



First Row Transition Metal Complexes Derived from N, N'-Substituted Thiourea: Synthesis, Geometrical Structures and Cyclic Voltammetry Probe: A Review

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Doi:10.29072/basjs.202117

Abstract

Thioureas or thiourea derivatives as organosulfur compounds are one of the most widely used ligands in different applications as we are going to discuss it extensively such as in coordination chemistry by involving them to rich sources of N, O and S atoms coordinating through S atom, S and O atoms in benzoyl derivatives or S, O and N atoms in pyridyl hetrocyclic benzoyl derivatives. These hard and soft donor sites facilitate the bonding between thiourea free ligand and metal ion through one or more to make ligands behave as mono, bi or multidentate ligands to form huge and stable series of the metal complexes. The tautomerism (thiol \leftrightarrow thione) inside the thiourea derivatives is responsible on their flexibility which make them easy capable to coordinate in different modes. Thiourea derivatives and their metal complexes are known in biological area by possess them antibacterial, antifungal, antimalarial, antitubercular, antithyroid and insecticidal activity features. Thioureas used as vital reagent to separate metal ions, catalyst to synthesize organic compounds or as starting material to form different hetrocyclic compounds. The wide range applications of thioureas and their metal complexes has motivated specialized researchers to search new applications for these compounds and to create a novel derivatives. The goal of this article is to present historical survey of thioureas and their metal complexes focusing on: firstly, the development of their synthetic routes by explore reactants, products, catalysis and the conditions of reactions. Secondly: investigation of the geometrical shapes of the produced complexes are reviewed as well as to the coordinated sites with metal centers. Lastly, the electrochemical manners have been lighted by employing cyclic voltammetry (CV) to study the electrochemical behavior of free ligands and their complexes to confirm the oxidation state of the metal ion in its complexes.

Article inf.

Received:
31/12/2020

Accepted

12/2/2021

Published

30/4/2021

Keywords

Thiourea derivatives, Synthetic methods, cyclic voltammetry, Four-coordinate complexes, Geometrical shape, Metal(II) complexes

1. Introduction

Thiourea or thiocarbamide compound, $\text{CS}(\text{NH}_2)_2$, which is in its original physical phase is a white powder, is derived from urea $\text{CO}(\text{NH}_2)_2$ compound with exchange oxygen atom by sulfur atom. The variation in electronegativity between oxygen and sulfur atoms make the properties of thiourea different than urea in spite of the similarity of their structure [1]. Thiourea by itself has some applications such as starting material to prepare thiourea dioxide which is used as reducing agent in textile treatment, producing flame delaying resins [2-4] vulcanization expediter [5] and copy papers for example diazo papers. Thioureas compounds are involving under its banner, big series of substances with public formula $(\text{R}^1 \text{R}^2 \text{N})(\text{C}=\text{S})(\text{R}^3 \text{R}^4 \text{N})$, R in general indicates to alkyl or aryl group (See Figure 1).

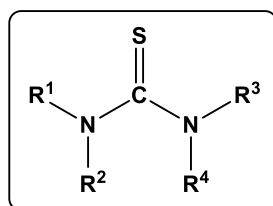


Figure 1: Public formula of thiourea derivatives.

According to the general form of thiourea derivatives and the former studies, two structural forms, trans and cis stereo isomers are probable to observe in N- alkyl thiourea derivatives with form $(\text{R}^1 \text{R}^2 \text{N})(\text{C}=\text{S})(\text{NH}_2)$. While three various isomer structures are conceivable to notice in N,N'-dialkyl thiourea derivatives with form $(\text{R}^1 \text{R}^2 \text{N})(\text{C}=\text{S})(\text{R}^3 \text{H N})$ and $(\text{R}^1 \text{H N})(\text{C}=\text{S})(\text{R}^3 \text{R}^4 \text{N})$ [6]. (See **Figure 2**). In previous studies, different techniques like X-rays, Raman and FT-IR used to confirm the cis structure of N-methyl thiourea $(\text{CH}_3 \text{NH})(\text{C}=\text{S})(\text{NH}_2)$ [7]. However, it was found that N,N'-dimethylthiourea $(\text{CH}_3 \text{NH})(\text{C}=\text{S})(\text{CH}_3 \text{NH})$ and N,N'-diethyl thiourea $(\text{CH}_3 \text{CH}_2 \text{NH})(\text{C}=\text{S})(\text{CH}_3 \text{CH}_2 \text{NH})$ arranged theirself in trans-trans structure [8-9].

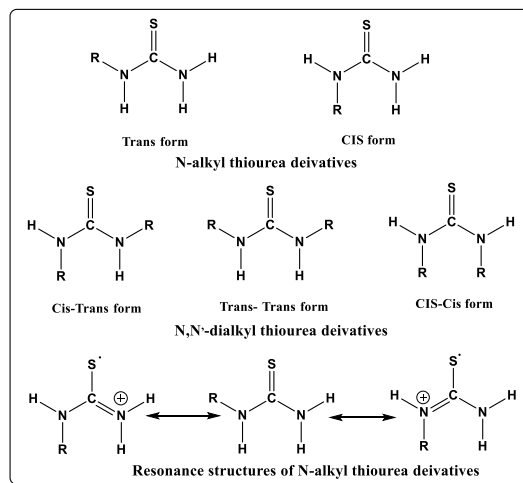
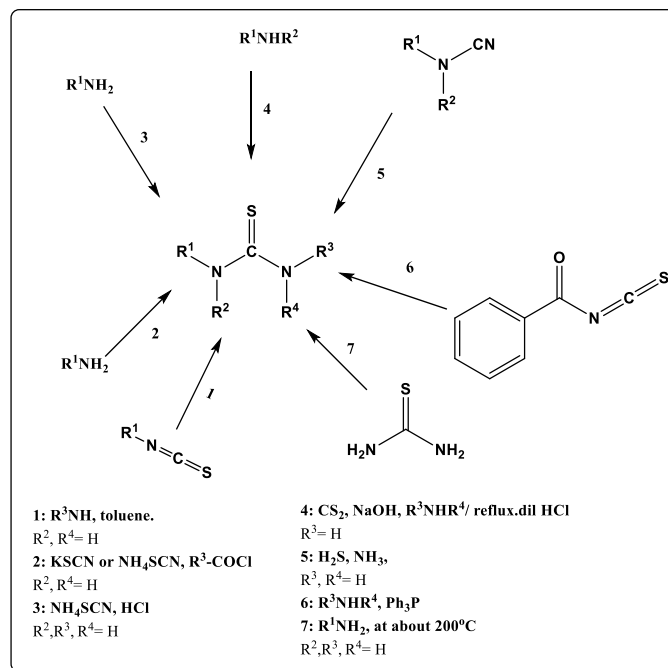


Figure 2: Conformational forms of N-alkyl and N,N'-dialkyl thiourea derivatives.

Different synthetic routes to create Thioureas

Valuable Descriptive methods of *thiourea compound and its derivatives have been generated from its preparation from the first time till now*. A widespread paths of these methods are summarized and collected in **Scheme 1**:

1: Alkyl isothiocyanate stirred at room temperature with amines in toluene solvent [10]. **2:** The reaction of potassium thiocyanate or ammonium thiocyanate with acid chloride and then adding of primary amine, lastly base hydrolysis is employed [11]. **3:** Acidic medium is used to react NH_4SCN and R-NH_2 to result the desired thioureas [12]. **4:** Secondary amine condensate with carbon disulfide in alkali media, then primary amine added. The mixture is refluxed with adding dilute acidic solution [13]. **5:** The mixture of Cyanamide derivatives and H_2S in NH_3 solution are stirred to form derived thiourea [14]. **6:** Condensation of benzoyl isothiocyanates and secondary amines with existence of $\text{HC}\equiv\text{C-COOR}$, $\text{R} = \text{alkyl}$ and Ph_3P employed to synthesis thiourea derivatives [15]. **7:** Thiourea as ligand reflux with primary amine at about 200°C to produce the required thiourea derivative [16].



Scheme 1: The familiar methods to create thiourea derivatives.

2. Thioureas applications in coordination chemistry and biological activity

Organic substances involving oxygen, sulfur and nitrogen donor centers act as a specific and privilege chelating agents in coordination chemistry. Thiourea compounds are classified from the most important class of organic substances and this is attributed to their broad range applications in many areas. In coordination chemistry, previous published studies have focused on the role of thiourea derivatives being functional ligands. Thiourea ligands coordinate mostly by oxygen and sulfur atoms with the metal center to form MOS skeletal structure [17-19]. In addition to the active role of thiourea derivatives in coordination chemistry, they have been known for using as construction component to form a big assortment heterocyclic derivatives [20-22], strong selectivity of ruthenium, rhodium, palladium, osmium, iridium, and platinum metals in liquid-liquid extraction process [23]. Recently, researchers have shown an increased interest in thiourea derivatives due to their wide range of pharmacological activity as antimicrobial [24], antifungal [25] and antiviral agents [26]. They have been promoted to be anion-binding centers in a hydrogen bonding sensors [27]. The transition metal complexes of thioureas coat a widespread range of different applications due to their behavior enhancement through the nature of sulfur atom and e^- distribution in the metal center [28]. In recent years, a considerable literature has grown up around the metal complexes of thioureas containing nitrogen, oxygen and sulfur atoms in biological activity field [29-31].

