



Synthesis, Characterization and Structural Study of New Ethyl Thiourea Compounds and the Preliminary Naked-eye Sensors for Mercury and Argentum Metal Ions

SITI AISHAH HASBULLAH*, SYAHIDATUL MUNIRAH RAFFIK, NURNADZIRAH MAT NOH, EMMA IZZATI ZAKARIAH, FATIMATUL AKMA AWANG NGAH, HAMZA MILAD ABOSADIYA and BOHARI YAMIN

School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

*Corresponding author: aishah80@ukm.edu.my

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ABSTRACT

Novel ethyl thiourea compounds **1a**– **1f** have been synthesized in good to high yields. The structure of all compounds were identified using FT-IR, ¹H NMR, ¹³C NMR spectroscopies, and ESI-Mass spectrometry. The compound 1-ethyl-3-(3-methoxyphenyl) thiourea **1e** was obtained in crystalline form by recrystallization from DMSO. Single crystal X-ray analysis revealed that **1e** molecule crystallized in a monoclinic crystal system with space group of P21/n and the unit cell dimensions are a = 11.0797(7) Å, b = 8.6081(6) Å, c = 11.9698(7) Å, α = 90°, β = 104.543(2)°, γ = 90°, Z = 4 and V = 1105.04(12) Å³. The preliminary optical sensor properties for metal ions of **1a**, **1b** and **1d** were investigated using naked-eye. The results determined that all compounds have the ability as naked eye sensors for mercury (Hg) and argentum (Ag) metal ions.

Keywords: Synthesis; Structural study; Ethyl thiourea; Naked-eye Sensors

INTRODUCTION

Thiourea is similar to urea compound except the oxygen atom in urea is replaced by the presence of sulphur atom in thiourea compound.¹ The chemical properties of both compounds are different because of the oxygen and sulphur atoms in urea and thiourea. These atoms have different in electronegativity where oxygen has

greater electronegativity compare to sulphur. Many applications can be done on behaviours.² Thiourea is a chemically interesting compound where it has more than two functional groups in a compound: amino, imino and thiol.³ Thiourea derivatives are mostly crystalline compounds and thermally stable. They can be produced in good yields from available starting material by simple syntheses.³ Thiourea is also one of the most famous studied compounds on

metallic electrodes.⁴ It can absorb to metal surface and the absorption blocks the active sites.⁴ It is also one of the important industrial chemical products.⁵ Now a days, the situation of environmental pollution by heavy metals is one of the critical issues due to the development of modern industries and agriculture.

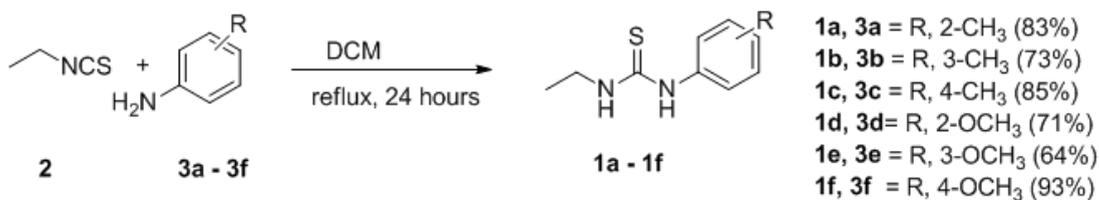
Many of heavy metals can be dangerous towards human or animal health. Mercury (Hg^{2+}) is one of the most toxic and hazardous between all the heavy metals.⁶ Mercury can cause cells damage and some diseases related to brain,⁷ kidney, and central nervous system. These are because the mercury is unable to decay naturally and accumulates in animal and human bodies.⁸ Silver ions (Ag^+) also have long been known to have strong inhibitory and antimicrobial activities.⁹ Silver nano particles are showing very toxic effects on human health and the environment due to the antibacterial activity. Then, chronic exposure to silver also can causes negative effects such as permanent bluish-grey discoloration of the skin (argyria) and eyes (argyrosis). Besides that, it also may produce other toxic effects like liver and kidney damage, irritation of the eyes, skin, respiratory and intestinal tract and changes to blood cell.¹⁰ For the above reasons, there is a high demand for tracking these metal ions.¹¹ The aim of the present study was to synthesis thiourea compounds having alkyl and aryl group substitutes.

