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(2-1) Chemicals and techniques**1. Chemicals:**

The following chemicals are used in this work..

<i>Compounds</i>	<i>Purity</i>	<i>Supplied from</i>
Anhydrous sodium carbonate	Purim	Fluka
Acetone	99%	Fluka
Carbon disulfide	98%	Fluka
Copper chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	95%	Fluka
Cobalt chloride $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$	99%	Fluka
Cadmium chloride $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$	98%	BDH
DMF	95%	BDH
DMSO	95%	BDH
Ether	98%	BDH
Ethanol (abs.)	99%	Fluka
Ferrous ammonium sulfate $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	Purim	Fluka
Hydrochloric acid	30%	Merck
Manganese chloride $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	90%	Merck
Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	99%	BDH
Palladium chloride PdCl_2	59% Pd	Merck
Sodium chloride	98%	Fluka
Sodium hydroxide	99%	BDH
Thiosemicarbazide	95%	Merck
Vanadyl sulphate $\text{VO}\text{SO}_4 \cdot \text{H}_2\text{O}$	90%	Merck

2. Techniques:

A- Fourier Transform Infrared Spectrophotometer (FT-IR)

The Infrared Spectra were recorded on a Shimadzu 8300 Fourier Transform Infrared Spectrophotometer (FT-IR) by using the (CsI) in the wave number range $(4000-200)\text{cm}^{-1}$.

B- Electronic Absorption Spectra

The electronic spectra of the complexes were obtained using: (Shimadzu UV-Vis 160A) Ultraviolet Spectrophotometer and using the quartz cell in the range at wave length range (1100-200 nm).

C- Magnetic Susceptibility Measurements

The magnetic Susceptibility values for the prepared complexes were obtained at room temperature using (Magnetic Susceptibility Balance), Johnson Matthey catalytic system division, England.

D- Melting Point Instrument

Gallenkamp M.F.B 600.01 of melting point apparatus was used to measure the melting points of all the prepared compounds.

E- Metal Analysis

The metals content of the complexes was measured using atomic absorption technique by **PERKIN-ELMER 5000** atomic absorption spectrophotometer for the determination of Pd^{+2} , Ni^{+2} , Cu^{+2} , Co^{+2} , Fe^{+2} , Cd^{+2} , Mn^{+2} , V^{+4} .

F- Conductivity measurements

The conductivity measurements were obtained using Corning Conductivity Meter 220.

(2-2) Preparation of starting materials

1. Preparation sodium tetrachloropalladate(II) Na_2PdCl_4

To palladium chloride (1g, 5.64mmole) that dissolved in ethanol (5ml), sodium chloride (1.32g, 22.5mmole) was added; the mixture was then warmed in water bath. The resulting brown precipitate was filtered, washed with diethyl ether and dried under vacuum, yield (60%).

2. Preparation of 2-amino-5-mercapto-1,3,4-thiadiazole (AMT)

To thiosemicarbazide (3.64g, 40mmole) suspended in anhydrous ethanol (14ml), anhydrous sodium carbonate (3.2g, 30mmole) and carbon disulfide (3ml) were added. The mixture was warmed with stirring under reflux for 1 hour, then heated on steam-bath for 4 hours. The solvent was largely removed, and the residue dissolved in water (16ml) and just acidified with concentrated hydrochloric acid (3ml) to give pale yellow product, this product was filtered and washed with ethanol and dried under reduce pressure, yield (78%), m.p. 230-232°C (decomp.), (Lit. 232°C).⁽⁶⁸⁾

3. Preparation of sodium N-(5-mercapto-1,3,4-thiadiazole) dithiocarbamate (NaMTD)

To AMT (2g, 15mmole) that dissolved in 50% mixture of ethanol-water (V/V), sodium hydroxide (0.6g, 10mmole) and carbon disulfide (1ml) were added with stirring at 15°C for 2 hours, a yellow precipitate was formed, this precipitate was filtered and washed with ethanol and dried under reduce pressure, yield (60%), m.p. 125-127°C, (Lit. 126,129°C).⁽⁶⁹⁾