The derived benzoyl thioureas (**Figure 3**) are one of the most widely used compounds of thiourea derivatives due to their easy synthesis accompanying with high percentage of product [32-35]. Interestingly, synthesis of novel benzoyl thiourea derivatives is remarkably growing fast due to

their exhibition valuable efficiency in different applications such as analytical [36-38], and biological fields as insecticidal, antifungal, antithyroid, antitubercular, antibacterial, antitumor, antiviral and herbicidal [39-46], as well as to use them as selective agents to extract several specific worth metals like copper, cobalt, nickel, silver, palladium and gold to form more stable metal chelates [47-48]. In coordination chemistry, studies over the past decade have interested with transition metal complexes of benzoyl thioureas and provided important information on their properties [49-51]. This interesting is related with the structural form of benzoyl thioureas which have carbonyl and C=S functional groups leading them to act as privilege chelating agents because of their capability to surrounding through the coordinating group metal centers [52]. In addition, It has previously been investigated the thermal behavior of the metal complexes of thioureas [53-55]. Thioureas have been probed as catalyst and present good efficiency for electrochemical reduction of positive metal ions such as Zn^{+2} and Cd^{+2} [56-57]. Thioureas Catalysts control and convert the mechanism and the kinetic of reactions depending on the force of M-S bond that form by the tautomerism in thiourea [58].

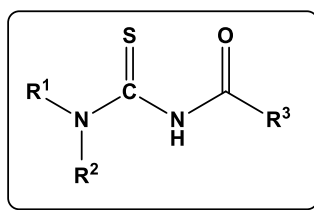


Figure 3: general structure of benzoyl thiourea derivatives.

3. Thioureas applications in electrochemistry

Broadly, thiourea ligands include a specific substituents having various electron withdrawal or donor atoms and this may acquire them remarkable electrochemical behavior. In recent years and due to these properties, more attention has focused on the studying electrochemical features of generally derived thioureas and in particular benzoyl thiourea derivatives [59-61]. The existence of oxygen and nitrogen atoms, and sulfur atom which are considered as hard and soft atoms respectively, in the vertebral column of thiourea derivatives contribute to obtain fast reaction between thiourea free ligands and metal ions producing stable complexes [62]. Thioureas played a vital role to precipitate metals by electrochemical participation as well as to inhibit the growing of corrosion operation [63-64].

4. Historical survey of thioureas and their metal complexes: synthesis methods, geometrical structures and electrochemical studies using cyclic voltammetry technique.

In spite of the huge applications of thiourea derivatives in many areas as mentioned above, the electrochemical behavior especially cyclic voltammetry of their transition metal complexes has not been profusely investigated. We are trying here to display historical review of thioureas and their metal complexes with connection among the synthetic routes, geometry and their cyclic voltammograms. Since 2001, Yao Feng Yuan and its group were interested to synthesis thiourea derivatives. They synthesized N-ferrocenoyl-N'-arylalkylthioureas, Fc-CO-NH-CS-N'HR (Fc=ferrocenyl; R=phenyl, p-methoxy phenyl, p-acetyl phenyl, o-methyl phenyl; o- chloro phenyl). When they react these thiourea derivatives with copper (II) chloride at room temperature in alcoholic solution, they got unusual results through formation of the corresponding Cu(I) complexes instead of what was expected as Cu(II) complexes. The reducing of Copper(II) ion to Copper(I) through the coordination reaction is attributed to the role of thiourea free ligands as reducing agents due to the high affinity of the S-atom to copper(I) ion. These compounds were confirmed by spectroscopic techniques and x-ray single crystal structures. Thiourea free ligands tend to coordinate as a monodentate ligands by the sulfur atom with three coordinated Cu(I) ion in a (S-MCl-S) model to form a trigonal planar geometry (**Figure 4**). Obviously, the Copper(I) ion coordinated with two sulfur atoms in two separated molecules of free ligands and the third bond was with the chloride ion.

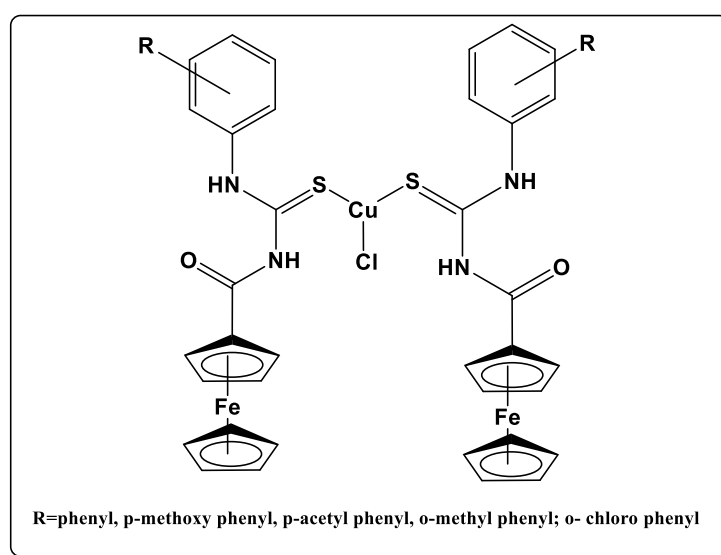
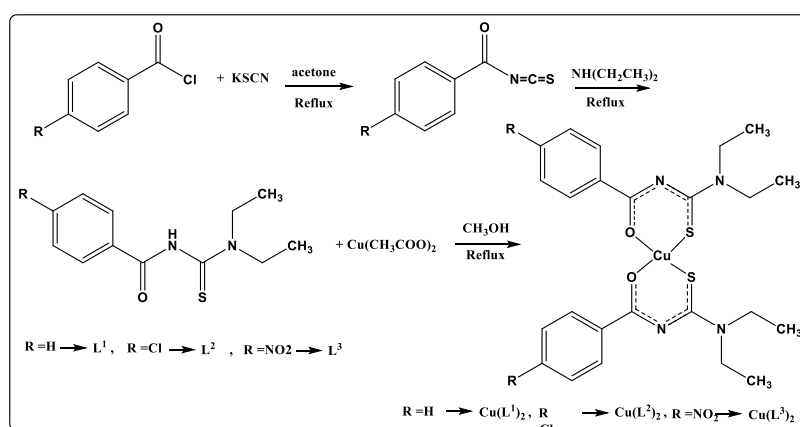


Figure 4: Trigonal planar Copper(I) complexes of N-ferrocenoyl- N'-arylalkylthioureas.

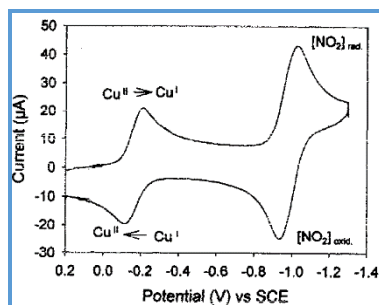
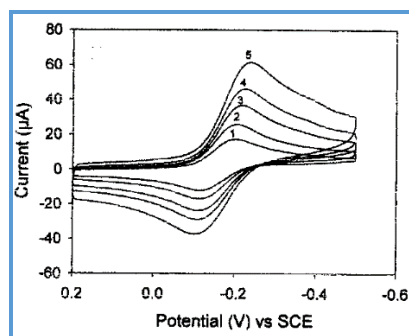
The electrochemical behavior of Copper(I) complexes of N-ferrocenoyl-N'-arylalkylthioureas has been investigated in methylene di chloride solvent by CV technique. All unbonded ligands and their complexes exhibited ferrocene/ferrocenium redox couple for ferrocenyl fragments through one reversible redox peak attributing to Ferric/ Ferrous peak at 0.72-0.79 Volts.