Chemical sensor is generally consisting of two units; receptor unit and signalling unit, but in some cases spacer is also used to provide the shape and geometry in two armed molecule.¹² Detecting metal cations is one of the great interests to many scientists.¹³ Thioureas are well known having good affinity towards metals via thiono group ($\text{C}=\text{S}$) make them applicable as ion sensors.¹⁴ The nitrogen, oxygen and sulphur atom are donor atoms of thiourea that can donate electrons to form bonding and

provide a multitude of bonding possibilities.^{15,16} The structural characterization of the thiourea derivatives were performed using FTIR, ^1H NMR, ^{13}C NMR spectroscopy devices and ESI-MS spectrometry. In order to investigate the sensor properties, the interaction of all compounds with metals in solvent media was investigated using naked-eye sensor.

MATERIALS AND METHODS

All reactions were performed under conventional reflux method. Chemicals and solvents were purchased from Sigma Aldrich and Across and used directly without any further purification. Melting points were recorded on the open tube capillary method using Electrothermal 9100 instrument (Electrothermal, England) and are uncorrected. All compounds were analyzed using FTIR Perkin Elmer Model Spectrum GX in the range $400\text{-}4000\text{ cm}^{-1}$ using KBr method, ^1H and ^{13}C NMR spectrometer model Bruker Advance 400 MHz and Liquid Chromatography Mass Spectroscopy (ToF) model Dionex/BrukerMicroToF Q. Single-crystal X-ray experiments were performed on a Bruker D-QUEST diffractometer (Bruker, AXS Inc., Madison, WI, USA) using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\gamma = 0.71073\text{ \AA}$). The ω -scan measured the intensity data at room temperature. The full-matrix least-squares fit of 25 reflections determines the accurate cell parameters and orientation matrix. Intensity data were collected for Lorentz and polarization effects. Empirical absorption correction was carried out using multi-scan. The structure was solved by direct methods and least-squares refinement of the structure was performed by the SHELXL-2007 program.¹⁷ All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in the calculated positions except those of the terminal nitrogen atoms of thiourea moieties located from Fourier maps and refined isotropically.



Scheme 1 Synthesis of ethylthioureas 1a – 1f

General procedure for synthesis of compounds 1a-1f

A solution of ethylisothiocyanate (0.1394 g, 0.0016 mol) in dichloromethane (20 mL) was added dropwise to a suspension of toluidine **1a**, **1b** or **1c** (0.1714 g, 0.0016 mol) and anisidine **1d**, **1e** or **1f** (0.1968 g, 0.0016 mol) in dichloromethane. The reaction mixture was refluxed for 24 hours and was monitored using thin layer chromatography (TLC) until the reaction was completed. The white precipitate was formed and filtered out. The solid product was purified by recrystallization method using ethanol: dichloromethane mixture.

1a Mp: 81.9 – 83.6 °C. IR (KBr), NH: 3193.00 cm^{-1} , C-N: 1371.00 cm^{-1} , C=S: 1245.00 cm^{-1} . ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 1.14 (3H, t, $J=7.2\text{Hz}$, CH_3), 2.29 (3H, s, CH_3), 3.63 (2H, s, CH_2), 5.65 (1H, s, NH), 7.25 (1H, d, $J=10.8\text{Hz}$, ArCH), 7.26 (1H, t, $J=7.8\text{Hz}$, ArCH), 7.28 (1H, t, $J=7.8\text{Hz}$, ArCH), 7.30 (1H, d, $J=10.8\text{Hz}$, ArCH), 7.84 (1H, s, NH). ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 14.5 (CH_3), 17.8 (CH_3), 40.2 (CH_2), 127.5–131.8 (4 x ArCH), 135.9 (ArC), 134.4 (ArC), 180.6 (C=S). m/z (ESI) (H^+ , $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$ requires 195.09)

1b Mp: 84.9 – 85.6 °C. IR (KBr), NH: 3011.00 cm^{-1} , C-N: 1355.00 cm^{-1} , C=S: 1148.00 cm^{-1} . ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 1.18 (3H, t, $J=7.2\text{Hz}$, CH_3), 2.36 (3H, s, CH_3), 3.66 (2H, s, CH_2), 6.01 (1H, s, NH), 7.30 (2H, d, $J=7.2\text{Hz}$, ArCH), 7.32 (2H, d, $J=7.6\text{Hz}$, ArCH), 8.20 (1H, s, NH). ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 14.4 (CH_3), 21.4 (CH_3), 40.3 (CH_2), 122.2 (2 x ArCH), 129.9 (2 x ArCH), 136.1

