2024, 21(3): 0990-1005
https://dx.doi.org/10.21123/bsj.2023.7872
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

First Transition Metal Complexes Salts of Diazonium Derived from Nitrogen Heterocyclic Compound, Synthesis, Characterization and Biological Activity

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Received 02/10/2022, Revised 10/03/2023, Accepted 12/03/2023, Published Online First 20/08/2023, Published 01/03/2024

Abstract

Metal complexes chrome(III), manganese(II), iron(III), cobalt(II), nickel(II), cupper(II) and zinc(II) with diazonium of 3-amino-2-chloropyridine of general formula $[2\text{-Cl-}C_5H_3N{\equiv}N]_n[MX_m]$, where n=2 or 3 for divalent and trivalent metal, m= 4 or 6 were synthesized. The complexes have been characterized by flame atomic absorption, (C.H.N), molar conductance, magnetic susceptibility UV-vis spectra, infrared spectra,^{1}H-NMR spectroscopy and thermo gravimetric analysis (TGA and DTA). The measurements showed that the divalent metal ion complexes (M^{2+}) have (1:2) M:L ratio with tetrahedral geometry around metal ions while the trivalent metal ions (M^{3+}) formed (1:3) metal: ligand ratios with octahedral geometry. Furthermore, the complex salts were displayed for antibacterial activity versus two types of bacteria Gram, positive *(Staphylococcus aureus*) and Gram negative *(Klebsiella pneumonia)*. The complex 2 Mn(II) and 3 Fe(III), exhibited moderate activity against the two tested bacteria, while the complexes 1 Cr(III), 4 Co(II) 6 Cu(II) and 7 Zn(II) showed high activity .The complex 5 Ni(II) displayed moderate and weak against the type one and type two of bacteria respectively.

Keywords: biological activity, diazonium salts, metal chloro ions, ionic complex, pyridinium salts.

Introduction

Aromatic diazonium halides are necessary intermediate substances, for preparation of different organic and inorganic materials. Diazonium can be prepared by treating aromatic amines with sodium nitrite, and hydrochloric acid in an aqueous solution at $0C^o$ to $5C^o$ [1,2].The diazonium salts solution forms stable double salts with inorganic compounds like $ZnCl_2$, $HgCl_2$, etc., to form inorganic salts of formula $[ArN_2]_2^{2+}[ZnCl_4]$[2, 3]. Despite aromatic diazonium salts and metal halide stabilized and well known, little work has been done in the literature [4], the tetramethylammonium;tetraethylammonium tetrachlorozincate(II)$[(C_2H_5)_4N]_2[ZnCl_4][(CH_3)_4N]_2[ZnCl_4]$ have been prepared and their crystal structure was investigated by means of single x-ray different diffraction at room temperature and Raman spectra, the crystal can be regarded a layered of repeated $[TMA]_2[ZnCl_4]$. The reaction of

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arenediazonium chloride with $CuCl_2$ to form arenediazonium tetrachlorocuprate (II) $[ArN^+]_2[CuCl_4]$ has been published [5].
Diazonium salts found several applications in different fields such as photo- chemical reactions, analytical chemistry, DNA cleavage, precursors for surface [6,7], grafting antibacterial and antioxidant [8].

There has been great efforts to develop and synthesis of heterocyclic substitutions to find cheap and safe new medicine; pyridine ring and their derivatives are among these heterocyclic compounds which are the core structure of several natural synthetic products and drugs[9-11].The natural products possess tremendous application in pharmaceuticals, antibacterial and anticancer due to their therapeutic and chemotherapeutic properties [12-13] .

In this study we aimed to synthesize a new metal complex salts of chrome (III), manganese (II), iron (III), cobalt (II), nickel(II), cupper(II) and zinc(II) with pyridine diazonium derivative and by physio-chemical properties were studied by different techniques. The biological activity of these salts investigated towards Gram, positive (*Staphylococcus aureus)*, Gram, negative (*Klebsieiaella pneumonia).*

Materials and Methods

Experimental

Materials, Methods and Instruments

All chemicals, reagents and solvents were of analytical grads. 3-amino-2-chloro pryidindiazonium chloride was prepared according to the method reported in the literature[14], and melting points were measured on Stuart-SMP melting point limited.

The electronic spectra were measured using Shimadzu UV-1800, device, infrared spectra were registered within range 400-4000 $cm^{-}1$ using KBr discs, magnetic susceptibilities were recorded by Gouy method on Sherwood scientific at 298 k^o using mercury tetrathiocynatocobalt as the calibrant. Diamagnetic correction was calculated from Pascal's constant. The conductivity of salts was determined in 0.001 M dimethyl sulfoxide solution using Jenway 4070. The (C.H.N.) of complex salts were determined, while metal analysis was carried out by using an AAS 240F VARIN instrument, proton NMR signals measured in DMSO-d^6 at room temperature on Varian agillent 500 MHZ spectrometer. The DTG-TGA were measured under dry N_2 gas at 1.0 C°/ minute.

Preparation of 3-amino-2-chloro Pyridine Diazonium Chloride

The diazonium salt was synthesized by adding dropwise 10 mmole $NaNO_2$ in distilled water to cold solution of 10 mmole 3-amino-2-chloro pyridine chloride in concentrated hydrochloride acid with continuous stirring. The resulting mixture was kept at 0-5C^o for 1 hour to be used for complexes preparation[1].

Synthesis of Complex Salts $[C_6H_5N_2Cl]_n[MCl_m]$

n=3, m=6 for Cr^{+3} and Fe^{+3}, n=2, m=4 for manganese (II), cobalt (II), nickel (II), cupper (II) and zinc (II).

The $MnCl_2.4H_2O$, $CrCl_3.6H_2O$,$FeCl_3.6H_2O$,$CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2.2H_2O$ (10^{-3} mole) in distilled water was poured into 2-chloro pyridine diazonium chloride solution ($2*10^{-3}$ mole) and was stirred for 1 hour, the resulting solid salt was recrystallized from absolute ethanol and dried to 60 C^o for 5 hours, Scheme 1.