As well as, It is noted in cyclic voltammograms for complexes that no redox processes of copper(I)/ copper(II) couple appeared [65]. In 2005, Wilfredo Hermindez and its group synthesized acyl thiourea derivatives: N,N-diethyl-N'-benzoyl thiourea (HL^1), N,N-diethyl-N'-O-chloro benzoyl thiourea (HL^2) and N,N-diethyl-N'-P-nitro benzoyl thiourea (HL^3). Then they prepared Cu(II) complexes of these thiourea derivatives. The full characterization like 1H -NMR, ^{13}C -NMR, Mass spectra, IR, UV-visible and CHN especially X-ray single crystallography confirmed the square-planer geometry of Cu(II) complexes with formula $Cu(L)_2$ accompanied by tetra dentate thiourea ligands through coordination via O and S atoms in a cis stereochemistry with removal of two protons of ligands. Acyl thiourea derivatives (HL^1 , HL^2 and HL^3) were created through the refluxing of the corresponding acid chloride with KSCN in acetone and then adding the $NH(CH_2CH_3)_2$. While Cu(II) complexes were prepared by the stirring of the (HL^1 - HL^3) ligands with $Cu(CH_3COO)_2$ in a mole ratio of 2:1 (L:Cu) to form $Cu(L)_2$ [66-67]. (**Scheme 2**).



Scheme 2: Synthesis of acyl thiourea compounds and their Copper(II) complexes.

The electrochemical data for $[Cu(L^1)_2]$, $[Cu(L^2)_2]$ and $[Cu(L^3)_2]$ complexes were investigated by the cyclic voltammetry through the study of the reduction/oxidation system in 10^{-3} M solution of dimethylsulfoxide solvent using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. The free ligands HL^1 - HL^3 do not show any redox peak excepting HL^3 ligand that gave -1.05 volt reduction peak attributed to the reduction of p-nitro phenyl moiety. CV of the Copper(II) complexes present a quasi-reversible peak for the copper(II)/ copper(I) with three reductive peaks in the range from -0.21 to -0.3 volts and slight effect were observed of the electrochemical features by additional of the Cl and NO_2 groups to the ph-(CO)- group [68]. (**Figures 5 and 6**).

Figure 5: CV of $\text{Cu}(\text{L}^3)_2$ complexFigure 6: CV of the $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ redox process at different scan rate ($50\text{-}500 \text{ m.volts}^{-1}$) of $\text{Cu}(\text{L}^3)_2$ complex

F.A. Saad and his research team reported in 2012 the synthesis of Bis(6-benzoylthiourea-2-pyridylmethyl)(2-pyridylmethyl) amine L and its Nickel(II), Cobalt(II) and Copper(II) complexes. L ligand was synthesized by the gradually adding of benzoyl isothiocyanate to the ethanolic solution of Bis(6-amino-2-pyridylmethyl)(2-pyridylmethyl)amine (BAPA). The mixture was stirred at 40°C to a few minutes to get the desired product. The preparation of transition metal complexes were achieved by the stirring of the mixture of the free ligand in acetonitrile and the metal perchlorate salt. The crystals were arising at room temperature by the diffusion of di ethyl ether vapor into its mixture solution. This research article showed the different geometries of transition metal complexes, six coordinated octahedral Nickel(II) complexes with NiN_4S_2 core and the Co(II) and Cu(II) complexes adopted five coordinated trigonal bipyramidal with MN_4S core as shown in Fig. 7.

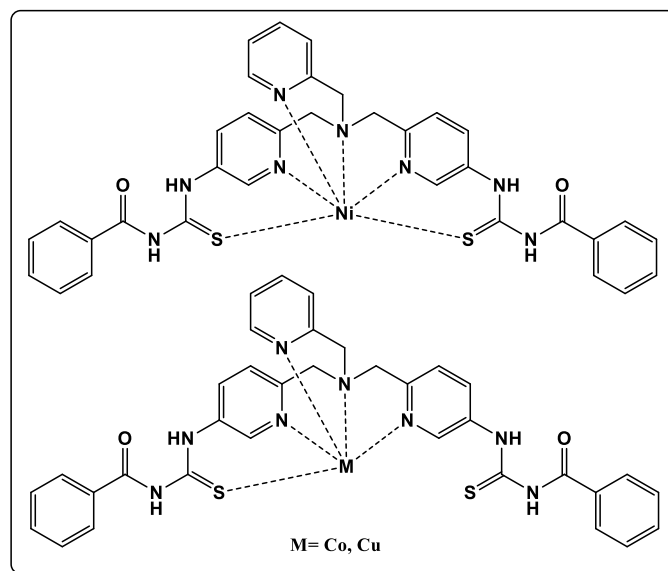


Figure 7: Octahedral NiL and trigonal bipyramidal CoL and CuL complexes.

The electrochemical behavior of free ligand L and its Nickel(II), Cobalt(II) and Copper(II) complexes have been studied in acetonitrile solution at working and counter platinum electrodes and Ag/AgNO₃ as reference electrode. CV of the Nickel(II) complex exhibited two irreversible reduction peaks at -1.78 V and -1.37 V while the Cobalt(II) complex showed a single reversible system at anodic potential of +0.36 V which is assigned to Cobalt(II)/Cobalt(III) redox couple. The Copper(II) complex present an electrochemically one reversible Copper(II)/Copper(I) redox process at -0.35 V [69] (see Figure 8).

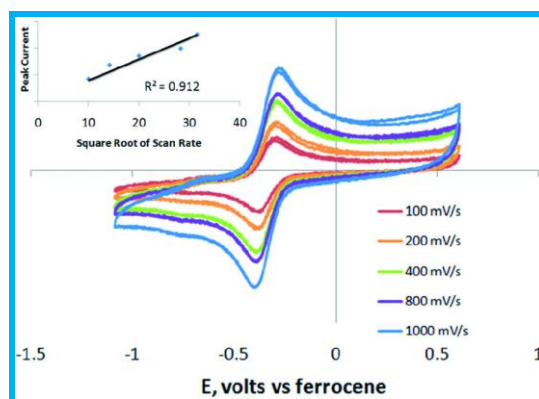
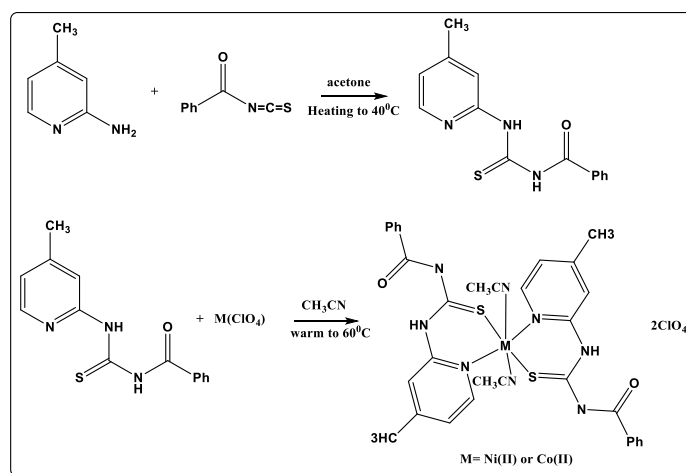


Figure 8: CV of the Copper(II)/Copper(I) redox process at different scan rate(100-1000 m.volts⁻¹) of CuL complex.

Again F. A. Saad in 2014 exhibited an interesting with study the cyclic voltammogram of another thiourea derivatives. He synthesized 1-Benzoyl-3-(4-methylpyridin-2-yl) thiourea ligand

and their complexes with Nickel(II) and Cobalt(II) ions (**Scheme 3**). The thiourea ligand and their Nickel(II) and Cobalt(II) complexes were investigated through full characterization. An octahedral geometry for the complexes were proposed according to UV-visible spectral data and with the complete confirmation by x-ray single crystals. The IR spectra of the complexes showed blue shift of the C=N and C=S bonds as compared to free ligand and this is confirmed the coordination through metal ion with nitrogen and sulfur atoms respectively [70-71].

The reduction/oxidation core plays as a redox catalyst and its capability to carry electrons is described by the redox potential making it as an essential variable factor in electrochemical studies. In coordination chemistry, especially in the transition metal complexes, cyclic voltammetry technique is extremely important to discover the oxidation state of the metal ion which perhaps influenced through the complex preparation depends on the base number of the free ligand. The efficiency of CV issues from its tendency to speedy provide considerable data on the reduction/oxidation manners along a broad potential extent. Pt-wire was employed as counter electrode and silver/ silver nitrate was employed as reference electrode immersing in the mixture of 0.1 Molar of tetrabutylammonium perchlorate in acetonitrile solvent to accomplish the electrochemical studies. The cyclic voltammograms for Ni(II) and Co(II) complexes reflected two consecutive irreversible peaks for one electron transfer system. The reduction peaks are attributed to Metal(II)/Metal(I) and Metal(III)/Metal(II) and It was noticed at -0.5 V and -0.35 V, and at -1.65 V and -1.73 V of the Nickel(II) and Cobalt(II) derivatives respectively [72-73].