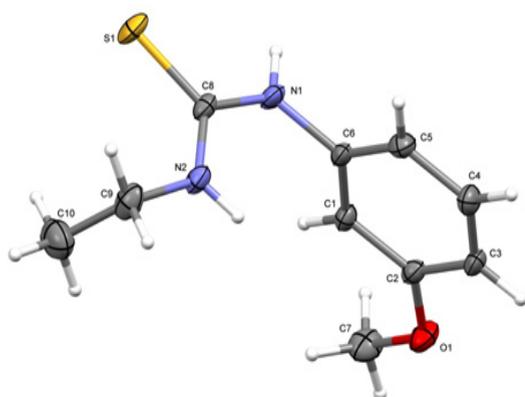


Fig. 1: ORTEP diagram of 1-Ethyl-3-(3-methoxyphenyl)thiourea **1e**

(ArC), 140.4 (ArC), 180.2 (C=S). m/z (ESI) (H^+ , $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$ requires 195.09)

1c Mp: 97.4 – 98.8 °C. IR (KBr), NH: 3198.00 cm^{-1} , C-N: 1317.00 cm^{-1} , C=S: 1249.00 cm^{-1} . ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 1.16 (3H, t, $J=7.2\text{Hz}$, CH_3), 2.36 (3H, s, CH_3), 3.64 (2H, s, CH_2), 5.95 (1H, s, NH), 7.10 (1H, d, $J=7.6\text{Hz}$, ArCH), 7.20 (1H, d, $J=7.6\text{Hz}$, ArCH), 7.32 – 7.33 (2H, m, ArCH), 8.06 (1H, s, NH). ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 14.3 (CH_3), 21.1 (CH_3), 40.3 (CH_2), 128.0 – 130.8 (4 x ArCH), 133.4 (ArC), 137.5 (ArC), 180.4 (C=S). m/z (ESI) (H^+ , $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$ requires 195.09)

1d Mp: 72.5 – 72.5 °C. IR (KBr), NH: 3335 cm^{-1} , C-C aromatic: 1528 cm^{-1} , C=S: 1263 cm^{-1} . ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 1.20 (3H, t, $J=7.2\text{Hz}$, CH_3), 3.67 (2H, sex, $J=5.6\text{Hz}$, CH_2), 3.85 (3H, s, OCH_3), 6.11 (1H, s, NH), 6.98 (1H, t, $J=7.6\text{Hz}$, ArCH), 7.23 (1H, td, $J=6.4\text{Hz}$ and 1.6Hz, ArCH), 7.31 (1H, s, ArCH), 7.52 (1H, s, NH). ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 14.3 (CH_3), 40.3 (CH_2), 55.7 (OCH_3), 112.0 – 124.9 (4 x ArC), 127.5 (ArC), 152.4 (ArC), 180.3 (C=S). m/z (ESI) (Na , $\text{C}_{10}\text{H}_{14}\text{N}_2\text{OS}$ requires 233.27g/mol)

1e Mp: 112.5 – 117.5 °C. IR (KBr) NH: 3343 cm^{-1} , C-C aromatic: 1550 cm^{-1} , C=S: 1284 cm^{-1} . ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm) 1.19 (3H, t, $J=7.2\text{Hz}$, CH_3), 3.67 (2H, sex, $J=5.4\text{Hz}$, CH_2), 3.80 (3H, s, OCH_3), 6.11 (1H, s, NH), 6.78 (1H, dd, $J=6.0\text{Hz}$ and 2.0Hz, ArCH), 6.74 (1H, t, $J=2.0\text{Hz}$, ArCH), 6.82 (1H, dd, $J=6.0\text{Hz}$ and 2.4Hz, ArCH), 7.32 (1H, t, $J=8.0\text{Hz}$, ArCH), 7.95 (1H, s, NH). ^{13}C