(2-3) Preparation of the new complexes

1. Palladium(II) complex (Pd-MTD)

(0.08g, 0.34mmole) of ligand (NaMTD) was dissolved in acetone and mixed with (0.1g, 0.34mmole) of Na_2PdCl_4 that dissolved in acetone, the mixture then was refluxed for 1 hour, a red-brown precipitate was formed, and then filtered and washed with ethanol and dried under reduced pressure, yield (73)%, m.p. 273 °C

2. Palladium(II)–Copper(II) complex (Pd-MTD-Cu)

(0.4g, 1.17mmole) of complex(Pd-MTD) was dissolved in DMF, the solution was added to(0.1g,0.58mmole) of copper chloride(II), dissolved in DMF, the mixture was then heated for 2 hours, a red precipitate was formed, this precipitate was filtered, washed with diethyl ether and dried under reduce pressure yield(65)%, m.p. 183 °C

3. Palladium(II)–Nickel(II) complex (Pd-MTD-Ni)

To (0.16g, 0.42mmole) of complex(Pd-MTD) that dissolved in DMF, (0.05g, 0.21mmole) of nickel chloride(II) dissolved in DMF was added, the mixture was warmed in water bath, a red precipitate was formed, which was filtered, washed with ether and dried under reduced pressure, yield (78)%, m.p. 305 °C

4. Palladium(II)–Cobalt(II) complex (Pd-MTD-Co)

A solution of (0.1g, 0.6mmole) of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in ethanol was added to a solution of (0.46g, 1.2mmole) of complex (Pd-MTD) in DMF. A blue complex was immediately formed. The product was digested on a water bath for an hour, then the product filtered, washed with ether and dried in vacuum desiccators for about 6 hours, yield (65%), m.p. 243°C

5. Palladium(II)–Iron(II) complex (Pd-MTD-Fe)

A solution of (0.5g, 0.74mmole) of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ dissolved in ethanol was treated with a solution of (0.56g, 1.5mmole) of complex (Pd-MTD) in DMF. The resulting solution was digested on a water bath for an hour when a red-brown precipitate was formed, and then the resulting product was filtered and washed with ether, yield (68) %, m.p. 187°C

6. Palladium(II)–Manganese(II) complex (Pd-MTD-Mn)

A solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.2g, 1mmole) in acetone was added to a solution of complex (Pd-MTD) (0.77g, 2mmole) in DMF. The mixture was heated under reflux for 15min. then cooled to room temperature and the solvent was removed under reduced pressure. A yellow solid product was formed, this product was washed with ether, yield (70%), m.p. 321°C

7. Palladium(II)–Vanadyl(IV) complex (Pd-MTD-V)

A warm solution of $\text{VO}\text{SO}_4 \cdot \text{H}_2\text{O}$ (0.1g, 0.55mmole) in ethanol was added to a solution of complex (Pd-MTD) (0.42g, 1.1mmole) in DMF. The mixture was heated on a steam bath for 10min. Then the solvent was removed by evaporation, a green precipitate was formed, which was washed with ether and dried under reduced pressure, yield (80%), m.p. 203°C

8. Palladium(II)–Cadmium(II) complex (Pd-MTD-Cd)

A solution of (0.1g, 0.46mmole) of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol was treated with a solution of complex (Pd-MTD) (0.35g, 0.93mmole) in DMF. The mixture was heated on water bath for 30min. a brown solid product was formed, which was filtered, washed with ether and dried under reduced pressure, yield (65) %, m.p. 143 °C

Chapter One

Introduction

Chapter TWO

Experimental Part

Chapter Three

Results and Discussion

Chapter FOUR

Biological Activity

Micro-organisms cause different kinds of diseases to human and animals. Discovery of chemotherapeutic agents played a very important role in controlling and preventing such diseases.

Chemotherapeutic agents are isolated either from living organisms known as antibiotics like penicillin and tetracycline etc., or they are chemical compounds prepared by chemist such as the sulfa drugs etc.,^{(170)rehab} micro-organisms have the ability to develop resistance to these chemotherapeutic agents and such strains which are resistant causing major problem in treatment of microbial infection.