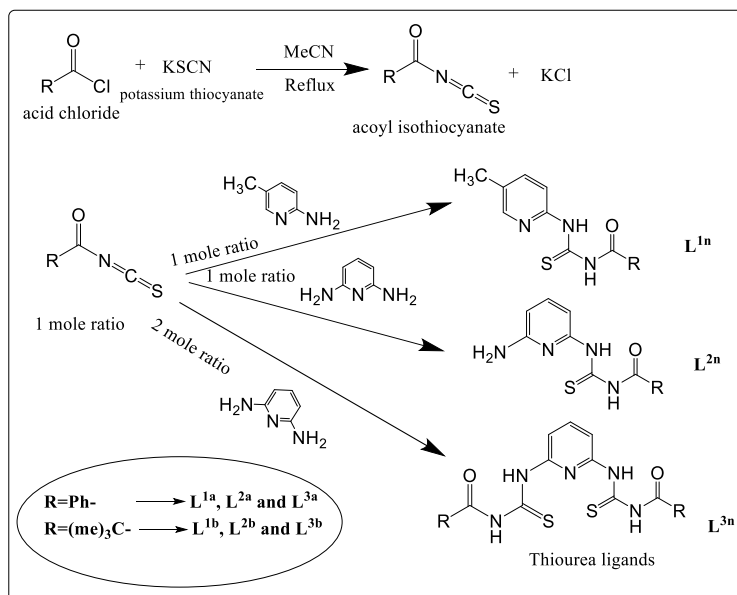
Scheme 3: Experimental steps for Synthesis of 1-Benzoyl-3-(4-methylpyridin-2-yl) thiourea ligand and their Nickel(II) and Cobalt(II) complexes.

Series of benzoyl thiourea and pivaloyl thioureas and their transition metal complexes were focused, created with full characterization by Ali A. A. AL-Riyahee in 2016 [74]. The preparation of

(L^{1a}-L^{3b}) ligands was performed by refluxing the corresponding acid chloride with KSCN, then the filtrate, benzoyl or pivaloyl isothiocyanate was refluxed with 5-methyl-2-amino pyridine in equimolar ratio from the reactants or with 2,6-di amino pyridine in equimolar and bimolar from the starting materials [75], (see **scheme 4**). The transition metal complexes were prepared through the stirring of (L^{1a}-L^{3b}) ligands with Cu(ClO₄)₂ and Ni(ClO₄)₂ salts in the required solvent. Full characterization techniques especially UV-visible, magnetic susceptibility measurements and x-ray single structures confirmed the square planer four coordinate system around Ni(II) complexes with L^{1a}, L^{2a}, L^{1b} and L^{2b} ligands and six coordinated octahedral for the Nickel(II) complexes with L^{3a} and L^{3b}. The Cu(I) complexes with the same ligands were confirmed too to show tetrahedrally coordinated Cu(I) ion with two bidentate ligands, each one coordinates by the sulfur C=S group and nitrogen atom in pyridine ring. In the other hand, L^{3a} and L^{3b} ligands act as tridentate ligands by their coordination by nitrogen pyridyl group and two sulfur atoms from thiourea giving trigonal planer environment around Ni(II) and Cu(I) metal ions in (1:1) L: M and octahedral geometry in (2: 1) L: M mole ratio.

The cyclic voltammograms of Copper(I) complexes exhibited a quasi-reversible system in the reductive side (-0.23 – -0.3 volt) which is corresponding to copper I/ Copper II. Big peak to peak separation and the less i_{pc}/i_{pa} ratio confirmed the quasi-reversible nature. **Figure 9** and **10** present cyclic voltammograms for [Cu(L^{1a})₂]ClO₄ and [Cu(L^{3a})₂]ClO₄. The Ni(II) complexes displayed two irreversible peaks from -1.11 to -1.134 volt and from -1.63 to -1.99 volt corresponding to ligand based [76] and Nickel II/ Nickel I process respectively. **Figure 11** shows cyclic voltammograms for [Ni(L^{1a})₂](ClO₄)₂. The cyclic voltammetry experiments were performed in CH₃CN solvent and 10⁻³ Molar of the sample under study and 10⁻¹ Molar of supporting electrolyte [Bu₄N][PF₆]. Three electrodes system was used to accomplish all these experiments containing Pt-disk, platinum wire and silver/silver chloride as working, counter and reference electrodes sequentially. Dry N₂ gas or He gas are necessary passed in the mixing solution before measure CV to guarantee of remove the O₂ gas which shows peak in cyclic voltammogram.





Scheme 4: Synthesis of benzoyl and pivaloyl thiourea ligands (L^{1a} – L^{3b}).

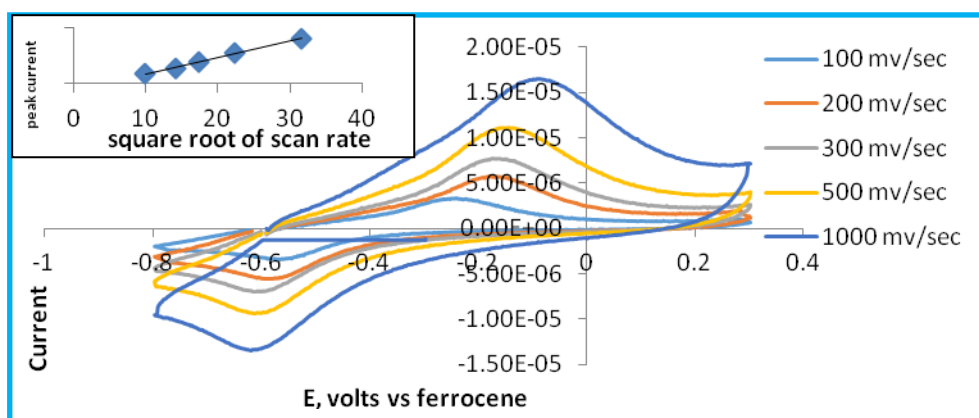


Figure 9: CV of $[Cu(L^{1a})_2]ClO_4$ shows quasi-reversible peak.

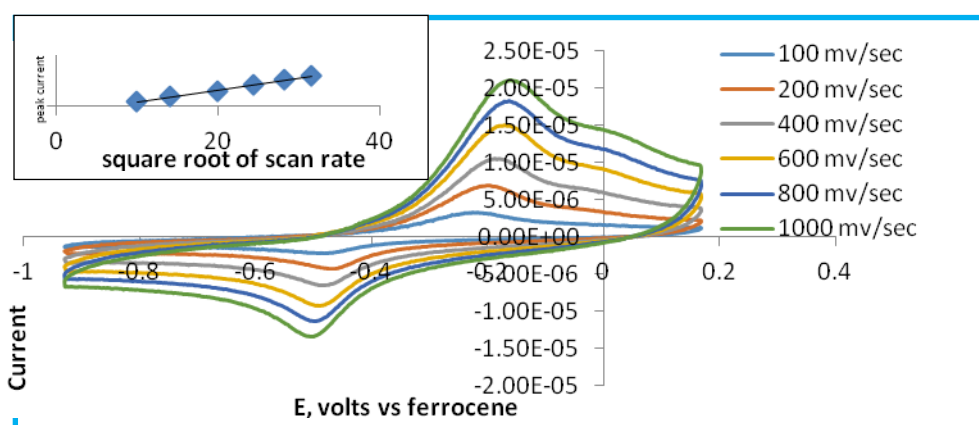


Figure 10: CV of $[Cu(L^{3a})_2]ClO_4$ shows quasi-reversible peak.

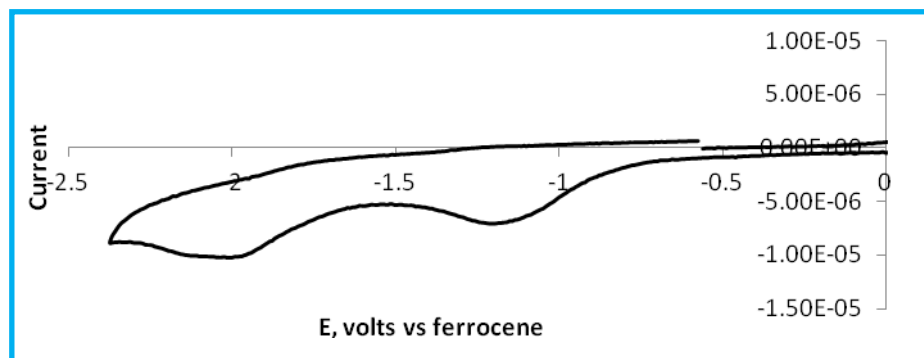


Figure 11: CV of $[\text{Ni}(\text{L}^{1\text{a}})_2](\text{ClO}_4)_2$.