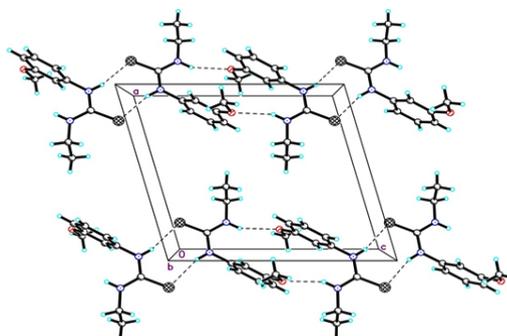


Fig. 2: Molecular packing of 1-ethyl-3-(3-methoxyphenyl)thiourea **1e** viewed down the *b* axis. The dashed lines denote the N–H···S and N–H···O hydrogen bonds

NMR (400 MHz, CDCl₃-d₆) δ (ppm) 14.3(CH₃), 40.4(CH₂), 55.5(OCH₃), 110.7-130.9(4 x ArC), 137.3 (ArC), 160.9 (ArC), 180.1(C=S). m/z (ESI) (Na, C₁₀H₁₄N₂OS requires 233.27g/mol)

1f Mp: 121.5 – 124.5 °C. IR(KBr), NH:3297 cm⁻¹, C-H:2988 cm⁻¹ C-C aromatic: 1520 cm⁻¹, C=S:1289 cm⁻¹. ¹H NMR (400 MHz, CDCl₃-d₆) δ (ppm) 1.15(3H, t, J=7.2Hz, CH₃), 3.64(2H, sex,

J=5.6Hz, CH₂), 3.82(1H, s, OCH₃), 5.78(1H, s, NH), 6.93(1H, d, J=8.8Hz, ArCH), 7.14(1H, d, J=8.8Hz, ArCH), 7.72(1H, s, NH). ¹³C NMR (400 MHz, CDCl₃-d₆) δ (ppm) 14.4 (CH₃), 40.2(CH₂), 55.5(OCH₃), 115.2 – 127.7(4 x ArC), 128.6(ArC), 158.8 (ArC), 180.8(C=S). m/z (ESI) (Na, C₁₀H₁₄N₂OS requires 233.27g/mol)

General procedure for naked-eye sensor

For naked-eye sensor detection of metal ions (Fe²⁺, Pb²⁺, Hg²⁺, Ni²⁺, Zn²⁺, Ag⁺, Cu²⁺, and Sn²⁺), compounds **1a**, **1b** and **1d** were dissolved in 25 ml dimethyl sulfoxide (DMSO) to form 1 x 10⁻³ M solution. Metal ion sources were prepared in deionized water to form 1 x 10⁻³ M stock solution except SnCl₂ in DMSO. The color changes were observed by naked eyes and the data were collected.

RESULTS AND DISCUSSIONS

All ethyl thiourea compounds **1a** – **1f** were synthesized in moderate to high yields from the reaction of ethylisothiocyanate **2** with isomers of toluidine **3a** – **3c** and anisidine **3d** – **3f** in dichloromethane under reflux condition. Scheme 1 outlines the synthesis of ethyl thiourea compounds **1a** – **1f**.

FT-IR spectra were taken with KBr pellets between 4000 and 400 cm⁻¹. In the FT-IR spectra of all the synthesized compounds show sharp and strong absorption band in the region of 3011 – 3335 cm⁻¹ and it were attributed to the stretching vibration of NH group, respectively. In addition, synthesized compounds show strong intensity C=S stretching vibration in the 1213 – 1284 cm⁻¹ range. The proton

Table 1: Crystal data and structure refinement of 1-ethyl-3-(3-methoxyphenyl)thiourea 1e

Crystal parameters	Data/values
Empirical formula	C ₁₀ H ₁₄ N ₂ OS
Formula weight	210.29
Temperature	302(2) K
Wavelength λ	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 11.0797(7) Å α = 90° b = 8.6081(6) Å β = 104.543(2)° c = 11.9698(7) Å γ = 90°
Volume	1105.04(12) Å ³
Z	4
D, cal (Mg/m ³)	1.264
Absorption coefficient	0.263 mm ⁻¹
F(000)	448
Crystal dimension (mm ³)	0.44 x 0.37 x 0.29
Theta range for data collection	2.89 to 28.40°
Reflections collected	40490
Ranges/indices (h,k,l)	-14, 14; -11, 11; -15, 15
Completeness to theta	28.40°, 99.6%
Independent reflections	2753 [R(int) = 0.0791]
Max. and min. transmission	0.9275 and 0.8929
Data / restraints / parameters	2753 / 2 / 137
Goodness of fit on F ²	1.100
R1, wR2 ($\geq 2\sigma(I)$)	R1 = 0.0580, wR2 = 0.1072
R1, wR2 indices (all data)	R1 = 0.1024, wR2 = 0.1220
Largest diff. peak and hole	0.230 and -0.285 e.Å ⁻³