For this reason searching for new antimicrobial agents is continuous process and great efforts have been employed to find new antibiotics or new chemical compounds with good antimicrobial activity which might be suitable to be used as chemotherapeutic agents.

It is only in recent times, following development in chemistry, biochemistry and related disciplines, that logical bases have been established for understanding the roles of inorganic species in medicine, and promise for the logical design of inorganic therapeutic agents that are relatively innocuous to the host, while being toxic to unwanted types of cells organisms, either directly or by depriving them of essential ions or other cell components.

In spite of the large amount of literature dealing with the metal metabolism of living organisms, only limited attempt appear to have been made to bring together what might be described as inorganic medicinal chemistry.

The transition metals have many characteristic properties of which is the ability to have multiple oxidation states, and having a strong tendency to form ionic and neutral complexes of varying degree of complexity. This can fruitfully be utilized in selective preparation of a very wide rang of chemotherapeutic agent containing transition metals and study the

complexing behavior of biological ligands involved in various biological processes.⁽⁸⁵⁾

(4-1) Experimental

(4-1-1) Chemicals:-

1. Dimethylsulphoxid (DMSO).
2. Nutrient agar medium from Maknus Lab company.
3. Solution of the new tested compound in DMSO.

(4-1-2) Apparatus:-

1. Petri dishes.
2. Incubator type Memmert incubator.
3. Autoclave from Hiraymama company.

(4-1-3) Types of bacteria

1. *Escherichia coli* (gram negative).
2. *Staphylococcus aureus* (gram positive).

(4-1-4) Preparation of nutrient agar medium

The antimicrobial activity was carried out by agar diffusion method⁽⁸⁶⁾. The principles of this method⁽⁸⁷⁾ are to allow the drug to diffuse through a solid medium.

(20g) of dry nutrient agar were added to (1L) of distilled water in conical flask and stirring the solution with heating until it was completely dissolve.

The flask was stoppered by cotton and the medium was sterilized by placing it in an autoclave for (20min) at 121 C^0 under pressure of 15bound/inch². After that the medium was cooled to $(45-55)\text{ C}^0$ and placed in Petri dish about (15-20) ml for each one, and was left to cooled and solidified.

Therefore the medium was ready for bacteria growth. The studied bacteria were placed on the nutrient agar surface using loop and by streaking

processor. After that the disc saturated with the tested compound solution was placed in the dishes which was then incubated for 24hour at 37C⁰

(4-2) Results and discussion

Table (4-1), show the activity of NaMTD and its metal complexes on the growth of *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative), the result show the following observations:-

- 1- NaMTD was inactive against *Staphylococcus aureus*. While it is moderately active against *Escherichia coli*.
- 2- Complexes of mono Pd-MTD, Pd-MTD-Cu and Pd-MTD-Cd were active against both, especially the last one show a high activity against both bacteria.
- 3- The complexes of Pd-MTD-Ni, Pd-MTD-Co and Pd-MTD-Fe were active only against *Escherichia coli*.
- 4- Pd-MTD-Mn complex was active against *Staphylococcus aureus*.
- 5- The Pd-MTD-V complex was totally inactive in both cases.

The differences in effectiveness of the different compound against the two types of bacteria might be attributed to the difference in the cell wall structure of bacteria, and to the charge, size and geometry of the complex, in addition to the type of the metals forming the complex, the last effect is known as synergistic effect.

The high activity of cadmium complex against both bacteria came in accordance with a previous study of Z. Muhi-Eldeen, et.al.⁽⁸⁸⁾ about the effect of some transition metal complexes of five members heterocyclic rings on a number of bacteria.

Table (4-1) show the activity of MTD and its complexes on the growth efficiency of *Staphylococcus aureus* and *Escherichia coli*

Compound	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>
Control (DMSO)	-	-
NaMTD	-	++
Pd-MTD	+	++
Pd-MTD-V	-	-
Pd-MTD-Mn	+	-
Pd-MTD-Cu	+	+++
Pd-MTD-Fe	-	++
Pd-MTD-Cd	+++	+++
Pd-MTD-Ni	-	++
Pd-MTD-Co	-	+

Where **6-8mm (+)**
 8-10mm (++)
 > 10mm (+++)

The concentration of all compounds were 10mg/ml





ACKNOWLEDGMENTS

I wish to express my deepest gratitude and great appreciation to my supervisors Prof. Dr. Ayad H. Jassim and Prof. Dr. Subhi A. Al-Jibori for their patient and supervision. Sincere thanks are also to the dean of the college of science and the head of chemistry department Dr. Shahbaz A. Maki and the staff members of the department of the chemistry. Finally, sincere thanks and deep respect goes to all my teachers, friends, and my family for their help and support.

