

## SYNTHESIS OF NOVEL COMPLEXES DERIVED FROM METHYL OR BENZYL 4-AMINO ANTIPYRINYL DITHIOCARBAMATES WITH DIVALENT Mn(II), Co(II), Ni(II), Zn(II) and Cu(II)

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(Received September 21, 2024; Revised November 11, 2024; Accepted November 12, 2024)

**ABSTRACT.** Two new ligands, methyl 4-amino antipyrinyl dithiocarbamates (MAC) and benzyl 4-amino antipyrinyl dithiocarbamates (BAC), were synthesized from 4-amino antipyrine and corresponding methyl or benzyl halides with potassium hydroxide in dimethylformamide. Then they were coordinated with five divalent transition metals: M = Mn, Co, Ni, Zn, and Cu(II) to produce ten novel complexes,  $[M(\text{MAC})_2]\text{Cl}_2$  **I(a-e)** and  $[M(\text{BAC})_2]\text{Cl}_2$  **II(a-e)**, which were characterized by some physical properties and spectral methods, elemental analyses, molar conductance, and magnetic susceptibility, in addition to <sup>1</sup>H NMR, FT-IR and UV-Vis. Spectroscopy proved that all metal complexes **I(a-d)** and **II(a-d)** have octahedral geometries, except those of copper complexes (**Ie**) and (**IIf**), which have square planer geometry (D<sub>4h</sub>). Following screening for biological activity against Gram-positive bacteria (*Streptococcus pyogenes*) and Gram-negative bacteria (*Pseudomonas aeruginosa*), the results of these novel complexes' investigations showed no effect except the complexes of  $[\text{Zn}(\text{BAC})_2]\text{Cl}_2$  **II(a)**,  $[\text{Zn}(\text{MAC})_2]\text{Cl}_2$ , **I(a)**,  $[\text{Mn}(\text{MAC})_2]\text{Cl}_2$ , **I(b)** and the ligand (MAC) are given promising data.

**KEY WORDS:** 4-Amino antipyrine, Dithiocarbamates, Dithiocarbamate complexes, Biological activity

### INTRODUCTION

The important ligands dithiocarbamates  $[\text{Ar}_1\text{NSSCH}_2\text{Ar}_2]$  are organosulfur esters that can coordinate with metals to form a stable complex [1, 2]. Depending on the type of amine being used, these ligands can be found in dialkyl- and mono-dithiocarbamates [3]. Dithiocarbamates can quickly coordinate with the transition elements through the process of the primary or secondary amine reaction [4]. Regarding the significance of complexes originating from these dithiocarbamate derivatives complexes, at the beginning of the current century, Much research has proven that gold or copper complexes exert antineoplastic activity because of their capability to affect the critical enzyme responsible for the elimination of superoxide radicals, the superoxide dismutase (SOD), This made it critical to the anti-oxidant in aerobic cells [5]. Also, copper complexes of these moieties were used in PET imaging. Some complexes treat tiny cadmium poisoning [6].

The interaction of amines with CS<sub>2</sub> in the presence of sodium or potassium hydroxides to form dithiocarbamates, solvents most commonly used were the carbon disulfide itself, ethanol, or dimethylformamide. Alkylation may occur without separating the intermediate salts [7]. The starting amine used was 4-aminoantipyrine, which was reported to exhibit the following pharmaceutical activity: Analgesic, Anti-inflammatory, Antiviral, Antibacterial, and others [8].

Thus, and as part of a continuous program directed toward the study of important biologically active agents, it has become of interest to stimulate our interest to prepare a novel new series of complexes derived from methyl or benzyl 4-amino antipyrine dithiocarbamates with divalent such as "Mn(II), Co(II), Ni(II), Zn(II), Cu(II)" and others, and study of some physical properties,

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elemental analyses, molar conductance, magnetic susceptibility,  $^1\text{H}$  NMR, FT-IR, and UV-Vis spectroscopy, as well as biological activity [9-11].