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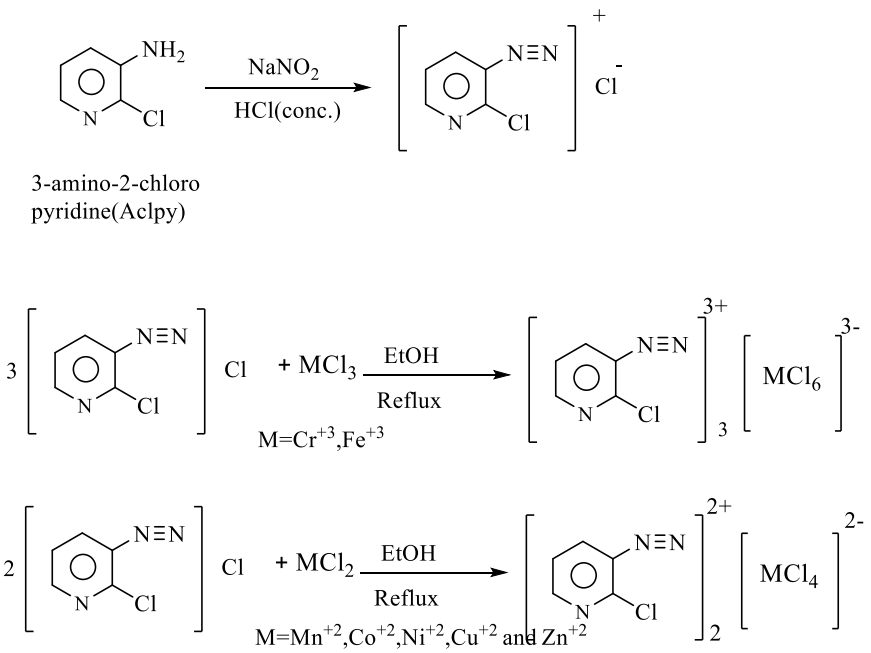

Scheme 1. preparation reaction of diazonium salt and their complexes

Antibacterial Activity

Antibacterial for complexes tested toward Gram positive (+) bacteria, *Staphylococcus aureus* and Gram negative (-) bacteria, *Klebsiella pneumonia* using the agar diffusion procedure and inoculation plate [15,16]. The tested complexes for antibacterial activity were dissolved in dimethyl sulfoxide at 30.0 μg/disc. A (6mm) diameter blank paper was cultivated at 37C° for 24 hours. The resulting diameter of complex inhibition zones in (mm) was determined and the resulting activity was estimated and compared with a standard disc of ciprofloxacin as control antibiotics.

Results and Discussion

All complexes are crystalline solid with a melting point or decomposition, colored, stable to air and soluble in most organic solvents. The metal complexes were characterized by elemental analysis (C.H.N and metal analysis), malar conductance Table 1, IR, UV-vis., and ^{1}H-NMR, which gave a good agreement with the calculated values results from the expected formulation of prepared complexes. The data value revealed that metal to ligand is 1:2 for divalent metal complexes Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), while (1:3) for trivalent metal complexes Cr(III), Fe(III)[17, 18] . The magnetic susceptibilities of complexes were consistent with tetrahedral geometry for divalent metal complexes $[C_5H_3ClN_3]_2[MCl_4]$ and octahedral geometry around metal for trivalent metals $[C_5H_3ClN_3]_3[MCl_6]$.

The chloride content were determined quantitatively on the sodium fusion solution [14].

Table 1. Physical and analytical data for the complex salts.

No.	Formula of complex	Colour	Melting point,C°	Yield	Elemental analysis theoretical(practical)				Λ ohm^{-1}.cm^2.mole^{-1}
					C %,	H %,	N %,	M %	
1-	$[C_5H_3ClN_3]_3[CrCl_6]$	Brown	260	80	26.22 (25.77)	1.31 (1.29)	19.20 (18.90)	7.57 (7.15)	144

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2-	$[C_5H_3ClN_3]_2[MnCl_4]$	Pale yellow	273d	92	25.10 24.81	1.25 (1.12)	17.58 (17.23)	11.50 (11.24)	88
3-	$[C_5H_3ClN_3]_3[FeCl_6]$	Brown	205-207	75	26.10 (25.85)	1.30 (1.22)	18.25 (17.91)	8.10 (7.86)	129
4-	$[C_5H_3ClN_3]_2[CoCl_4]$	Green	254	90	24.91 (24.50)	1.24 (1.11)	17.43 (17.16)	12.04 (11.87)	72.6
5-	$[C_5H_3ClN_3]_2[NiCl_4]$	Light green	262	97	24.91 (24.68)	1.25 (1.05)	17.44 (17.10)	12.18 (11.75)	80.6
6-	$[C_5H_3ClN_3]_2[CuCl_4]$	Yellow	268	88	24.66 (24.13)	1.23 (1.07)	17.26 (16.91)	13.06 (12.88)	76
7-	$[C_5H_3ClN_3]_2[ZnCl_4]$	White	186-188	93	24.57 (24.19)	1.23 (1.07)	17.2 (16.82)	13.40 (13.2)	85.2

d=decomposed

Infrared spectra

Infrared spectra of prepared complexes exhibited a broad band between 3053-3210cm^{-1} due to vibration of C-H aromatic, while C=N and C-Cl aromatic groups appeared strong vibration bands at 1595-1690 cm^{-1} and 1056-1150cm^{-1} respectively [19,20] .It is clear that a shift of these vibrations in compare with 3-amino-2-chloro pyridine. Infrared spectrum of the complexes showed a weak band at 2200-2350cm^{-1} belongs to triple bond ν (N≡N) which is in a good agreement with the previous publications [21]. Table 2 and Figs. 1-3 show the results of the infrared study.

Table 2. Selected infrared bands of prepared complex salts (cm^{-1}).