Table 2: Selected bond lengths and angles of 1-Ethyl-3-(3-methoxyphenyl)thiourea 1e

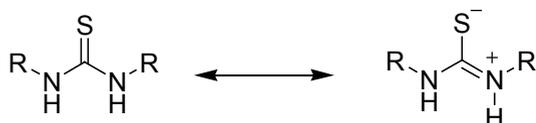
Bond	Length Å	Bond	Angles°
S1-C8	1.6917(18)	C2-O1-C7	118.32(16)
O1-C2	1.366(2)	C8-N1-C6	124.92(16)
O1-C7	1.420(3)	C8-N2-C9	124.91(17)
N1-C8	1.339(3)	O1-C2-C3	115.78(16)
N1-C6	1.436(2)	O1-C2-C1	124.25(18)
N2-C8	1.326(3)	C5-C6-N1	119.26(18)
N2-C9	1.456(3)	C1-C6-N1	119.36(17)

NMR spectrum (^1H and ^{13}C) were in agreement with compounds **1a** – **1f**. The peaks in the region of 7.60 – 8.20 ppm were attributed to NH proton near the aromatic ring. This singlet NH resonance is more de-shielded due to anisotropic effect. The distinctive broad singlets in the range of 5.65 – 6.20 ppm were attributed to NH proton attached to the ethyl terminal ring. The present of electron donating ethyl moieties increased the electron density and shifted the protons of NH to the upfield position. The protons at aromatic ring were assigned at 6.80 – 7.36 ppm. The protons for methyl (**1a** – **1c**) and methoxy (**1d** – **1f**) at aromatic ring exhibited signal as singlet in the range of 2.28 – 2.36 ppm and 3.80 – 3.85 ppm, respectively. The peaks in the region of 1.1 to 3.7 ppm were due to the protons of methylene and methyl of ethyl ring. According to the ^{13}C NMR spectra, the signal of C=S ring was found around 180.2 ppm and indicated the formation of thiourea moiety. The aromatic carbons were observed in the range of 110.7 – 160.9 ppm for all compounds. The methyl (**1a** – **1c**) and methoxy (**1d** – **1f**) carbons for aromatic ring were resonated at 21.0 and 55.5 ppm, respectively. All other carbons at the ethyl terminal ring were resonated in the region of

14.3 – 40.3 ppm. The signal related to $[\text{M} + \text{H}]^+$ and $[\text{M} + \text{Na}]^+$ for compounds **1b** and **1d** in the MS spectrum were observed at 195.09 and 233.27, respectively.

X-ray diffraction study indicates that the compound **1e** crystallizes in the monoclinic crystal system with space group of P21/n and the unit cell dimension are $a = 11.0797(7) \text{ \AA}$, $b = 8.6081(6) \text{ \AA}$, $c = 11.9698(7) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.543(2)^\circ$, $\gamma = 90^\circ$, $Z = 4$ and $V = 1105.04(12) \text{ \AA}^3$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1493627. Summary of the data collections and details of the structure refinement is given in Table 1.

Fig.1 shows the molecular structure with numbering scheme of compound **1e** which is analogous to the previously reported 1-(2-Hydroxyethyl)-3-(3-methoxyphenyl)thiourea (Choi *et al.* 2010) except in **1e** compound, there is no hydroxyl group bonded to the terminal carbon of ethyl group.



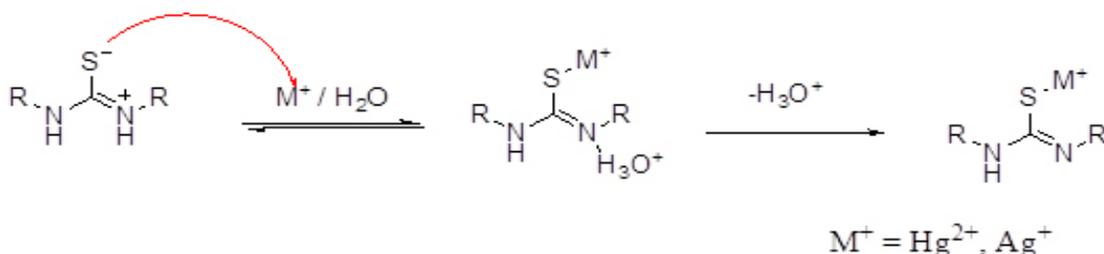
Scheme 2: Resonance structure of thiourea