The coordination chemistry of N-((6-methylpyridin-2-yl)carbamothioyl)thiophene-2-carboxamide ligand (HL) with Cobalt(II), Copper(II) and Nickel(II) ions were investigated in 2016 by Tuncay Yeşilkaynak [77]. Two moles of HL bidentate ligand coordinated with metal ions by sulfur with oxygen atoms to compose square planer geometry in ML_2 system. Thiophene carboxylic acid chloride was refluxed with potassium thiocyanate in acetone and the filtrate was stirred with solution of 6-methyl-2- amino pyridine in acetone. The collected solid is the desired compound [78]. Tuncay Yeşilkaynak interested with study the electrochemical manner of HL and Copper(II) complex by using BAS 100 W (Bioanalytical, USA) electrochemical apparatus which have individual unit with three electrodes. These electrodes are glassy carbon working electrode, silver/silver chloride reference electrode and pt-wire counter electrode. The cyclic voltammogram revealed two irreversible peaks, the first one in the anodic region at +0.52 volt and the other at -1.4 volt in the cathodic region. **Figure 12** showed CV of the Copper(II) complex at various sweep rate [79].

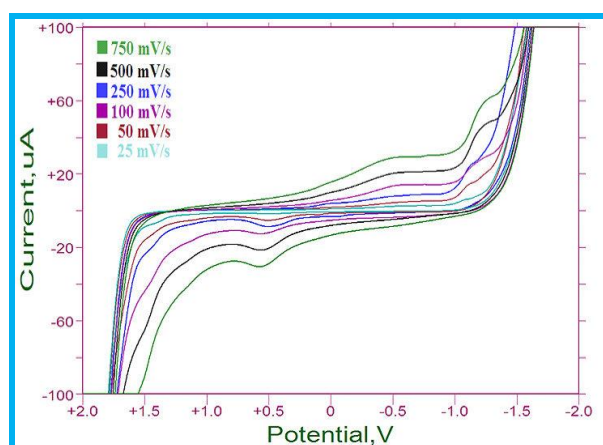


Figure 12: CV of the $[\text{HLCu}]$ with HL ligand at various sweep rate (25- 750 mV/ Sec).

In 2018, Copper(II) and Nickel(II) complexes of N-(dimethylcarbamothioyl)-4-fluorobenzamide (HL) were created with fully characterization by Gun Binzet and his work team [80]. The spectrographic analysis of the ligand and its complexes is compatible to square planer structure of the prepared complexes in the general form $[ML_2]$ and the metal center coordinated with two bidentate thiourea ligand (HL) through two sulfur atoms from C=S bond and two oxygen atoms from carbonyl groups. HL was created by amendment of the method reported by G. Benzit to rectify the coordination feature [54]. Synthesis of HL ligand accomplished by the preparation of 4-fluorobenzoyl isothiocyanate from the refluxing the mixture of 4-fluoro benzoyl chloride and KSCN in acetone. $(CH_3)_2NH_2$ in acetone was stirred with 4-fluorobenzoyl isothiocyanate to obtain HL ligand. The metal complexes of HL were produced by stirring the mixture of $Cu(CH_3COO)_2$ or $Ni(CH_3COO)_2$ in with the free ligand in methanolic solution to form $[CuL_2]$ and $[NiL_2]$ complexes [81]. The $[L_2Cu]$ and $[L_2Ni]$ complexes exhibited significant electro active response towards cyclic voltammetry. Cyclic voltammograms are achieved in dichloromethane solvent and NBu_4PF_6 employed as supporting electrolyte to enhance the conductivity of solutions under study. Cyclic voltammograms of $[L_2Cu]$ and $[L_2Ni]$ complexes are presented in **Figures 13** and **14**. The $[L_2Cu]$ complex showed one reversible redox process centered at -0.085 volt against Ag/AgCl resulting to copper II/ copper I process at 0.01 mv/sec [82]. The cyclic voltammogram of $[L_2Ni]$ complex revealed a quasi-reversible and an irreversible oxidative systems at +0.59 volt and +1.38 volt sequentially. A quasi-reversible reduction/ oxidation peak caused by Nickel(II)/Nickel(III) process while the irreversible oxidation peak is related with the ligand L component [83-84].

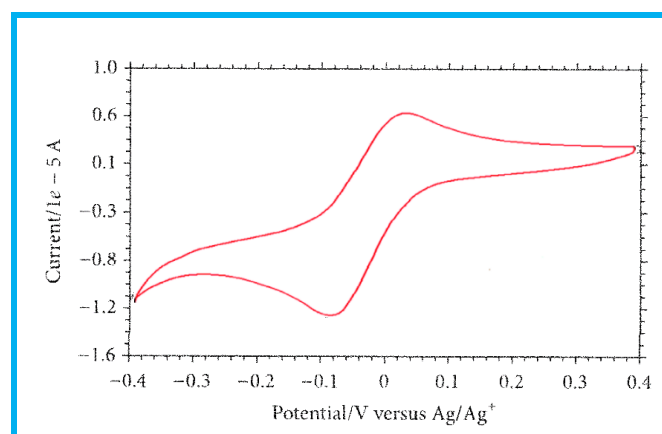


Figure 13: The Cyclic voltammogram of $[L_2Cu]$ complex.

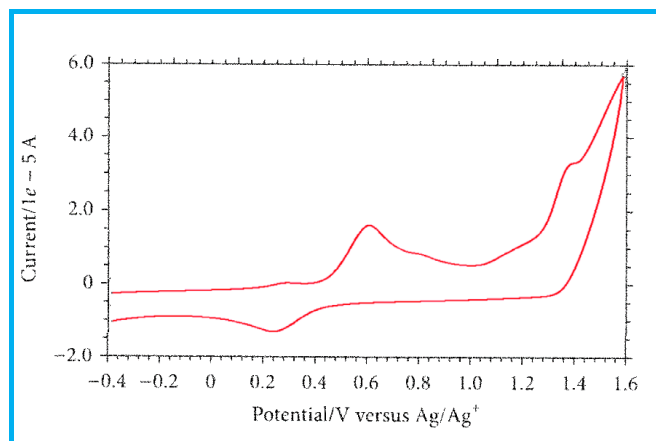


Figure 14: The Cyclic voltammograms of [L₂Ni] complex.

Conclusions

This article review has focused and discussed extensively the different employments of thioureas with their complexes. Undoubtedly, thioureas act good role in biological system with high efficiency as antibacterial, antifungal, antimalarial, antitubercular, antithyroid and insecticidal. The heteroatoms involving in the structure of thiourea derivatives earned them additional characteristics to their pharmacophore features by easy forming complexes with metal ions. This research was oriented to explore variable geometry structure of thioureas complexes depending on free ligand structure to form four coordinate, square-planar and tetrahedral geometry, six coordinate octahedral geometry. Generally, it is easy to form thioureas with high yield through two steps: first, the reaction between potassium thiocyanate with acid chlorides and second, the filtrate from the first step is reacted with the corresponding amine. So many of researchers depended on this procedure to synthesis acyl thiourea derivatives. Electrochemical studies almost investigate and confirm the reduction/oxidation process corresponds Metal(II)/Metal(III) ions or Metal(I)/Metal(II) ions in the oxidation part and Metal(III)/Metal(II) ions or Metal(II)/Metal(I) ions in the reduction part through reversible or quasi-reversible electron transfer process. Sometimes thioureas moiety exhibits irreversible system.