Comp. No	N≡N	C=N	C=C	C-H	C-Cl
ACLPY	----	1690 $_{(s)}$	1480$_{(S)}$	3010$_{(b)}$	1150$_{(m)}$
1-	2200$_{(w)}$	1627$_{(S)}$	1404$_{(S)}$	3167$_{(b)}$	1076$_{(m)}$
2-	2500$_{(w)}$	1629$_{(S)}$	1406$_{(S)}$	3210$_{(b)}$	1056$_{(m)}$
3-	2350$_{(w)}$	1610$_{(S)}$	1458$_{(S)}$	3086$_{(b)}$	1091$_{(m)}$
4-	2250$_{(w)}$	1619$_{(S)}$	1409$_{(S)}$	3011$_{(b)}$	1079$_{(m)}$
5-	2200$_{(w)}$	1616$_{(S)}$	1408$_{(S)}$	3105$_{(b)}$	1058$_{(m)}$
6-	2370$_{(w)}$	1595$_{(S)}$	1406$_{(S)}$	3053$_{(b)}$	1070$_{(m)}$
7-	2310$_{(w)}$	1620$_{(S)}$	1407$_{(S)}$	3062$_{(b)}$	1081$_{(m)}$

S=strong, m=medium, b=broad, w=week

ACLPY= 3-amino-2-chloro pyridine

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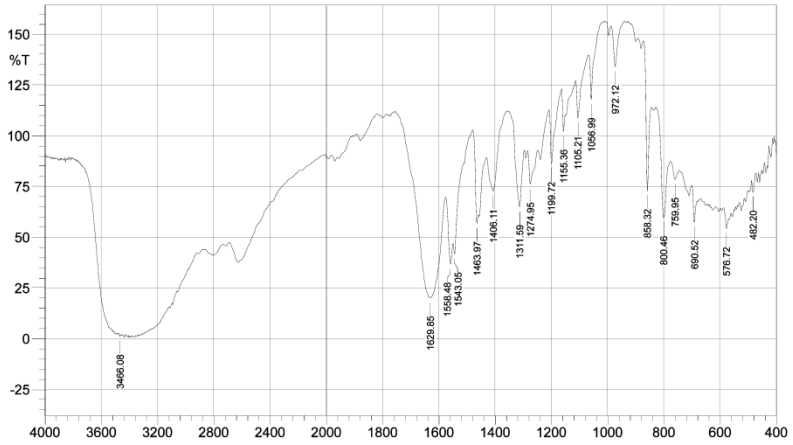

Figure 1.The infrared for $[C_5H_3ClN_3]_2[MnCl_4]$ complex.

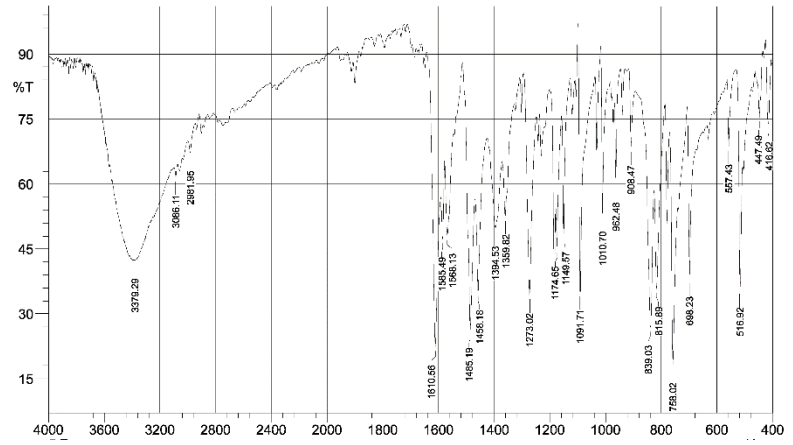

Figure 2.The infrared for $[C_5H_3ClN_3]_3[FeCl_6]$ complex.

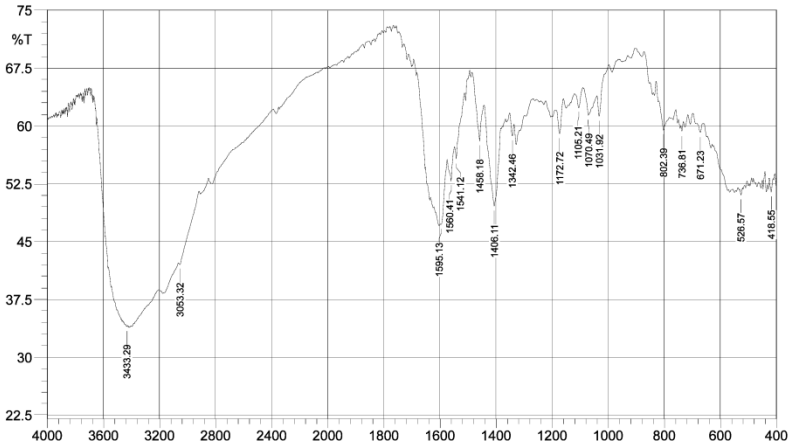

Figure 3.The infrared for $[C_5H_3ClN_3]_2[CuCl_4]$ complex.

Electronic Spectra and Magnetic Properties

The absorption spectroscopy and magnetic moment of metal complexes are listed in Table 3 and Fig. 4 we present the absorbance bands between 32051-37062cm^{-1} in UV- visible region due to n-π* transition of C=N group and the charge transfer [22,23].

The Iron(III) complex exhibits prominent two transition bands at (15723,10121cm^{-1}) near infrared and visible regions corresponding $^6A_1$ (^6S)

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$\rightarrow {}^4T_1({}^4G)(\nu_2)$ and ${}^6A_1({}^6S) \rightarrow {}^4Eg(\nu_3)$ transition of Fe^{+3} respectively due to the spin forbidden transition of high spin octahedral around ferric ion [24,25] .

The magnetic moment value of the Fe(III)complex was 4.95 B.M which is a little low in value compared with the calculated value of Iron (III) complexes[26] .

The reflectance spectrum of Mn (II) complex does not give d-d transition as it is expected [27,28] for tetrahedral geometry and this was confirmed by magnetic moment value (5.9B.M) [25].

The electronic spectrum of Cr(III) complex salt Table 3 and Fig. 4 displayed two bands at 15723 and 10121 cm^{-1} assigned to $4A_2g \rightarrow {}^4T_2g$ and ${}^4A_2 \rightarrow {}^4T_1g$ respectively [29,30]. Furthermore the μ_{eff} (4.7B.M) is another proof for confirming the octahedral shape of Cr (III) complex [31,32].

The spectrum of Ni(II) complex displayed absorbance band at 23809 cm^{-1} this band due to the electronic transition of type ${}^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) indicates a tetrahedral geometry [29] .This geometry was confirmed by a magnetic moment (3.2B.M), the high value may be attributed to the orbital contribution[33].

The spectrum of the prepared Co(II) salt shows a peak in the uv.vis. region (18518 cm^{-1}) referring to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ (ν_3) transition the position of this band confirms the tetrahedral shape of Co(II) compound [29,34,35] Table 3 .

The value of μ_{eff} of the Co(II) complex salt, was 4.53 B.M, which agrees the tetrahedral geometry [29] .

