G. K.; Dogen, A.; Arslan, H. Synthesis, characterization, crystal structure, and antimicrobial studies of novel thiourea derivative ligands and their platinum complexes. *J. Coord. Chem.* **2018**, *71* (2), 200–218.

[5]. Solmaz, U.; Keskin, E.; Arslan, H. Palladium(II) complexes of thiobenzamide derivative ligands: Synthesis, crystal structure, supramolecular architecture, Hirshfeld surface analysis, and in vitro antibacterial and antifungal activities. *J. Mol. Struc.* **2024**, *1308*, 138103.

[6]. Uysal, M. E.; Solmaz, U.; Arslan, H. Ruthenium(III) acyl thiourea complex: A catalyst for transfer hydrogenation of nitroarenes. *Polyhedron* **2024**, *247*, 116707.

[7]. Uysal, M. E.; Solmaz, U.; Arslan, H. Ru(II) and Ru(III) complexes containing *N*-acylthiourea ligands: Supramolecular structures and synthons, reduction, and reaction pathway of aromatic nitro compounds. *Applied. Organom. Chem.* **2023**, *37* (7), e7107 https://doi.org/10.1002/aoc.7107.

[8]. Oztaslar, A.; Arslan, H. N–((2–Acetylphenyl)carbamothioyl) benzamide: Synthesis, crystal structure analysis, and theoretical studies. *Karbala Inter. J. Modern Sci.* **2023**, *9* (3), https://doi.org/10.33640/2405-609X.3304.

[9]. Alizada, A.; Arslan, H. Experimental and theoretical studies of a thiourea derivative: 1-(4-chloro-benzoyl)-3-(2-trifluoromethyl-phenyl)thiourea. *J. Mol. Struc.* **2023**, *1279*, 134996.

[10]. Solmaz, U.; Arslan, H. Spectral, crystallographic, theoretical, and catalytic activity studies of the PdII complexes in different coordination modes of benzoylthiourea ligand. *J. Mol. Struc.* **2022**, *1269*, 133839.

[11]. Solmaz, U.; Ince, S.; Yilmaz, M. K.; Arslan, H. Conversion of monodentate benzoylthiourea palladium(II) complex to bidentate coordination mode: Synthesis, crystal structure and catalytic activity in the Suzuki-Miyaura cross-coupling reaction. *J. Organometal. Chem.* **2022**, *973-974*, 122374.

[12]. Keskin, E.; Solmaz, U.; Gumus, I.; Arslan, H. Di- and tetra-nuclear oxorhenium(V) complexes of benzoylthiourea derivative ligands: Synthesis, structural characterization, and catalytic applications. *Polyhedron* **2022**, *219*, 115786.

[13]. Abosadiya, H. M. Synthesis, crystal structure and antioxidant evaluation of N-(4-formylpiperazine-1-carbonothioyl)benzamide. *Eur. J. Chem.* **2020**, *11* (2), 156–159.

[14]. Arslan, H.; Duran, N.; Borekci, G.; Koray Ozer, C.; Akbay, C. Antimicrobial Activity of Some Thiourea Derivatives and Their Nickel and Copper Complexes. *Molecules* **2009**, *14* (1), 519–527.

[15]. Abosadiya, H. M.; Anouar, E. H.; Yamin, B. M. Synthesis, X-Ray, spectroscopic characterization (FT-IR, NMR, UV–Vis) and quantum chemical calculations of some substituted benzoylthiourea derivatives. *J. Mol. Struc.* **2019**, *1194*, 48–56.

[16]. Li, Z.; Zhang, Y.; Wang, Y. Synthesis and Characterization of N-benzoyl-N′-carboxyalkyl Substituted Thiourea Derivatives. *Phosphorus, Sulfur, Silicon Related Elements* **2003**, *178* (2), 293–297.

[17]. Abosadiya, H. M.; Yamin, B. M.; Ngah, N. *N*-Benzoyl-*N*′-(3-hydroxyphenyl)thiourea. *Acta. Crystallogr. E Struct. Rep. Online.* **2007**, *63* (5), o2403–o2404.

[18]. Abosadiya, H. M.; Hasbullah, S. A.; Yamin, B. M.; Fadzil, A. H. 1-(4-Bromophenyl)-3-(3-chloropropanoyl)thiourea. *Acta. Crystallogr. E Struct. Rep. Online.* **2014**, *70* (6), o685–o685.

[19]. Abosadiya, H. M.; Hasbullah, S. A.; Yamin, B. M.; Fadzil, A. H. 1-(4-Chlorobutanoyl)-3-(3-chlorophenyl)thiourea. *Acta. Crystallogr. E Struct. Rep. Online.* **2014**, *70* (6), o675–o675.

[20]. Jumal, J.; Latip, J.; Yamin, B. M. 2-(4-Fluoroanilino)-4,5-dimethyl-1,3-thiazole. *Acta. Crystallogr. E. Struct. Rep. Online.* **2006**, *62* (8), o3305–o3306.

[21]. Jumal, J.; Yamin, B. M. 2-Anilino-4,5-dimethyl-1,3-thiazole. *Acta. Crystallogr. E Struct. Rep. Online.* **2006**, *62* (7), o2893–o2894.

[22]. Sheldrick, G. M. A short history of *SHELX*. *Acta. Crystallogr. A Found. Crystallogr.* **2007**, *64* (1), 112–122.

[23]. Roman, R.; Pintilie, L.; Nuţă, D. C.; Căproiu, M. T.; Dumitraşcu, F.; Zarafu, I.; Ioniţă, P.; Marinaş, I. C.; Măruţescu, L.; Kapronczai, E.; Ardelean, S.; Limban, C. Contribution to the Synthesis, Characterization, Separation and Quantification of New N-Acyl Thiourea Derivatives with Antimicrobial and Antioxidant Potential. *Pharmaceutics* **2023**, *15* (10), 2501.

[24]. Huong, D. Q.; Bay, M. V.; Nam, P. C. Antioxidant activity of thiourea derivatives: An experimental and theoretical study. *J. Mol. Liquids* **2021**, *340*, 117149.

[25]. Terao, J.; Kambe, N. Cross-Coupling Reaction of Alkyl Halides with Grignard Reagents Catalyzed by Ni, Pd, or Cu Complexes with π-Carbon Ligand(s). *Acc. Chem. Res.* **2008**, *41* (11), 1545–1554.

[26]. Kambe, N.; Iwasaki, T.; Terao, J. Pd-Catalyzed Cross-Coupling Reactions of Alkyl Halides. *Chem. Soc. Rev.* **2011**, *40* (10), 4937–4947.

[27]. Saeed, A.; Shaheen, U.; Hameed, A.; Naqvi, S. H. Synthesis, characterization and antimicrobial activity of some new 1-(fluorobenzoyl)-3-(fluorophenyl)thioureas. *J. Fluorine. Chem.* **2009**, *130* (11), 1028–1034.

[28]. Othman, E. A.; Soh, S. K.; Yamin, B. M. *N*-(3-Chloropropionyl)-*N*′-phenylthiourea. *Acta. Crystallogr. E Struct. Rep. Online.* **2010**, *66* (3), o628–o628.