## EXPERIMENTAL

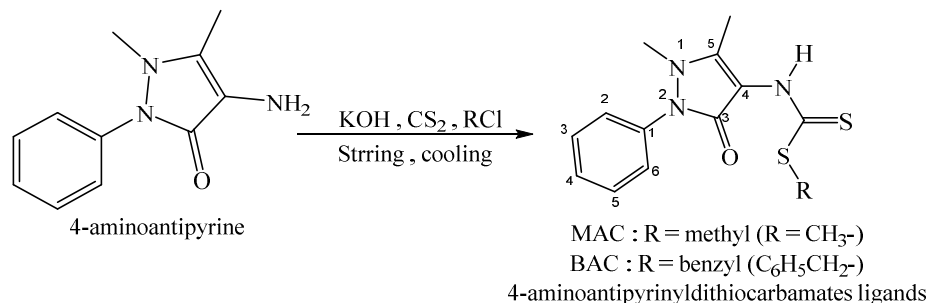
### Material and measurements

Fluka provided the chemical reagents and divalent "Mn(II), Co(II), Ni(II), Zn(II), and Cu(II) chlorides," which were used as directed. The Fourier-transform infrared spectra were recorded using cesium iodide discs and an 8300 Shimadzu spectrophotometer. Ethyl alcohol's ultraviolet light-visible spectra in the 200–1000 nm range were measured using a Shimadzu light-visible 160 spectrophotometer. The magnetic susceptibility balance model MSB-MKI and the flame atomic absorption of the Shimadzu AA-670 elemental analyzer were used to determine the metal. The CHNS Carlo Erba elemental analyzer model 5500. For elemental analysis, Gallen Kamp M.F.B.600.010 F was utilized.

### General synthesis of the ligands [7]

#### Methyl 4-amino antipyrinyl dithiocarbamates (MAC) and Benzyl 4-amino antipyrinyl dithiocarbamates (BAC)

A mixture of potassium hydroxide (0.56 g, 0.01 mol) and a solution of the appropriate 4-amino antipyrine (0.203 g, 0.01 mol) in 8 mL dimethyl formamide was kept below 20 °C. Carbon disulfide (0.76 g, 0.01 mol) was added dropwise to this reaction mixture for 15 min with stirring. This was followed by a dropwise addition of 0.01 mol of methyl iodide for ligand (MAC) and benzyl bromide for ligand (BAC) with continuous stirring for a further three hours. After cooling, the reaction mixture was poured into 100 mL ice-cold water. The resulting precipitate was filtered and then repeatedly cleaned with water. Diluted hydrochloric acid, and then water again and recrystallized from ethanol. Scheme 1 shows the general equation of ligands preparation. A few physical characteristics and an elemental study of the two ligands (MAC) and (BAC) are listed in Table 1.



Scheme 1. General equation of ligands preparation.

### Synthesis of complexes I(a-e) and II(a-e) [1]

The aqueous solution of 0.01 mol of appropriate bivalent metal chloride was added with constant stirring to 0.02 mol of (MAC) or (BAC) ligands. For two hours, the reaction mixture was swirled

at room temperature. The yellow precipitates were obtained. The precipitates were filtered, washed with water, then methanol, and dried over calcium chloride in the desiccator. Some physical properties and elemental analysis of the novel complexes **I** and **II** are listed in Table 1.

Table 1. Specific physical characteristics and an elemental study of the two ligands (MAC) and (BAC) and their complexes.

Compounds	Color	Yield %	Molecular formula (Mol. Wt.)	Found (Calc.) %				
				C	H	N	S	M
(MAC)*	Yellow	68	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> OS <sub>2</sub> (293.40)	53.33 (53.22)	5.19 (5.15)	14.39 (14.32)	22.00 21.85	----
[Zn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(a)</b>	Yellow	64	C <sub>26</sub> H <sub>30</sub> N <sub>6</sub> O <sub>2</sub> S <sub>4</sub> Zn (652.19)	48.00 (47.88)	4.70 (4.64)	13.00 (12.89)	19.70 (19.66)	9.99 (10.02)
[Mn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(b)</b>	Yellow	66	C <sub>26</sub> H <sub>30</sub> MnN <sub>6</sub> O <sub>2</sub> S <sub>4</sub> (641.74)	48.71 (48.66)	4.79 (4.71)	13.15 (13.10)	21.11 (19.98)	8.56 (8.99)
[Co(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(c)</b>	Green	68	C <sub>26</sub> H <sub>30</sub> CoN <sub>6</sub> O <sub>2</sub> S <sub>4</sub> (645.72)	48.39 (48.36)	4.68 (4.68)	13.01 (13.01)	20.01 (19.86)	9.19 (9.13)
[Ni(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(d)</b>	Green	72	C <sub>26</sub> H <sub>30</sub> N <sub>6</sub> NiO <sub>2</sub> S <sub>4</sub> (645.50)	48.40 (48.38)	4.77 (4.68)	13.12 (13.02)	19.90 (19.87)	9.12 (9.09)
[Cu(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(e)</b>	Green	64	C <sub>26</sub> H <sub>30</sub> CuN <sub>6</sub> O <sub>2</sub> S <sub>4</sub> (650.35)	48.12 (48.02)	4.77 (4.65)	12.90 (12.92)	19.79 (19.72)	9.80 (9.77)
(BAC)*	Yellow	79	C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> OS <sub>2</sub> (369.50)	61.80 (61.76)	5.18 (5.14)	11.39 (11.37)	17.33 (17.35)	----
[Zn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(a)</b>	Yellow	82	C <sub>38</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> S <sub>4</sub> Zn (804.38)	56.8 (56.74)	4.77 (4.76)	11.00 (10.45)	16.01 (15.94)	18.01 (8.13)
[Mn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(b)</b>	Off white	84	C <sub>38</sub> H <sub>38</sub> MnN <sub>6</sub> O <sub>2</sub> S <sub>4</sub> (793.94)	57.55 (57.49)	4.90 (4.82)	10.60 (10.59)	16.20 (1.65)	6.99 (6.92)
[Co(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(c)</b>	Green	66	C <sub>38</sub> H <sub>38</sub> CoN <sub>6</sub> O <sub>2</sub> S <sub>4</sub> (797.94)	57.33 (57.20)	4.80 (4.80)	10.90 (10.53)	16.12 (16.07)	7.44 (7.39)
[Ni(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(d)</b>	Green	66	C <sub>38</sub> H <sub>38</sub> N <sub>6</sub> NiO <sub>2</sub> S <sub>4</sub> (797.70)	57.30 (57.22)	4.88 (4.80)	10.99 (10.54)	16.00 (16.08)	7.50 (7.36)
[Cu(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(e)</b>	Brown	78	C <sub>38</sub> H <sub>38</sub> CuN <sub>6</sub> O <sub>2</sub> S <sub>4</sub> (802.55)	56.95 (56.87)	4.85 (4.77)	10.50 (10.47)	16.11 (15.98)	8.02 (7.92)