Spectra of copper (II) complex salt displayed a band at 11235 cm^{-1} due to the ${}^2T_2 \rightarrow {}^2E$ transition as

characterized for Cu(II) ion in tetrahedral geometry Fig 4. This geometry was confirmed by the magnetic measurement value (2.2B.M) [36].

The zinc (II) complex, showed strong peak at 3627 cm^{-1} could be allocated to π-π^* transition, however, taking into account the configuration at zinc(II) ion a tetrahedral shape could be assumed[29].

Table 3. The electronic spectra and μ_{eff} data for the complex salts.

Complex no.	μ_{eff} B.M	Electronic spectra (cm^{-1})	
		C.T	d-d transition
1	4.7	32051	15723,10121
2	5.9	32890	
3	4.8	35211	15723,10121
4	4.52	36231	18518
5	3.23	37313	23809
6	2.20	34129	14705
7	Dia	36527	

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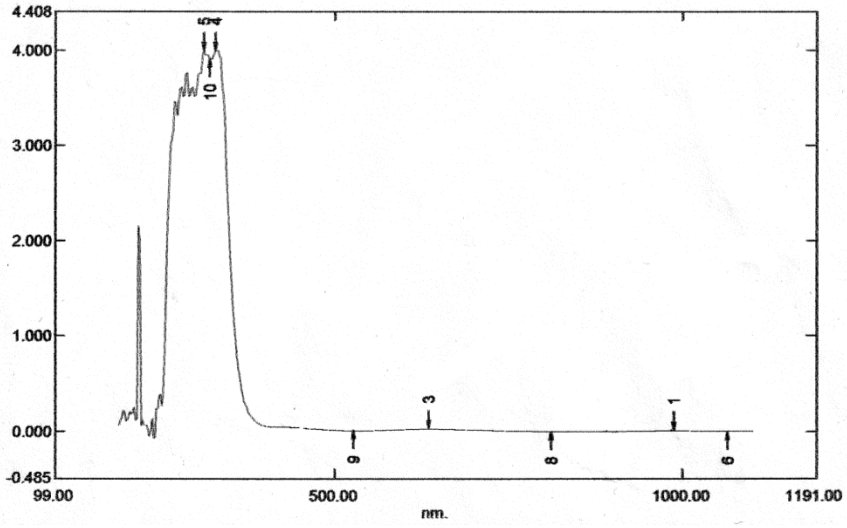
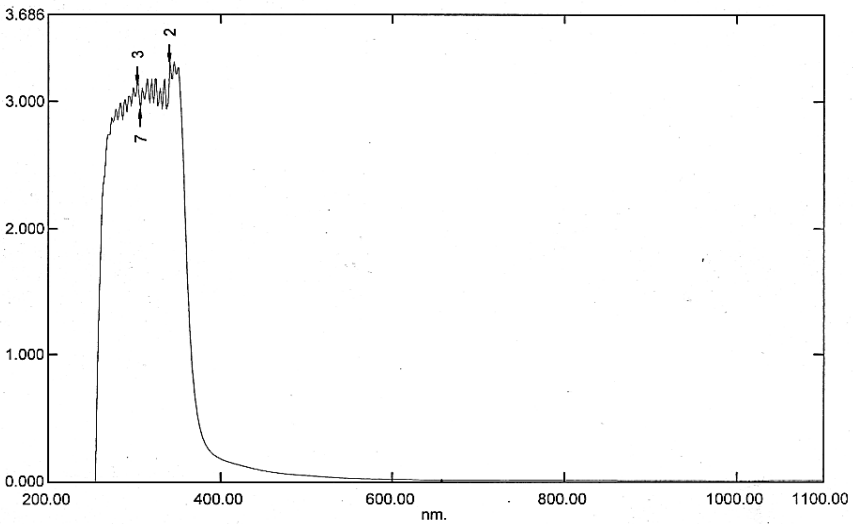
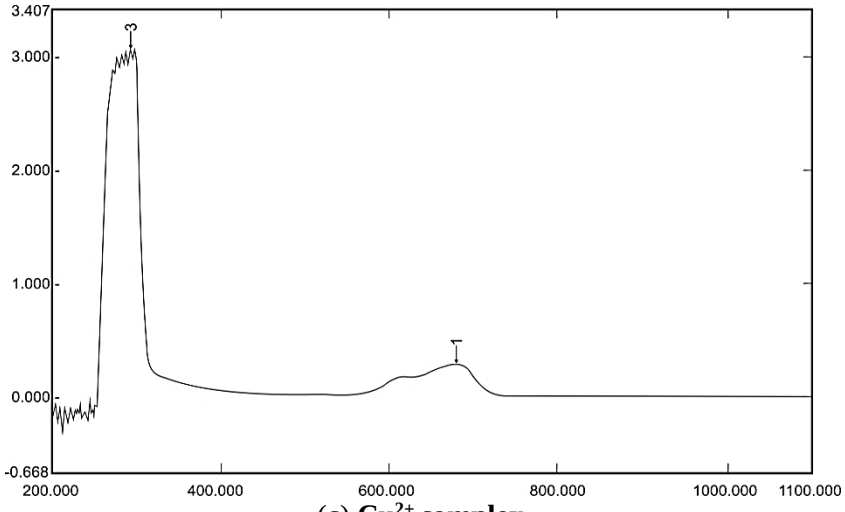


(a) Cr^{3+} complex.



(b) **Mn^{2+} complex.**



(c) **Cu^{2+} complex.**

Figure 4. Electronic spectra of some typical complex salts.

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^{1}H-NMR Spectra:

The ^{1}H-NMR spectra of complex salts (1and7) are recorded in DMSO-d^{6} on BruckerBioSpin GmbH (400 MHz) spectrophotometer. The chemical shifts were expressed in ppm using TMS as internal standard.

The ^{1}H-NMR spectrum of $[C_5H_3ClN_3]_2[ZnCl_4]$ complex (1), Fig .5 shows three separated signal bands at chemical shift 7.71,8.06 and 8.34 ppm assigned to the protons of 4H,5H and 6H of pyridinium ring respectively [37,38]. The peaks at 2.5 and 3.49 ppm refer to tetramethylsilane (TMS) and the trace of moisture in DMSO-d6 solvent.

