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

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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 benzyol derivatives or S, O and N atoms in pyridyl hetrocyclic benzyol 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↔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.
1. Introduction

Thiourea or thiocarbamide compound, CS(NH₂)₂, which is in its original physical phase is a white powder, is derived from urea CO(NH₂)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 (R¹ R² N)(C=S)(R³ R⁴ 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 (R¹ R² N)(C=S)(NH₂). While three various isomer structures are conceivable to notice in N,N-dialkyl thiourea derivatives with form (R¹ R² N)(C=S)(R³ H N) and (R¹ H N)(C=S)(R³ R⁴ 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 (CH₃ NH)(C=S)(NH₂) [7]. However, it was found that N,N-dimethyliourea (CH₃NH)(C=S) (CH₃ NH) and N,N-diethyl thiourea (CH₃CH₂NH)(C=S)(CH₃CH₂NH) 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$_4$SCN 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$_2$S in NH$_3$ solution are stirred to form derived thiourea [14].

6: Condensation of benzoyl isothiocyanates and secondary amines with existence of HC≡C-COOR, R= alkyl and Ph$_3$P employed to synthesis thiourea derivatives [15].

7: Thiourea as ligand reflux with primary amine at about 200$^\circ$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 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.](image)

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 spectroscographic 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.](image)

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/ferrocinium redox couple for ferrocenyl fragments through one reversible redox peak attributing to Ferric/ Feroxous peak at 0.72-0.79 Volts.
As well as, It is noted in cyclic voltammmograms 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 (HL¹), N,N-diethyl-N’-O-chloro benzoyl thiourea (HL²) and N,N-diethyl-N’-P-nitro benzoyl thiourea (HL³). Then they prepared Cu(II) complexes of these thiourea derivatives. The full characterization like ¹H-NMR, ¹³C-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 tetradentate thiourea ligands through coordination via O and S atoms in a cis stereochemistry with removal of two protons of ligands. Acyl thiourea derivatives (HL¹, HL² and HL³) were created through the refluxing of the corresponding acid chloride with KSCN in acetone and then adding the NH(CH₂CH₃)₂. While Cu(II) complexes were prepared by the stirring of the (HL¹-HL³) ligands with Cu(CH₃COO)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(L¹)₂], [Cu(L²)₂] and [Cu(L³)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 HL¹-HL³ do not show any redox peak excepting HL³ 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 NO₂ groups to the ph-(CO)- group [68]. (Figures 5 and 6).
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 NiN₄S₂ core and the Co(II) and Cu(II) complexes adopted five coordinated trigonal bipyramidal with MN₄S core as shown in Fig. 7.
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).

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, benzyol 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(ClO_4)_2 and Ni(ClO_4)_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_p/c/ i_p/a ratio confirmed the quasi-reversible nature. Figure 9 and 10 present cyclic voltammograms for [Cu(L^1a)_2]ClO_4 and [Cu(L^3a)_2]ClO_4. The Ni(II) complexes displayed two irreversible peaks from -1.11 to -1.1.34 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](ClO_4)_2. The cyclic volammetry experiments were performed in CH_3CN solvent and 10^{-3} Molar of the sample under study and 10^{-1} Molar of supporting electrolyte [Bu4N][PF_6]. 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 N_2 gas or He gas are necessary passed in the mixing solution before measure CV to guarantee of remove the O_2 gas which shows peak in cyclic volammoram.
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.
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 ML₂ 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 voltammogramm 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 11: CV of [Ni(L₁ᵃ)₂(ClO₄)₂].

Figure 12: CV of the [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 [ML₂] 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. (CH₃)₂NH₂ 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(CH₃COO)₂ or Ni(CH₃COO)₂ in with the free ligand in methanolic solution to form [CuL₂] and [NiL₂] complexes [81]. The [L₂Cu] and [L₂Ni] complexes exhibited significant electro active response towards cyclic voltammetry. Cyclic voltammograms are achieved in dichloromethane solvent and NBu₄PF₆ employed as supporting electrolyte to enhance the conductivity of solutions under study. Cyclic voltammograms of [L₂Cu] and [L₂Ni] complexes are presented in Figures 13 and 14. The [L₂Cu] 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 voltammogramm of [L₂Ni] 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 [L₂Cu] 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.
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معقدات العناصر الانتقالية للدورة الأولى المشتقة من مركبات N,N'-ثيولوثيريا الموضوعة: التخليق، استقصاء الأشكال الهندسية والفولتامترية الحالقي: مقالة مراجعه

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المستخلص

تعتبر مشتقات الثيولوثيريا كمركبات الكبريت العضوي واحدة من أكثر المركبات المستخدمة وعلى نطاق واسع في تطبيقات مختلفة.

كما سيتم مناقشتها بصورة مستقلة في هذه المقالة. على سبيل المثال استخدامها في الكيمياء التطبيقية بسبب اعتبارها كمصادر غنية للذرات مثل ذرات النتروجين والأوكسجين والكربون والتي يمكن أن تتناسق في مشتقات البنزوليثيولوثيريا من خلال ذرة الكبريت أو ذرة الكبريت وذرة الأوكسجين أو تناسق في مشتقات البنزوليثيولوثيريا من خلال ذرات الكبريت والأوكسجين والنتروجين. تتم هذه المواقع الماءية الصلبة والناجحة على تحسين الترابط بين ليازات الثيولوثيريا الحر والأيون المعين من خلال ذرة واحدة أو أكثر لجعل هذه النيازات تتسل على أنها روابط أحادية أو ثنائية أو متعددة لتشكل سلسلة ضخمة ومستقرة من التحول بين حالتين الكبريت والثيانيون داخل مشتقات tautomerism (thiol↔thione) المعقدات المعدنية. إن وجود ظاهرة الثيولوثيريا هو المسؤول عن مرونة ليازات الثيولوثيريا مما يجعلها قادرة وبسهولة على التناسق في أوضاع مختلفة. تعد مشتقات الثيولوثيريا ومركباتها المعدنية من المركبات المعروفة في المجال البيولوجي باعتلاكها فعالية مضادة للجراثيم، ومضاد للفيروسات، ومضاد للملاريا، ومضاد للسل، ومضاد للعدوى الدقيقة ومضاد للعشرات. كما تستخدم مشتقات الثيولوثيريا ككافح حيوي لفصل أيونات المعادن، ومحفز لتحليل المركبات العضوية أو كمواد أولية لتكوين مركبات حلقيه مختلفة. لقد حفزت التدابير ذات الوعي لتكوين مركبات حلقيه مختلفة، لتمكيننا من تطوير الأنواع الجديدة وتحضير مشتقات جديدة.

الهدف من هذه الدراسة هو تقديم مسح تاريخي عن مشتقات الثيولوثيريا ومعداتها المعدنية المحدودين للمبحث عن تطبيقات جيدة لهذه المركبات وتحضير مشتقات جديدة. الدراسة تطور المسارات المختلفة لتحضيرها من خلال استكشاف المواد المتغطاة والمواد المشتراة والمواد المعروفة وظروف التفاعلات. ثانياً، استعراض الأشكال الهندسية للمعقدات الناتجة وكذلك مواقع التناسق بالأيونات المعينة. أخيراً، تم تلخيص النتائج على السلوكي الكهروكيميائي (Cyclic voltammetry) لدراسة السلوكي الكهروكيميائي للأيونات المعينة لاستكشاف الحالة المحدودة لأيون المعين في معقداتها.