The m.p. of MAC was 203 °C and BAC was 233 °C, all complexes m.p. were decomposed below 200 °C

## RESULTS AND DISCUSSION

*Synthesis of the two ligands dithiocarbamates, antipyrinyNSSCH<sub>3</sub> (MAC) and antipyrinyNSSCH<sub>2</sub>ph (BAC)*

In this paper, the two ligands dithiocarbamates [AntipyrinyNSSCH<sub>3</sub> and AntipyrinyNSSCH<sub>2</sub>ph] (abbreviated MAC and BAC), where the former is benzyl diethyldithiocarbamate and the latter is methyl diethyldithiocarbamate], and their IUPAC names are methyl or benzyl (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl).

These two ligands were prepared by reacting carbon disulfide with equimolecular amounts of the 4-amino antipyrine and potassium hydroxide in dimethyl formamide. The methyl or benzyl halide was added to this clear solution of potassium dithiocarbamate salt formed [1]. The general structure of these two ligands is shown in Scheme 1.

*Synthesis and characterization of new complexes [M(MAC)<sub>2</sub>]Cl<sub>2</sub> (a-d) and [M(BAC)<sub>2</sub>]Cl<sub>2</sub>(a-d)*

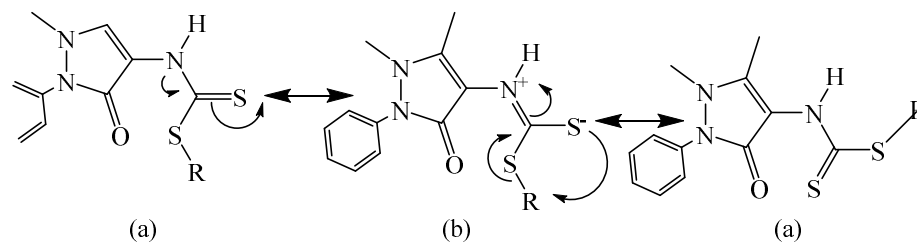
These target yellow complexes were synthesized, producing high yields by stirring an aqueous solution of appropriate bivalent metal chloride with the two ligands separately for 2 hours.

Reserving these complexes in a desiccator (these firmly anhydrous conditions keep them indefinitely stable) [12]. These complexes were soluble in (acetonitrile, chloroform, and dichloromethane).

#### IR study of all products

Because of the delocalization of the dithiocarbamates, nitrogen atom lone pair onto the sulfur atom, and so their complexes tend to have rich electrochemistry; dithiocarbamates usually bind to metals to form a symmetrical chelate mode with soft dithiocarbamate resonance forms [13]. In addition to the pi-donor characteristic of the amino nitrogen atom in dithiocarbamates the sulfur atom of C=S thioester is an anion, and this will enhance the basicity of the second thioester centre, which can be embodied by the resonance structure that a positive charge on N and negative charges on both which is called thioureide represented in Scheme 2b, which showed the C-N partial double bond character of high basicity.

These resonance effects on IR spectra in several ways: First, the characteristic stretching vibrations of the (C-N) of thioureide IR spectra show bands at  $1494.73\text{ cm}^{-1}$ ; these higher frequency bands (about  $20\text{ cm}^{-1}$ ) are probably due to the increase in C-N double bond character by the resonance at coordination to the metals ion. Second way, correspondingly, the characteristic stretching vibrations of the (C-S) of the complexes IR spectra showing bands at  $990\text{ cm}^{-1}$ , these higher frequency bands (about  $4\text{ cm}^{-1}$ ) probably due to the increase in C-S double bond character by the resonance at coordination to the metals ion. A third way, the lack of an absorption band between  $3400$  and  $3650\text{ cm}^{-1}$ , due to the stretching frequency of the functional group  $\text{-OH}$ , excludes the coordination of water.