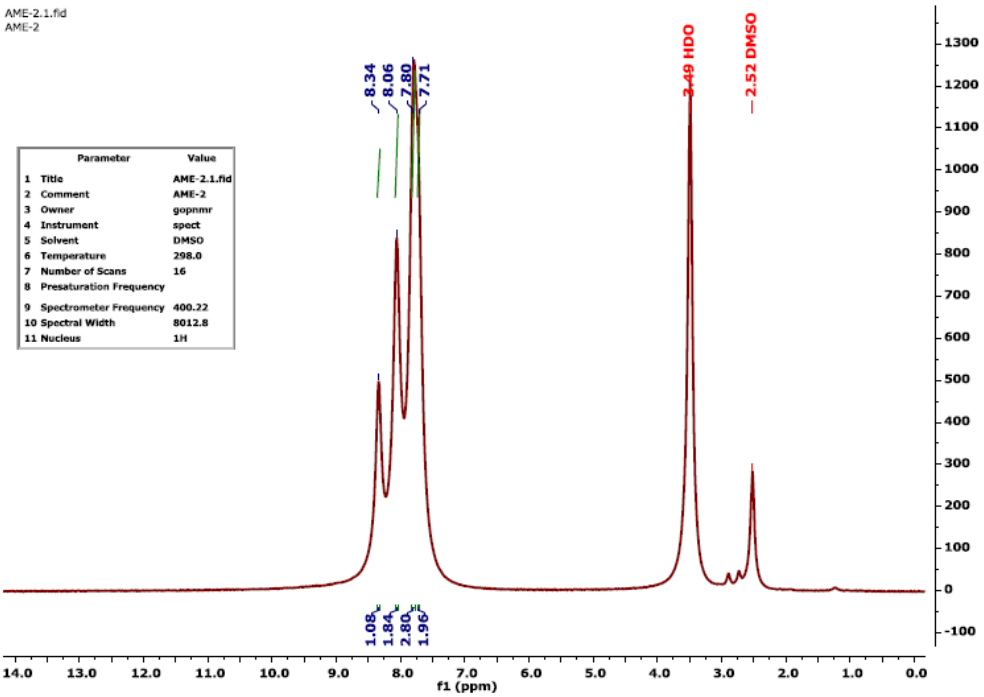

Figure 5. ^{1}H-NMR Spectrum of $[C_5H_3ClN_3]_2[ZnCl_4]$.

Thermal Analysis

Thermal stability of complexes 1, 5 and 6 were determined by placing 9-20 mg of the sample in an aluminum pan and heated between 30-450C^{o} at 20 C^{o}. min^{-1}. The total time given to reach the thermal stabilizing was 18.5 min. The thermal stability of prepared salts were studied with inorganic stabilizing anions, the studies indicated an important effect of the anions.

Correlation between the rate and diazonium nitrogen evaluation, the electronic configuration and the electronegativity of the metal ion has been elucidated [39].

The melting point of the synthesized complexes was measured by differential thermal analysis (DTA) to give peaks at 260, 268 C^{o} for complexes 1 and 6 respectively; while 5 shows a broad band at 100 C^{o} that may be due to the presence of moisture in this complex. The only one sharp transition band indicates that complexes are pure, Table 4 and Figs. 6-8.

The diazonium complexes salts under study were decomposed in three stages to evaluate moisture and nitrogen under their respective temperature 30-250 C^{o}. The onset of thermal decomposition for all complexes started between 260-450 C^{o} in which the bonds C-N and C-C started to break, while the loss of weight was 55-68% [40].

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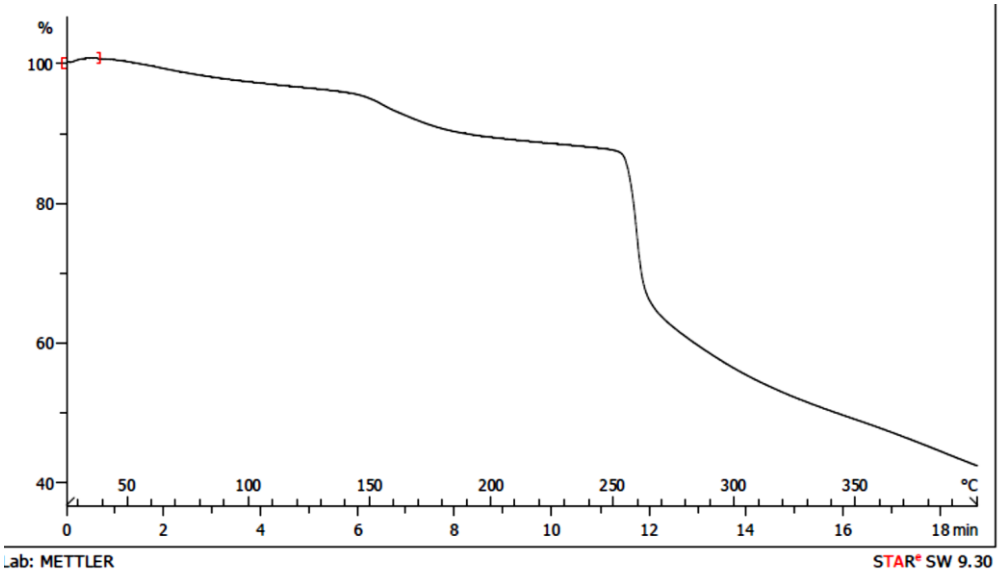
Table 4. Thermo-analysis results for the complexes 1, 5 and 6.

Complex No	TGA Cº	Mass loss%	Assignment	Residue
1	30-250	15	Moisture and N_2	Cr_2O_3+C
	260	----	m.p	
	260-450	55	C_5H_3-M-Cl	
5	30-250	13	Moisture and N_2	
	262	----	m.p	NiO+C
	260-450	65	C_5H_3+MCl	
6	30-250	25	Moisture and N_2	CuO+C
	268	----	m.p	
	260-450	68	C_5H_3+M-Cl	

(A)



(B)