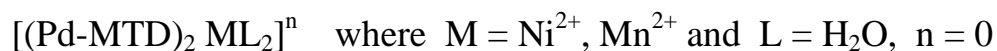
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Abstract

Derivatives of 1,3,4-thiadiazole ring show biological activities against different species of microbes, therefore mono- and poly-nuclear complexes of dithiocarbamate derivatives of 2-amino-5-mercapto-1,3,4-thiadiazole (AMT), have been prepared in an attempt to show the effect of introducing two centers in the structure of the ligand (NaMTD), as well as to investigate the coordination behavior of the ligand toward both transition metals and to compare the biological activity of the complexes with that of the ligand.

Dithiocarbamate derivatives of AMT (NaMTD), were prepared by condensation of CS₂ and AMT, which was itself prepared starting from thiosemicarbazide, in alcoholic sodium hydroxide solution, the product was isolated and characterized by FT-IR and U.V.-visible spectroscopy. The Pd(II) complex of NaMTD have been prepared using Na₂PdCl₄ in acetone, the product (Pd-MTD) was isolated and used as precursor to prepare a series of heteropolynuclear complexes with V⁴⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Cd²⁺ metal ions in DMF. Different fine crystalline, colored and stable complexes were isolated and studied using FT-IR and U.V.-visible spectroscopy, magnetic susceptibility and conductivity measurements, the metal content was determined using atomic absorption spectroscopy technique.

The complexes exhibit the general formula



While the vanadyl ion show complexes of a formula $[(\text{Pd-MTD})_4 \text{VO}]^{2-}$ and that of Fe(II) was $[(\text{Pd-MTD})_4 \text{Fe}]^{2-} \cdot 2(\text{H}_2\text{O})$.

While Co²⁺ and Cd²⁺ have the formula $[(\text{Pd-MTD})_2 \text{M}] \cdot 2\text{L}$,

L = DMF for Co²⁺ and H₂O for Cd²⁺.

A number of structural phenomena have been revealed during the study. The results helped to illustrate the bonding natures between metal ions and the different donor atoms of the ligand. NaMTD was found to coordinate with Pd(II) ion through sulfur of the dithiocarbamate group and the nitrogen of the ring. The thioamide group, on the other side, was left to coordinate to the several metal ions either through sulfur atom only (in case of VO^{2+} and Fe^{2+}), or chelating through nitrogen and sulfur (in case of $(\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Cd}^{2+})$ ions).

The structural formula were either octahedral for $(\text{Mn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+})$ ions, square pyramidal (in case of VO^{2+} ion), and tetrahedral for $\text{Cd}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$ ions. The antibacterial activity of the NaMTD and its mono- and poly-nuclear complexes were screened against gram (+) and gram (-) bacteria.

الخلاصة

من المعروف أن لبعض مشتقات حلقة ١،٣،٤- ثايدايازول فعالية بايولوجية تجاه أنواع مختلفة من البكتيريا، لذلك جرى تحضير معقدات احادية ومتعددة النواة لمجموعة ألدائثايوكاربامات لمشتق ٢- أمينو-٥- مركبتو-١،٣،٤- ثايدايازول (AMT) في محاولة لظهور تأثير ادخال مركزين فلزيين على تركيب المتعاضد (NaMTD)، كذلك لمعرفة أسلوبك ألتناسقي للمتعضد تجاه كلا العنصرين ألتنقاليين ولمقارنة ألعالية ألبايولوجية للمتعضد مع تلك ألعقدات ألعضرة.