The molecule is not planar. However, the thiourea fragment S1/N1/N2/C8/C9 and the benzene ring (C1–C6) are essentially planar with a maximum deviation of 0.003(2) \AA for N2 atom from the least square plane of the thiourea fragment. The

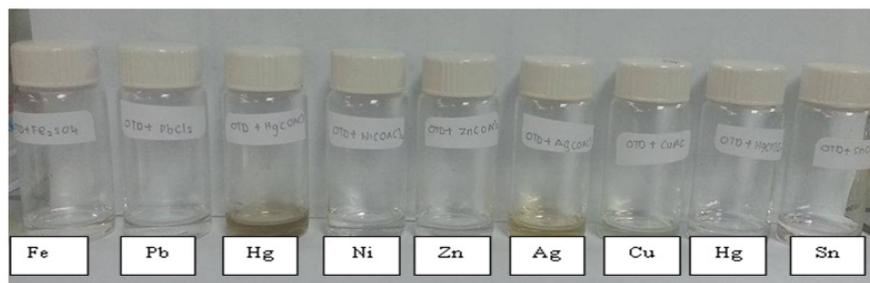
Table 3: Hydrogen geometric parameters (\AA) of 1-Ethyl-3-(3-methoxyphenyl)thiourea **1e**

D ⁱ H ⁱ ...A	D ⁱ H	H ⁱ ...A	D ⁱ ...A	D ⁱ H ⁱ ...A
N1 ⁱ H1A ⁱ ...S1 ⁱ	0.866(14)	2.528(16)	3.3678(18)	163.6(16)
N2 ⁱⁱ H2A ⁱⁱ ...O1 ⁱⁱ	0.865(19)	2.331(17)	3.126(2)	152.9(19)

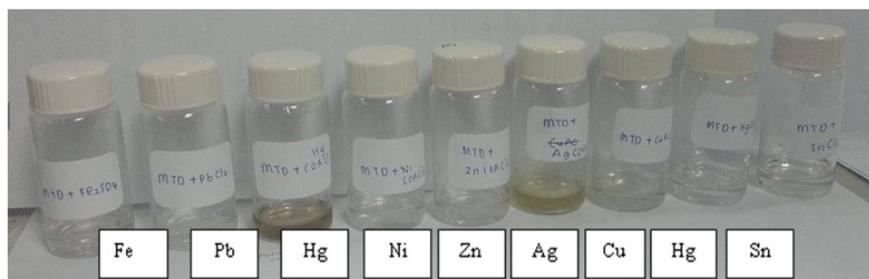
Symmetry codes: $i = -x, 1-y, -z$, $ii = -x, 1-y, 1-z$



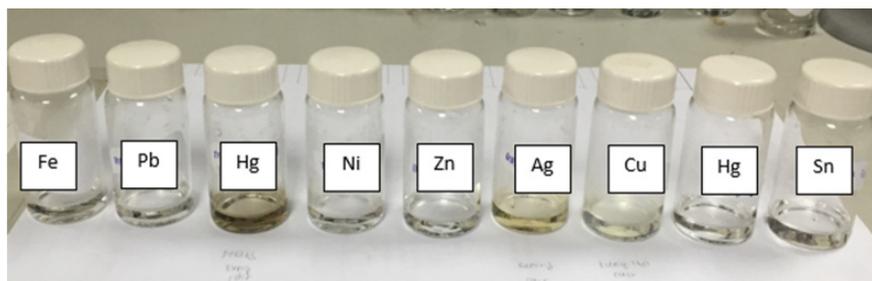
Scheme 3: Reaction scheme of thiourea binding with metal ions



1a



1b



1d

Fig. 3: The interaction of compound 1a, 1b and 1d with metal cations

two planes forming a dihedral angle of $88.54(9)^\circ$, which is considerably bigger than that found in 1-(2-Hydroxyethyl)-3-(3-methoxyphenyl)thiourea of $62.57(4)^\circ$. Other bond lengths and angles are comparable to those in the analog and lie in normal ranges (Table 2).