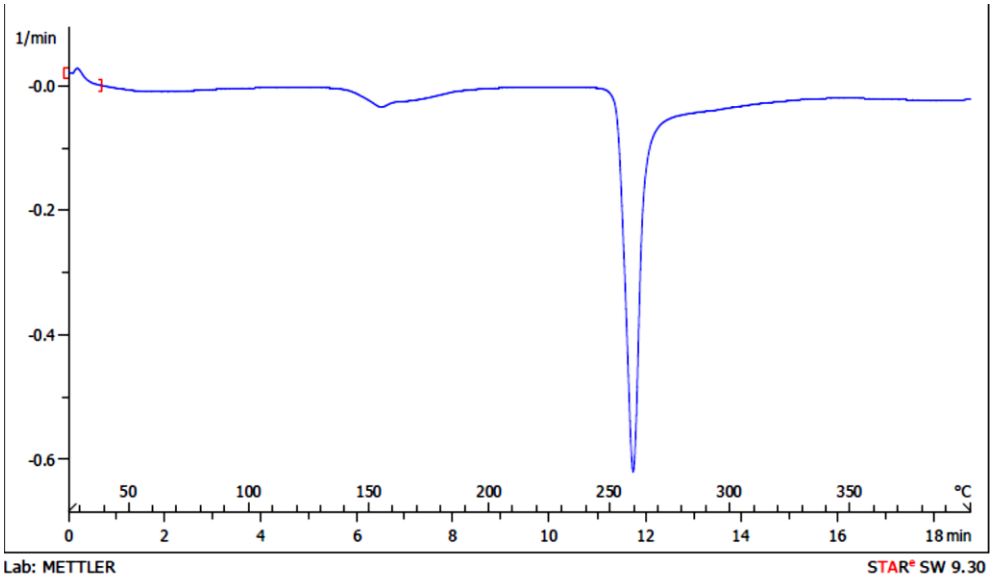


Figure 6. Thermo gravimetric analysis A- TGA and B-DTA of of $[C_5H_3ClN_3]_3[CrCl_6]$ complex.

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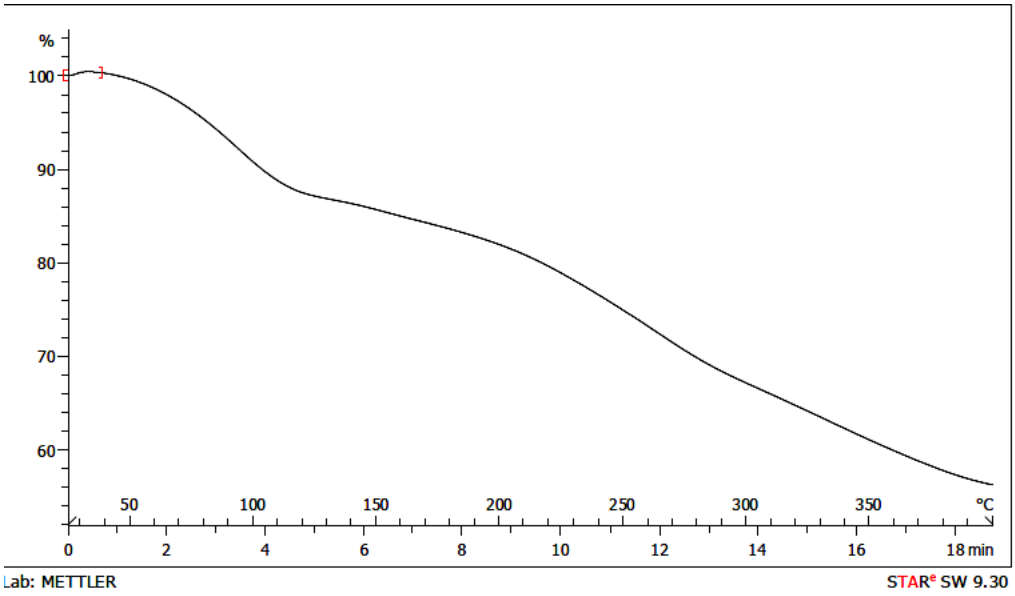
(A)



(B)

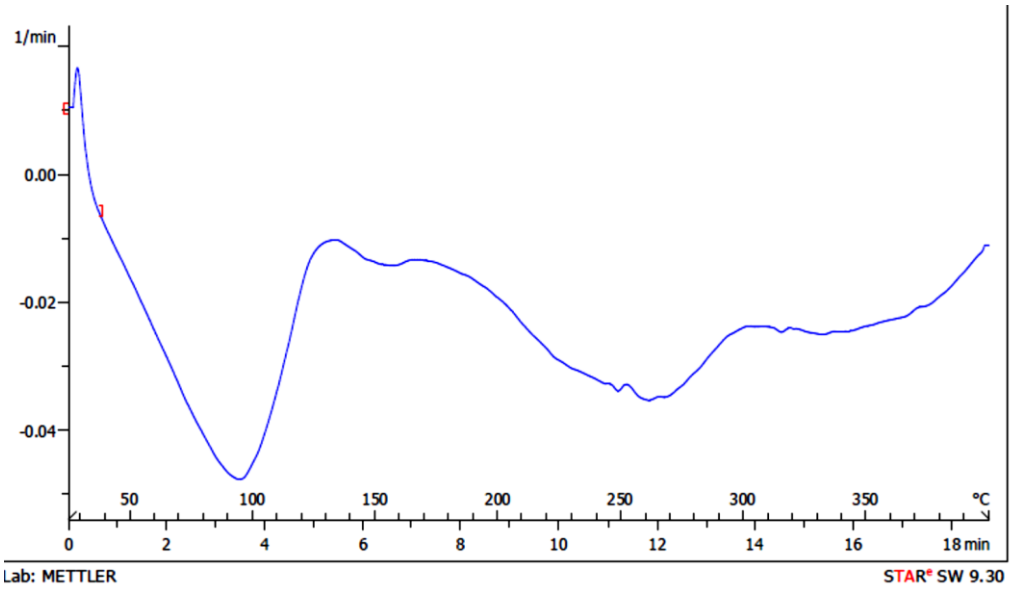


Figure 7. Thermo gravimetric analysis A- TGA and B-DTA of of $[C_5H_3ClN_3]_2[NiCl_4]$ complex.