جرى تحضير مشتق ألدائثايوكاربامات (NaMTD)، وذلك بمعاملة CS₂ و (AMT)، وأذي حضر أصلا من ألتايسيميكاربازيد في محلول هيدروكسيد الصوديوم ألكحولي، حيث تم عزل ألتنتاج ومن ثم تشخيصه باستعمال مطيافية الأشعة تحت الحمراء والأشعة فوق ألبنفسجية.

لقد جرى تحضير معقد ألبلاديوم ألتنائي للمتعضد NaMTD بأستعمال ملح NaPdCl₄ في مذيب (enaceto)، وتم عزل ألتنتاج (Pd-MTD) واستخدامه كمادة أساس لتحضير سلسلة من ألعقدات متعددة النواة غير متجانسة مع أيونات الفلزات (Ni²⁺، Cu²⁺، V⁴⁺، Mn²⁺، Fe²⁺، Co²⁺، Cd²⁺) في مذيب (DMF). حيث تم ألتحصول على معقدات بلورية دقيقة ملونة ومستقرة وجرى عزل هذه ألعقدات ودراستها بأستخدام مطيافية الأشعة تحت الحمراء والأشعة فوق ألبنفسجية و قياسات ألتحساسية المغناطيسية وألتوصيلية ألكهربائية وكذلك تم تعيين نسبة ألتفلز بأستخدام تقنية ألتامتصاص ألتذري ألتلهبي.

أظهرت ألعقدات ألعضرة ألتصيغة ألعامة $[(Pd-MTD)_2 ML_2]^n$

حيث $M = Ni^{2+}, Mn^{2+}$ and $L = H_2O, n = 0$

$M = Cu^{2+}$ and $L = DMF, n = 0$

بينما أظهر معقد ألتفناديوم ألترباعي ألتصيغة ألتالية $[(Pd-MTD)_4 VO]^{2-}$

وكانت صيغة معقد ألتحديد ألتنائي $[(Pd-MTD)_4 Fe]^{2-} \cdot 2(H_2O)$

$[(Pd-$ بينما كانت صيغة معقدي ألتكولبت وألتكاديوم ألتثنائيين هي

$MTD)_2 M]^{n-} \cdot 2L,$

حيث $L = DMF$ for Co^{2+} and H_2O for $Cd^{2+}, n = 0$

من خلال أبحاث تم اكتشاف عدد من الظواهر التركيبية. وقد ساعدت النتائج على توضيح طبيعة التآصر بين أيونات الفلزات مع الذرات الواهبة المختلفة الموجودة في المتعاضد NaMTD ، حيث وجد هذا المتعاضد أنه يتناسق مع (Pd^{2+}) من خلال ذرة (S) ألتابعة لمجموعة الدايتاويوكاربامات و(N) حلقة ألتايدايازول، في ألتانب ألتآخر للمتعاضد وجد أن مجموعة ألتاويوأمايد تتناسق مع ألتلزات ألتاضافية اما عن طريق ذرة (S) لوحتها (كما في حالة VO^{2+} و Fe^{2+})، أو بطريقة كلايية من خلال ذرتي (S) و(N) (كما في حالة Mn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+}).

استنادا للنتائج العملية والنظرية للمعقدات المحضرة تم اقتراح الشكل ألتهندسي ألتثماني السطوح لمعقدات $(Ni^{2+}$ ، Cu^{2+} ، $Mn^{2+})$ ، في حين كان لمعقدات $(Fe^{2+}$, Co^{2+} , $Cd^{2+})$ شكل رباعي ألتسطوح، كما تم اقتراح شكل هرم مربع ألتقاعدة لمعقد ألتفناديل الرباعي. وجرى أيضا في هذا ألتبحث دراسة ألتفاعلية ألتضادة للبكتريا لمركب (NaMTD) ومعقداته ألتأحادية وألتثنائية ألتنواة بألتخدام بكتريا موجبة وسالبة ألتصبغة.

ABBREVIATION

AMT	2-amino-5-mercapto-1,3,4-thiadiazole
NaMTD	Sodium N-(5-mercapto-1,3,4-thiadiazole-2-yl) dithiocarbamate
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
dppe	Diphenylphosphoethene
ν	Stretching
δ	Bending