References

- [1] C. Alkan, Y. Tek and D. Kahraman, "Preparation and characterization of a series of thiourea derivatives as phase change materials for thermal energy storage", *Turk. J Chem.*, 35(2011) 769–777.
- [2] B. Mertschenk, F. Beck and W. Bauer. "Thiourea and Thiourea Derivatives". *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH, (2002).
- [3] G. You, H. He, B. Feng, Y. Tang, Z. Cheng, F. Fan, "Synthesis and application of a novel phosphoryl thiourea-containing flame retardant for epoxy resin", *Chem. Pap.*, 74(2020)2403–2414.
- [4] G. Waris, H. M. Siddiqi, L. J. Twyman, R. Hussain, Z. Akhter and M. S. Butt, "Novel flame retardant poly(thiourea-sulfone-imide)s for high temperature applications: Synthesis and characterization", *Turk. J Chem.*, 37(2013) 946-958,
- [5] B. Rodgers, S. Soils, N. Tambe, B. B. Sharma and W.H. Waddell, "Thiourea accelerators in the vulcanization of butyl elastomers", *Rubber World*, 233(2006) 29-37.
- [6] M. J. Moloto, M. A. Malik, P. O'Brien, M. Motevalli and G. A. Kolawole, "Synthesis and characterisation of some N-alkyl/aryl and N,N'-dialkyl/aryl thiourea cadmium(II) complexes: the single crystal X-ray structures of $[\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHCH}_3)_2]_n$ and $[\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHCH}_2\text{CH}_3)_2]$ ", *Polyhedron*, 22(2003) 595–603.
- [7] G. Vassilev, V. Koleva, M. Ilieva and B. Galabov, "Spectra and conformations of substituted thioureas", *J Mol Struct*, 82(1982) 35–41.
- [8] Y. Mido, I. Kitagawa, M. Hashimoto and H. Matsuura, "Vibrational spectra and normal coordinate analysis of N-methylthiourea and three deuterated analogues" *Spectrochim Acta A*, 55(1999) 2623–2633.
- [9] X. Shen, X. Shi, B. Kang, Y. Liu, Y. Tong, H. Jiange and K. Chen, "Syntheses, crystal structures and properties of Zn(II) and Cd(II) complexes derived from N-(o-nitrophenyl)-N'-(methoxycarbonyl) thiourea(H₂omt) and 2,2'-bipyridine(bpy) or o-phenanthroline(phen)", *Polyhedron*, 17(1998)4049-4058.
- [10] M. Kiranmai, "Synthesis, Antimicrobial Activity and Docking Studies of Novel Urea and Thiourea Derivatives", *Iqsr-Jpbs*, 11(2016)10-16.
- [11] M. M. Milosavljević, I. M. Vukićević, V. Šerifi, J. S. Markovski, I. Stojiljković, D. Ž. Mijin and A. D. Marinković, "Optimization of the synthesis of N-alkyl and N,N'-dialkyl thioureas from waste water containing ammonium thiocyanate", *Chem. Ind. Chem. Eng. Q*, 21(2015) 501–510,
- [12] B. Loev, P. E. Bender, H. Bowman, A. Helt, R. McLean and T. Jen, "Amidines. 3. Thioureas possessing antihypertensive activity" *J Med Chem*, 15(1972) 1024–1027.
- [13] F. E. Critchfield and J. B. Johnson, "Reaction of Carbon Disulfide with Primary and Secondary Aliphatic Amines as Analytical Tool", *J Anal Chem*, 28(1956) 430–436.

- [14] S. Wang and S. Lv, " Notice of Retraction:: The Preparation Process of Thiourea from Cyanamide", 5th International Conference on Bioinformatics and Biomedical Engineering (2011), Conference Location: Wuhan, China.
- [15] I. Yavari, S. Zahra Sayyed-Alangi, M. Sabbaghan, R. Hajinasiri and N. Iravani, "One-pot synthesis of functionalized thioureas by reaction of benzoyl isothiocyanates, secondary amines, and alkyl propiolates", *Montash Chem*, 139(2008) 1025-1028.
- [16] J. Erickson, " Notes - Reactions of Long-Chain Amines. VI. Preparation of Thioureas", *J Org Chem*, 21(1956) 483-484.
- [17] M. Graser, H. Kopacka, K. Wurst, T. Müller and B. Bildstein, "Structurally diverse pyridyl or quinolyl enolato/enamido metal complexes of Li, Zr, Fe, Co, Ni, Cu and Zn", *Inorg. Chim. Acta*, 401(2013) 38-49.
- [18] A. Kossmann , R. Ehnert , A. Preuß , N. Ruffer , M. Korb , S. Schulze , C. Tegenkamp , F. Köster and H. Lang, "The di(thiourea)gold(I) complex $[Au\{S=C(NH_2)_2\}_2][SO_3Me]$ as a precursor for the convenient preparation of gold nanoparticles" *Z Naturforsch*, 75(2020) 239–249.
- [19] A. D. Burrows, M. D. Coleman and M. F. Mahon, "Platinum thiosemicarbazide and thiourea complexes: the crystal structure of $[PtCl(dppe)\{SC(NHMe)NHNMe_2-S\}](PF_6)$ and the influence of intramolecular hydrogen bonding on ligand co-ordination mode", *Polyhedron*, 18(1999) 2665–2671.
- [20] M. Kodomari, M. Suzuki, K. Tanigawa and T. Aoyama, " A convenient and efficient method for the synthesis of mono- and N,N-disubstituted thioureas" *Tetrahedron Lett.*, 46(2005) 5841–5843.
- [21] R-S Zeng, J-P Zou, S-J Zhi, J. Chen and Q. Shen, " Novel Synthesis of 1-Aroyl-3-aryl-4-substituted Imidazole-2-thiones", *Org Lett*, 5(2003) 1657–1659.
- [22] D. P. Singh, S. Pratap, S.K. Gupta and R.J. Butcher, " 3-[(Furan-2-yl)carbon-yl]-1-(pyrimidin-2-yl)thio-urea" *Acta Crystallogr E*, 68(2012) 3300–3301.
- [23] S. Bourne and K. R. Koch, " Dalton communications. Intramolecular hydrogen-bond controlled unidentate co-ordination of potentially chelating N-acyl-N'-alkylthioureas: crystal structure of cis-bis(N-benzoyl-N'-propylthiourea) dichloroplatinum(II)", *Dalton T*, 13(1993) 2071-2072.
- [24] F. Steppeler, D. Iwan, E. Wojaczyńska and J. Wojaczyński, "Chiral Thioureas-Preparation and Significance in Asymmetric Synthesis and Medicinal Chemistry", *Molecules*, 25(2020) 401.
- [25] T. Phuong, T. Khac-Minh, N. T. Van Ha and H. T. Ngoc Phuong, " Synthesis and antifungal activities of phenylenedithioureas", *Bioorg Med Chem Lett*, 14(2004) 653–656.
- [26] T. Venkatachalam, E. A. Sudbeck and F. M. Uckun, " Regiospecific synthesis, X-ray crystal structure and biological activities of 5-bromothiophenethyl thioureas", *Tetrahedron Lett*, 42(2001) 6629–6632.



- [27] L. Nie, Z. Li, J. Han, X. Zhang, R. Yang, W. X. Liu, F. Y. Wu, J. W. Xie, Y. F. Zhao and Y. B. Jiang, "Development of N-benzamidothioureas as a new generation of thiourea-based receptors for anion recognition and sensing", *J Org Chem*, 69(2004) 6449–6454.
- [28] M.T. Allen, A.D. Burrows and M.F. Mahon, "Hydrogen bond directed crystal engineering of nickel complexes: the effect of ligand methyl substituents on supramolecular structure" *Dalton T*, 2(1999) 215-222.
- [29] M. S. Refat and N. M. El – Metwaly, "Spectral, thermal and biological studies of Mn(II) and Cu(II) complexes with two thiosemicarbazide derivatives", *Spectrochim Acta A*, 92(2012) 336-346.
- [30] S. Rakhshani, A. R. Rezvani, M. Dušek and V. Eigner, "Design and fabrication of novel thiourea coordination compounds as potent inhibitors of bacterial growth" *J Antibiot*, 72(2019) 260-270.
- [31] K. S. Abou –Melha and N. M. El- Metwally, "Spectral and thermal studies for some transition metal complexes of bis(benzylthiocarbohydrazone) focusing on EPR study for Cu(II) and VO₂⁺" *Spectrochim Acta A*, 70(2008) 277-283.
- [32] R. Shardin, S. S. Tan, and M. Kassim, "Synthesis and structural characterization of N-bromobenzoyl-N-(1,10-phenanthroline-5-yl)thiourea derivatives," *Mjas*, 21(2017) 60–71.
- [33] G. Binzet, F. M. Emen, U. Flörke, T. Yeilkaynak, N. Külcü, and H. Arslan, "4-Chloro-N-[N-(6-methyl-2-pyridyl) carbamothioyl] benzamide," *Acta Crystallogr E*, 65(2009) 81-82.
- [34] D. S. Mansuroglu, H. Arslan, U. Flörke, and N. Külcü, "Synthesis and characterization of nickel and copper complexes with 2,2-diphenyl-N-(alkyl(aryl)carbamothioyl)acetamide: the crystal structures of HL1 and cis-[Ni(L1)₂]," *J Coord Chem*, 61(2008) 3134–3146.
- [35] K. R. Koch, "New chemistry with old ligands: N-alkyl- and N,N-dialkyl-N-acyl(aryl)thioureas in co-ordination, analytical and process chemistry of the platinum group metals," *Coordin Chem Rev*, 216(2001) 473–488.
- [36] M. Gemili, H. Sari, M. Ulger, E. Sahin, and Y. Nural, "Pt(II) and Ni(II) complexes of octahydropyrrolo[3,4-c]pyrrole N-benzoylthiourea derivatives: synthesis, characterization, physical parameters and biological activity," *Inorg Chim Acta*, 463(2017) 88–96.
- [37] D. Totur, S. S. Bozkurt, and M. Merdivan, "Use of pyrocatechol violet modified sodium dodecyl sulfate coated on alumina for separation and preconcentration of uranium(VI)," *J Radioanal Nucl Ch*, 292(2012) 321–327.
- [38] S. S. Hassan, M. M. Shoukry, R. N. Shallan and R. van Eldik, "Synthesis, characterization, speciation and biological studies on metal chelates of 1-benzoyl (1,2,4-triazol-3-yl) thiourea", *J Coord Chem*, 70(2017) 1761–1775.
- [39] S. Saeed, N. Rashid, P. G. Jones, M. Ali and R. Hussain, "Synthesis, characterization and biological evaluation of some thiourea derivatives bearing benzothiazole moiety as potential antimicrobial and anticancer agents," *Eur J Med Chem*, 45(2010) 1323–1331.