The intramolecular hydrogen bonds does not exists in the molecule while in the crystal packing the molecules are linked by $N1-H1A \cdots S1$ and $N2-H2A \cdots O1$ intermolecular hydrogen bonds (Table 3), to form infinite one-dimensional chains along the *c* axis (Fig. 2).

The ability and sensor features of compounds **1a**, **1b** and **1d** were investigated using

the naked-eye in DMSO solvent mixture in the presence of metals such as Fe, Pb, Hg, Ni, Ag, Cu and Sn. It was determined that ethyl thiourea as **1a – 1f** did not exhibit naked-eye sensor properties for Fe, Pb, Ni, Cu and Sn metals. However, the compounds exhibited selective sensor behavior for Hg^+ and Ag^+ metal ions (Fig. 3).

Thiourea derivatives contain a relatively basic C=S group that interacts with the metal ions. The C=S bond which was weak and had the resonance structure (Scheme 2) was the dominant resonance contributor.⁸ The resonance structure will be the nucleophile to attack the metal ions to form a stable complex (Scheme 3).

CONCLUSIONS

In the present work, ethyl thiourea **1a** – **1f** were prepared from the simple reaction method and are characterised using various spectral techniques. From the X-ray crystallography study of **1e**, molecule crystallized in a monoclinic crystal system with space group of P21/n and the unit cell dimensions are $a = 11.0797(7) \text{ \AA}$, $b = 8.6081(6) \text{ \AA}$, $c = 11.9698(7) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.543(2)^\circ$, $\gamma = 90^\circ$, $Z = 4$ and $V = 1105.04(12) \text{ \AA}^3$. Preliminary study

showed that ethyl thiourea **1a**, **1b** and **1d** have the ability as naked eye sensors for mercury (Hg) and argentum (Ag) metal ions.

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REFERENCES

1. Abdul Fattah, M. A.; Lusta, I. Z.; Zubi, A. E. *International Scholarly and Scientific Research & Innovation* **2014**, 8(2), 116-118.
2. Alkan, C.; Tek, Y.; Kahraman, D. *Turkish Journal of Chemistry* **2011**, 35(5), 769-777.
3. Mertschenk B.; Beck F.; Bauer W. Weinheim: Wiley-VCh Verlag GmbH & Co. KGaA. **1995**.
4. Zhao J.; Cui G. *International Journal of Electrochemical Science* **2011**, 6, 4048 - 4058.
5. Asieh Y.; Zahra G. *Eur. Chem. Bull.* **2013**, 2(8), 573-575.
6. Rurack, K.; Resch-Genger, U. *Chemical Society Reviews* **2002**, 31(2): 116-127.
7. Jae-Young L.; Boddu Ananda R.; Ji-Yong H.; and Young-A. S. *Sensors and Actuators B* **2015**, 220, 1070–1085.
8. Zhang, H.; Gu, C. D.; Huang, M. L.; Wang, X. L.; Tu, J. P. *Electrochemistry Communications* **2013**, 35, 108-111.
9. Berger, T.; Spadaro, J.; Chapin, S.; Becker, R. *Antimicrobial Agents and Chemotherapy* **1976**, 9(2), 357.
10. Panyala, N. R.; Peña-Méndez, E. M.; Havel, J. *J Appl Biomed*, **2008**, 6(3), 117-129.
11. Li, X.; Gao, X.; Shi, W.; Ma, H. *Chemical Reviews* **2013**, 114(1), 590-659.
12. Kumar V.; Kaushik M.P.; Srivastava A.K.; Pratap A.; Thiruvenkatam V.; Guru Row T. N. *Analytica Chimica Acta* **2010**, 663, 77–84.
13. Valeur, B.; Leray, I. *Coordination chemistry reviews* **2000**, 205(1), 3-40.
14. Abosadiya, H. M.; Siti Aishah Hasbullah; Bohari M Yamin. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2015**, 144, 115-124.
15. Saeed S.; Rizwan Hussain. *Eur. Chem. Bull.* **2013**, 2(7), 465-467.
16. Arslan H.; Duran N.; Borekci G.; Koray O.; Akbay C. *Molecules* **2009**, 14, 519-522.
17. Sheldrick, G. M. *SHELXTL. Version 6.14. Program for Crystal Structure Determination*. University of Gottingen: Gottingen, Germany **1997**.