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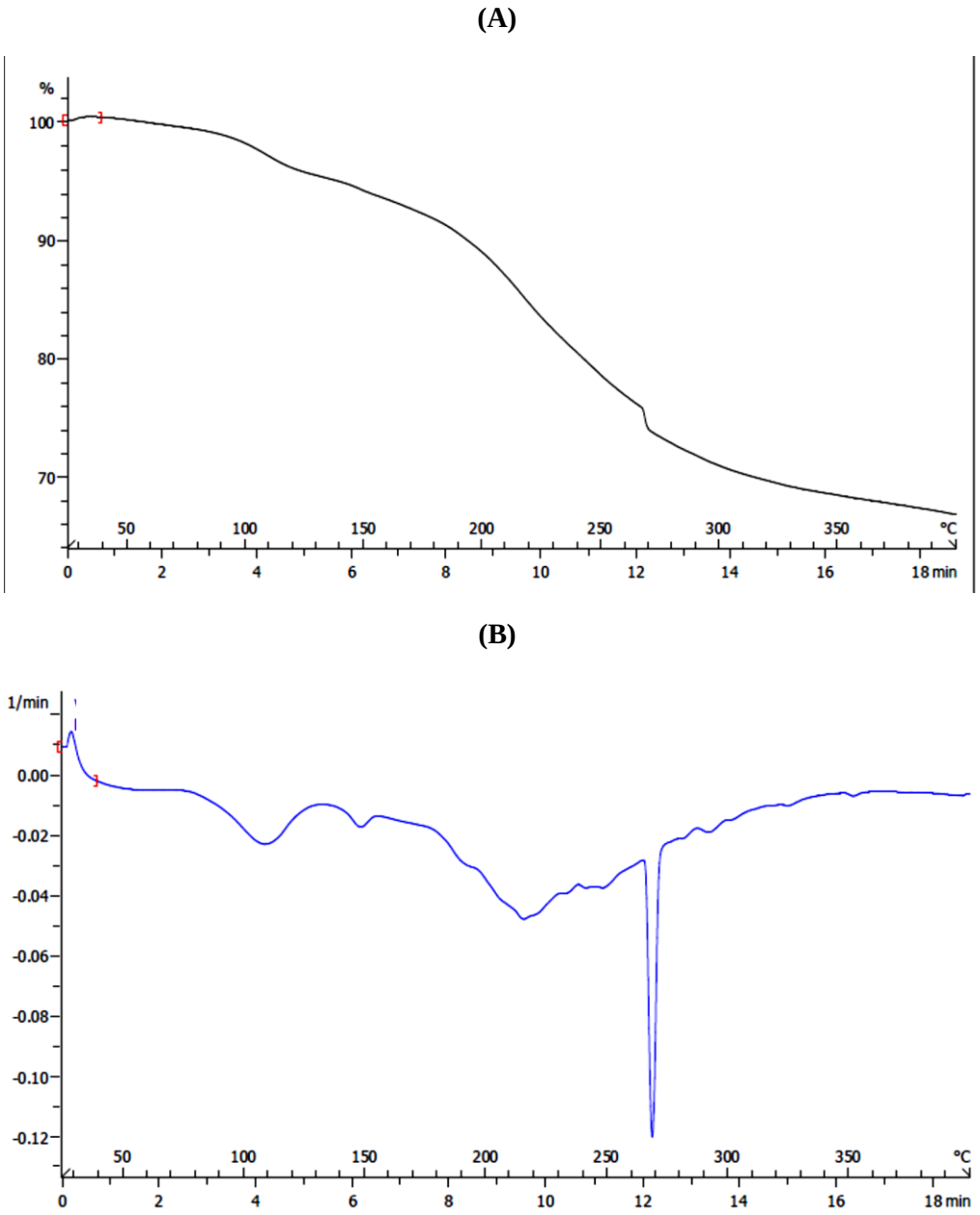

Figure 8. Thermo gravimetric analysis A- TGA and B-DTA of $[C_5H_3ClN_3]_2[CuCl_4]$ complex.

Antibacterial Activity

In this work, the synthesized complexes have been screened for their antibacterial activity against *Staphylococcus aureus* (G+) and Klebsiella pneumoniae **(G-)** compared with the standard drug ciprofloxacin as shown in Table 5 and Fig. 9. All complexes exhibited biological activity towards the two types of bacteria. It is observed that complexes 2 (Mn^{2+} complex) and3 (Fe^{3+}complex) have a weak activity against *Staphylococcus aureus* (G+) and moderate against *Klebsiella pneumoniae* **(G-)** , while complexes 1 (Cr^{3+} complex) ,4 (Co^{2+} complex), 6 (Cu^{2+} complex) and 7 (Zn^{2+} complex) displayed high activity against the two types of bacteria. The 5 (Ni^{2+} complex) exhibited moderate and weak against the type one and type two of bacteria respectively. The activity of metal complexes may be related to the metal chelate geometry of complexes and the electronic configuration of the Metal[38,41].

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Table 5. The antibacterial activity of the prepared complexes

Complex No.	*Staphlococcuss aureus (G+)*	*Klebsiella pneumoniae (G-)*
1	16	18
2	4	11
3	6	9
4	15	24
5	15	13
6	22	14
7	19	21
Control (ciprofloxacin)	25	28