- [40] D. Erşen, M. Ülger, S. Mangelinckx, M. Gemili, E. Şahin, and Y. Nural, "Synthesis and anti(myco)bacterial activity of novel 5,5-diphenylpyrrolidine N-arylthiourea derivatives and a functionalized hexahydro-1H-pyrrolo[1,2-c]imidazole", *Med Chem Res.* 26(2017) 2152–2160.
- [41] J. P. Barolli, P. I. S. Maia, L. Colina-Vegas, J. Moreira, A. M. Plutin, R. Mocelo, V. M. Deflon, M. R. Cominetti, M. I. Camargo-Mathias and A. A. Batista, "Heteroleptic tris-chelate ruthenium(II) complexes of N,N-disubstituted-N-acylthioureas: synthesis, structural studies, cytotoxic activity and confocal microscopy studies," *Polyhedron*, 126(2017) 33-41.
- [42] S. Naz, M. Zahoor, M. N. Umar, S. Alghamdi, M. U. K. Sahibzada, W. UlBari, "Synthesis, characterization, and pharmacological evaluation of thiourea derivatives" *Open Chem*, 18(2020) 764-777.
- [43] R. D. Campo, J. J. Criado, R. Gheorghe, F. J. González, M. R. Hermosa, F. Sanz, J. L. Manzano, E. Monte, E. Rodríguez-Fernández, "N-benzoyl-N-alkylthioureas and their complexes with Ni(II), Co(III) and Pt(II)—crystal structure of 3-benzoyl-1-butyl-1-methyl thiourea: activity against fungi and yeast," *J Inorg Biochem*, 98(2004) 1307–1314.
- [44] H. Siddiqui, S. Shafi, H. Ali and S. G. Musharraf, "Synthesis and Erythroid Induction Activity of New Thiourea Derivatives" *J Med Chem*, 17(2021) 121-133.
- [45] S. Saeed, N. Rashid, M. Ali and R. Hussain, "Synthesis, characterization and antibacterial activity of nickel (II) and copper (II) complexes of N-(alkyl(aryl)carbamoithiyl)-4-nitrobenzamide," *Eur. J. Chem.*, 1(2010) 200–205.
- [46] S. Saeed, N. Rashid, M. Ali, R. Hussain, and P. G. Jones, "Synthesis, spectroscopic characterization, crystal structure and pharmacological properties of some novel thiophenethiourea core derivatives," *Eur. J. Chem.*, 1(2010) 221–227.
- [47] M. Dominguez, E. Anticó, L. Beyer, A. Aguirre, S. Garcia-Granda and V. Salvadó, "Liquid–liquid extraction of palladium(II) and gold(III) with N-benzoyl-N',N'-diethylthiourea and the synthesis of a palladium benzoylthiourea complex", *Polyhedron*, 21(2002) 1429–1437.
- [48] U. A. Khan, A. Badshah, M. N. Tahir and E. Khan, "Gold(I), Silver(I) and Copper(I) Complexes of 2,4,6-trimethylphenyl-3-benzoylthiourea; Synthesis and biological applications", *Polyhedron*, 181(2020) 114485,
- [49] MH Ali, IE Zaghoul and MW Khalid, "Microwave Synthesis, Characterization, Biological Activity of N-(p-Chlorophenyl)-N'-Benzoyl Thiourea and its Complexes" *J Chem Sci*, 11 (2020) 1-13.
- [50] S. Parveen, K. K. H. Tong, M. K. Rauf, M. Kubanik, M. A. Shaheen, T. Söhnel, S. M. F. Jamieson, M. Hanif, C. G. Hartinger, "Coordination Chemistry of Organoruthenium Compounds with Benzoylthiourea Ligands and their Biological Properties" *Asian J Chem*, (2019).
- [51] C. Y. Panicker, H. T. Varghese, A. George, and P. K. V. Thomas, "FT-IR, FT-Raman and ab-initio studies of 1,3-diphenyl thiourea," *Eur. J. Chem*, 1(2010) 173–178.
- [52] R. Vivas-Reyes, E. Espinosa-Fuentes, J. Forigua, A. Arias, R. Gaitan, and E. Arguello, "Theoretical study of a series of N-(N-propyl)-N-(para-R-benzoyl)-thioureas with



trans[pt(py)₂Cl] through chemistry reactivity descriptors based on density functional theory," *J Mol Struct*, 862(2008) 92–97.

- [53] A. Saeed, A. Mumtaz, and U. Flörke, "Synthesis, characterization and crystal structure of 1-(4-methylbenzoyl)-3-(4-aminosulfonylphenyl)thiourea," *Eur. J. Chem.* 1(2010) 73–75.
- [54] G. Binzet, Synthesis and characterization of benzoylthiourea derivatives and their metal complexes [Ph.D. thesis], Mersin University, Mersin, Turkey (2009).
- [55] G. Kurt, F. Sevgi and B. Mercimek, "Synthesis, characterization, and antimicrobial activity of new benzoylthiourea ligands," *Chem Pap*, 63(2009) 548–553.
- [56] K. Sykut, J. Saba, B. Marczewska and G. Dalmata, "The influence of thiourea on the electroreduction of Zn ions in various supporting electrolytes in respect to the cap-pair effect", *J. Electroanal. Chem. Interf. Electrochem.*, 178(1984) 295-303.
- [57] R. M. Souto, S. Gonzales and A. Arevalo, "On the adsorption of cadmium(II) ions on a HMDE from KF+thiourea aqueous solution: A chronocoulometric study", *J. Electroanal. Chem. Interf. Electrochem.*, 216(1987)273-282.
- [58] C. A. Widring, C. Chung and M. D. Porter, "The electrochemical desorption of n-alkanethiol monolayers from polycrystalline Au and Ag electrode", *J Electroanal Chem*, 310(1991) 335–359.
- [59] G. Nanjappan, J Peter, S. W. Ng, E. Tiekink, and R. Karvembu, "Tris-chelate complexes of cobalt(III) with N[di(alkyl/aryl)carbamothioyl] benzamide derivatives: Synthesis, crystallography and catalytic activity in TBHP oxidation of alcohols," *J Mol Catal*, 353(2012) 156–162.
- [60] F. Asghar, S. Fatima, S. Rana, A. Badshah, I. S. Butler, M. N. Tahir, "Synthesis, spectroscopic investigation, and DFT study of *N,N'*-disubstituted ferrocene-based thiourea complexes as potent anticancer agents" *Dalton T*, 47(2018) 1868-1878.
- [61] S. Hussain, I. U. Din, A. Raheel, M. N. Tahir and I. Hussain "New bioactive Cu(I) thiourea derivatives with triphenylphosphine; synthesis, structure and molecular docking studies" *J Coord Chem.*, 73(2020) 1191-1207.
- [62] C. K. Ozer, H. Arslan, D. Vanderveer, and G. Binzet, "Synthesis and characterization of *N*-(alkyl(aryl)carbamothioyl) cyclohexanecarboxamide derivatives and their Ni(II) and Cu(II) complexes," *J Coord Chem.*, 62(2009) 266–276.
- [63] K. H. Lubert, L. Beyer and M. Guttman, "Voltammetric study of *N*-benzoythiourea and its *N'-N'* disubstituted derivatives as possible electrode modifiers". *Collect Czech Chem C*, 64(1999) 1937–1952.
- [64] D. Q. Huong, T. Duong and P. C. Nam, "Effect of the Structure and Temperature on Corrosion Inhibition of Thiourea Derivatives in 1.0 M HCl Solution" *ASC Omega*, 4(2019) 14478-14489.



- [65] Y. F. Yuan, J. T. Wang, M. C. Gimeno, A. Laguna, and P. G. Jones, "Synthesis and characterisation of copper complexes with N-ferrocenoyl-N'-aryl(alkyl)thioureas", *Inorg Chim Acta*, 324(2001) 309–317.
- [66] H. Hartmann and I. Reuther, *J Prak Chem-Chem Ztg.*, 315(1973) 144.
- [67] J. C. Brindley, J. M. Caldwell, G. D. Meakins, S. J. Plackett and S. J. Price, "N'-substituted N-acyl- and N-imidoyl-thioureas: preparation and conversion of N',N'-disubstituted compounds into 2-(N,N-disubstituted amino)thiazol-5-yl ketones", *J Chem Soc Perk T*, 1(1987) 1153-1158.
- [68] W. Gorritti, E. Spodine, L. Beyer, U. Schröder, R. Richter, J. Ferreira and M. Pavani, "Synthesis, Characterization And Antitumor Activity Of Copper(II) Complexes, [CuL₂] [HL¹⁻₃=N,N-Diethyl-N'-(R-Benzoyl)Thiourea (R=H, o-Cl and p-NO₂)]", *Bioinorg Chem Appl*, 3(2005) 299-316.
- [69] F. A. Saad, N. J. Burma, A. J. Amoroso, J. C. Knight, and B. M. Kariuki, "Co-ordination behaviour of a novel bithiourea tripodal ligand: structural, spectroscopic and electrochemical properties of a series of transition metal complexes," *Dalton T*, 41(2012) 4608–4617.
- [70] N.M. El-Metwaly and M.S. Refat, "Spectral, thermal, kinetic, molecular modeling and eukaryotic DNA degradation studies for a new series of albendazole (HABZ) complexes", *Spectrochim Acta A*, 78(2011) 196–204.
- [71] H. Sakiyama, Y. Watanabe, R. Ito and Y. Nishida, "Electronic spectral studies of dinuclear Cobalt(II) complexes with a phenol-based dinucleating ligand containing four methoxyethyl chelating arms", *Inorg Chim Acta*, 357(2004) 4309-4312.
- [72] F. A. Saad, "Synthesis, spectral, electrochemical and X-ray single crystal studies on Ni(II) and Co(II) complexes derived from 1-benzoyl-3-(4-methylpyridin-2-yl) thiourea", *Spectrochim Acta A*, 128(2014) 386–392.
- [73] E. Guillon, A. Mohamadou, I. Déchamps-Oliver and J. Barbier, "Synthesis and characterization of copper, nickel and cobalt complexes with N-disubstituted, N'-ethoxy carbonyl thioureas" *Polyhedron*, 15(1996) 947-952.
- [74] Ali A. A. Al-Riyahee, "An Exploration of the Synthesis, Coordination Chemistry and Properties of Novel Thiourea Ligands and their Complexes", PhD Thesis, Cardiff University, Cardiff, Wales, UK (2016). URI: <http://orca.cf.ac.uk/id/eprint/94404>.
- [75] W. Kaminsky, K. I. Goldberg and D. X. West, "Synthesis and structures of two N,N'-bis(2-pyridinyl)thioureas and N-(2-pyridinyl)-N'-(benzoyl)thiourea", *J Mol StructT.*, 605(2002) 9–15.
- [76] F. A. Saad, N. J. Burma, A. J. Amoroso, J. C. Knight and B. M. Kariuki, "Co-ordination behaviour of a novel bithiourea tripodal ligand: structural, spectroscopic and electrochemical properties of a series of transition metal complexes", *Dalton T*, 41(2012) 4608–4617.
- [77] T. Yeşilkaynak, "Synthesis and Characterization of N-((6-methylpyridin-2yl)carbamothioyl)thiophene-2-carboxamide And its Co(II), Ni(II) and Cu(II) Complexes: Calculation of the Molecular Orbitals and Antioxidant and Antitumor Activities", *Jotcsa*, 3(2016) 1-14.



- [78] G. Binzet, G. Kavak, N. Külçü, S. Özbey, U. Flörke, and H. Arslan, "Synthesis and characterization of novel thiourea derivatives and their nickel and copper complexes," *J Chem-Ny*, 2013(2013), Article ID 536562, 9 pages.
- [79] H. Muslu, A. Golcu, M. Tumer and M. Ozsoz, "Electrochemical investigation and DNA-binding studies of pefloxacin–metal(II/III) complexes", *J Coord Chem.*, 64(2011) 3393–3407.
- [80] G. Binzet, E. Turunc, U. Flörke, N. Külçü and H. Arslan, "Crystal Structure and Cyclic Voltammetric Studies on the Metal Complexes of N-(Dimethylcarbamothioyl)-4-fluorobenzamide", *J Chem-Ny*, (2018) ,
- [81] C. K. Ozer, H. Arslan, D. Vanderveer, and G. Binzet, "Synthesis and characterization of N-(alkyl(aryl)carbamothioyl) cyclohexanecarboxamide derivatives and their Ni(II) and Cu(II) complexes," *J Coord Chem*, 62(2009) 266–276.
- [82] M. H. Habibi, R. Mokhtari, M. Mikhak, M. Amirnasr, and A. Amiri, "Synthesis, spectral and electrochemical studies of Cu(II) and Ni(II) complexes with new N₂O₂ ligands: a new precursor capable of depositing copper nanoparticles using thermal reduction," *Spectrochim Acta A*, 79(2011) 1524–1527.
- [83] K. Das, A. Datta, S. Roy, Jack K. Clegg, E. Garrriba, C. Sinha, H. Kara, "Doubly phenoxo-bridged M-Na (M = Cu(II), Ni(II)) complexes of tetradentate Schiff base: structure, photoluminescence, EPR, electrochemical studies and DFT computation," *Polyhedron*, 78(2014) 62–71.
- [84] S. Kundu, A. K. Pramanik, A. S. Mondal, and T. K. Mondal, "Ni(II) and Pd(II) complexes with new N,O donor thiophene appended Schiff base ligand: Synthesis, electrochemistry, X-ray structure and DFT calculation," *J Mol Struct*, 1116(2016) 1–8.



معقدات العناصر الانتقالية لدوره الأولى المشتقة من مركبات N, N'- الثيويوريا المعوضه: التخليق،
استقصاء الأشكال الهندسية والفولتامتري الحلقي: مقالة مراجعة

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المستخلص

تعتبر مشتقات الثايويوريا كمركبات الكبريت العضوي واحدة من أكثر المركبات المستخدمة وعلى نطاق واسع في تطبيقات مختلفة كما سيتم مناقشتها بصورة مستفيضة في هذه المقالة. على سبيل المثال استخدامها في الكيمياء التناسقية بسبب اعتبارها كمصادر غنية للذرات مثل ذرات النتروجين والأوكسجين والكبريت والتي يمكن أن تتناسق في مشتقات البنزوايل بيريدائل ثايوريا من خلال ذرة الكبريت أو ذرة الكبريت وذرة الأوكسجين أو تتناسق في مشتقات البنزوايل بيريدائل ثايوريا من خلال ذرات الكبريت والأوكسجين والنتروجين. تعمل هذه المواقع المانحة الصلبة والناعمة على تسهيل الترابط بين ليكاند الثايويوريا الحر والأيون المعدني من خلال ذرة واحدة أو أكثر لجعل هذه الليكاندات تسلك على أنها روابط أحادية أو ثنائية أو متعددة لتشكل سلسلة ضخمة ومستقرة من المعقدات المعدنية. إن وجود ظاهرة (thiol ↔ thione) tautomerism والتحول بين حالتي الثايول والثيون داخل مشتقات الثايويوريا هو المسؤول عن مرونة ليكاندات الثايويوريا مما يجعلها قادرة وبسهولة على التناسق في أوضاع مختلفة. تعد مشتقات الثيوريا ومركباتها المعدنية من المركبات المعروفة في المجال البيولوجي بامتلاكها فعالية مضاده للجراثيم ، ومضاد للفطريات ، ومضاد للملاريا ، ومضاد للسُّل ، ومضاد للغدة الدرقية ومبيد للحشرات. كما تستخدم مشتقات الثايويوريا ككاشف حيوي لفصل أيونات المعادن ، ومحفز لتخليق المركبات العضوية أو كمواد أولية لتكوين مركبات حلقيه مختلفة. لقد حفزت التطبيقات الواسعة لمركبات الثايويوريا ومعقداتها المعدنية الباحثين المتخصصين للبحث عن تطبيقات جديدة لهذه المركبات وتحضير مشتقات جديدة. الهدف من هذه المقالة هو تقديم مسح تاريخي عن مشتقات الثايويوريا ومعقداتها المعدنية مع التركيز على: أولاً ، استعراض تطور المسارات المختلفة لتحضيرها من خلال استكشاف المواد المتفاعلة والنواتج والعوامل المحفزة وظروف التفاعلات. ثانياً: استعراض الأشكال الهندسية للمعقدات الناتجة وكذلك مواقع التناسق مع الايونات المعدنية. أخيراً ، تم تسليط الضوء على السلوك الكهروكيميائي للمعقدات من خلال استخدام تقنية مقياس الجهد الدوري (Cyclic voltammetry) لدراسة السلوك الكهروكيميائي لليكاندات الحرة ومعقداتها لتأكيد حالة التأكد لأيون المعدن في معقداته.