(A) **(B)**

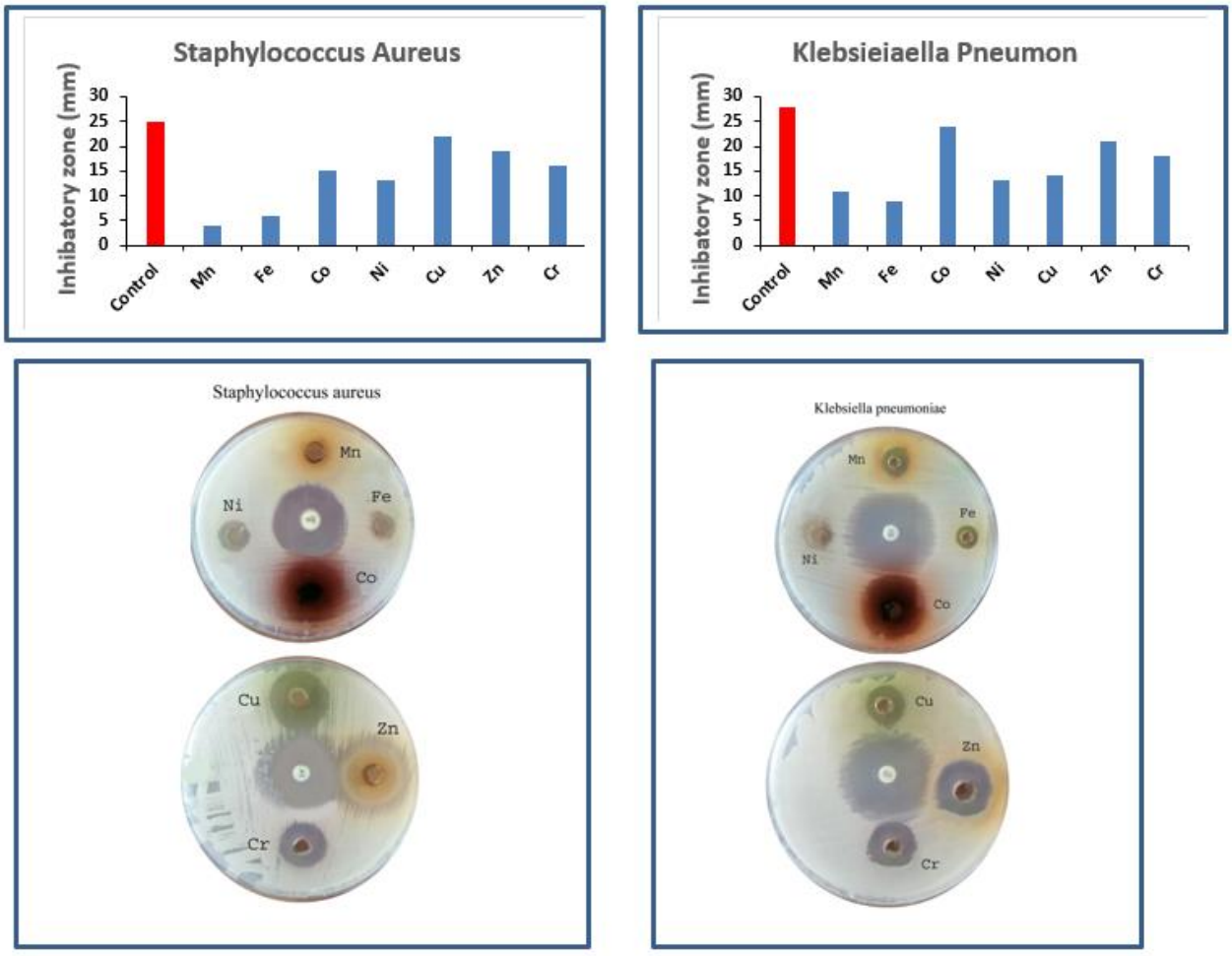

Figure 9. Antibacterial activity of prepared complexes against (a) *Staphlococcuss aureus* (b) *Klebsiella pneumoniae*

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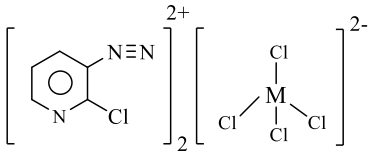
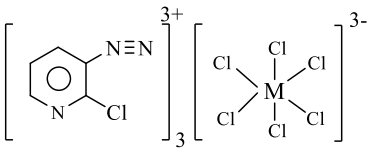
Conclusion

In this work, we described the synthesis of stable diazonium hexa and tetrachloro metal ions for Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The complexes were diagnosed by different techniques such as elemental analysis, IR-spectroscopy UV- visible spectrum, ^{1}H-NMR, and thermal analysis. The divalent metal ions and chloride ions were found to be tetrahedral geometry, Scheme 2a, while the trivalent metal ions and chloride ions formed an octahedral geometry around metal ions, Scheme 2b; in this type of ionic complexes there are electrostatic forces between negative and positive charges. In addition, the complexes were evaluated for their biological activity using the disc diffusion method; the prepared plate at 37C^{o} for 24 hours. The solution diffused and growth of the inoculated bacterial strains were influenced. Then the developed inhibition zone was proposed. The results of evaluation of biological activity of the complexes under study against *Staphlococcuss aureus* and *Klebsiella pneumonia.* The complexes 1 Cr(III), 4 Co(II) 6 Cu(II) and 7 Zn(II) showed a good biological activity against the two types of bacteria while the complex 2 Mn(II) and 3 Fe(III), exhibited moderate activity toward the two tested bacteria. The complex 5 Ni(II) displayed moderate and weak against type one type two of bacteria respectively.



a: M=Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) ions



b: M=Cr(III) and Fe(III)

Scheme 2. Geometry of the prepared complex salts

Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- The author has signed an animal welfare statement.
- Authors sign on ethical consideration's approval.
- Ethical Clearance: The project was approved by the local ethical committee in University of Mosul.

Authors' Contribution Statement

The two authors conducted experiments, data analysis, and biological activity. They performed all the necessary requirements to accomplish the project.

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P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

املاح الفلزات الانتقالية الأولى للدايازونيوم المشتق من مركب حلقي غير متجانس للنيتروجين تحضيرو تشخيص و الفعالية الحيوية

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الخلاصة

يتضمن البحث تحضيرمعقدات لايونات الكروم (III) والمنغنيز (II) والحديد (III) والكوبلت (II) والتيكل (II) والنحاس (II) والخارصين (II) مع (3- امينو -2- كلوروبيريدين) ديازونيوم ذات الصيغة $[Cl\text{-}C_5H_3N{=}N]_n[MX_m]$, حيث ان n=2 او 3 و m=4 او 6 للايونات ثنائية او ثلاثية التكافؤعلى التوالي . شخصت المعقدات المحضرة بوساطة الامتصاص الذري والتحليل الدقيق للعناصر .C.H.N والتوصيلية الكهربائية وطيف الاشعة تحت الحمراء والاطياف الالكترونية وطيف الرنين النووي المغناطيسي للبروتون وقياسات الحساسية المغناطيسية بالاضافة الى التحاليل الحرارية TGA و DTA اظهرت القياسات ان معقدات العناصر ثنائية التكافؤ تكون بنسبة مولية 1:2 (ليكند: فلز) وتمتلك شكل هندسي رباعي السطوح حول الايون الفلزي في حين تمتلك ايونات الفلزات ثلاثية التكافؤ شكل هندسي ثماني السطوح وبنسبة مولية (1:3) (ليكند: فلز) . ودرست الفعالية الحيوية تجاه نوعين من البكتريا (Gram, positive (*Staphylococcus aureus*) , Gram, negative (*Klebsieiaella pneumonia*) حيث اظهرت المعقدات 2 و 3 و 5 و 6 فعالية متوسطة في حين المعقدان 1 و 7 اظهرتا فعالية عالية مقارنة مع المادة القياسية.

الكلمات المفتاحية: النشاط البيولوجي ، أملاح الديازونيوم ، أيونات كلوريدات الفلزات ، المركب الأيوني ، أملاح البيريدينيوم.