Scheme 2. The resonance structure of the new ligands.

These three observations indicate that a symmetrical bidentate chelating mode forms between the ligand and the metal center [13, 14]. Moreover, their general complexes octahedral structure of metals Zn, Mn, Co, and Zn, i.e. **I(a-d)** and **II(a-d)**, Figure 1A, and the general complexes square planer structures of metal Cu, **I(e)** and **II(d)**, Figure 1B with some physical properties and elemental analysis, Table 1 and study of their UV-Vis, IR and NMR spectroscopy are described in the following sections.

The new dithiocarbamate ligands, MAC = methyl-4-amino antipyrinyl dithiocarbamate and BAC = benzyl-4-amino antipyrinyl dithiocarbamate were yellow crystals with melting points of  $203\text{ }^{\circ}\text{C}$  for the primer and  $233\text{ }^{\circ}\text{C}$  for the later. However, the prepared metal complexes of these ligands vary in color relative to the metal ions, as shown in Table 1.

All these new complexes were stable in the air. It is insoluble in water but in most organic solvents, giving stable solutions at room temperature. All complexes were 1:2 electrolytes in solution. Thus, the structures of all these novel complexes were suggested octahedral, Figure 1A, except those of copper complexes were square planer Figure 1B, according to the electronic absorptions spectra as the following investigations:

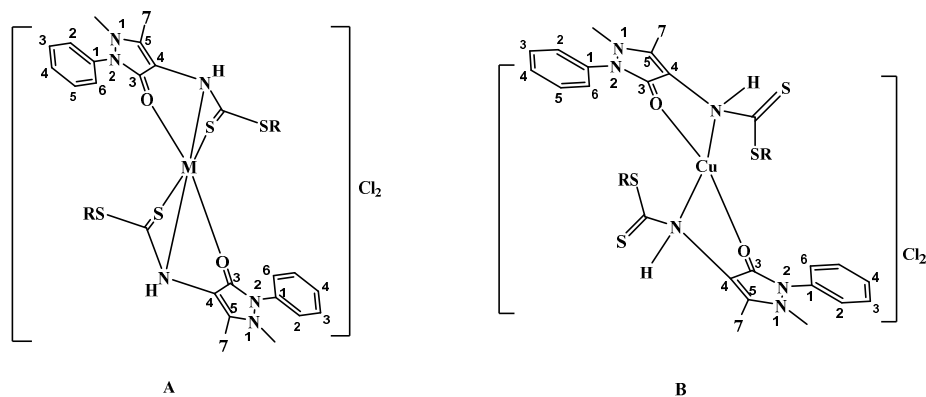


Figure 1. A: The general complexes structure; R = methyl or benzyl M = Zn, Mn, Co and Ni  
 B: The general complexes structure of copper; R = methyl or benzyl.

#### Electronic absorption spectra and magnetic moments studies

The electronic spectra for the free ligands have revealed that the bands corresponded to the chromophores of dithiocarbamate moiety of the  $\pi$ - $\pi^*$  transitions of the N-C-S, while the band that is assigned to  $\pi$ - $\pi^*$  of S-C-S group, in addition to the band  $n$ - $\pi^*$  transitions [15]. These transitions from ligands are consistent with the transition utilizing excitation of “Mn(II), Co(II), Ni(II), Zn(II), and Cu(II) ions”, which was called the d-d transition [16]. Absorption of ultraviolet or visible radiation with excitation of outer electrons was agreed with the works of literature [1]. These novel complexes’ electronic transitions consisted of  $\sigma$ ,  $\pi$ , and  $n$  electrons.

The electronic absorption spectra of divalent zinc-complexes (**Ia**) and (**Ib**) showed bands attributed to the presence of Zn $\rightarrow$ MAC or Zn $\rightarrow$ BAC at about 520-522 nm but did not display any d-d transitions. The obtained magnetic moment values show a diamagnetic character for these complexes [17]. These electronic spectra were recorded in absolute ethanol. These complexes showed three absorption bands at 928-930 nm, 648-650 nm, and 590-600 nm, which were assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(v1)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(p)(v3)$  transitions, respectively possessing an octahedral spatial arrangement. Finally, due to the absence of unpaired electrons, zinc complexes are diamagnetic [18].

The divalent manganese complexes **Ib** or **Ib** were shown three bands 480-490 nm, 530-525 nm, and 710-721 nm assignable to  ${}^4T_{1g} \rightarrow {}^6A_{1g}(G)$ ,  ${}^4T_{2g} \rightarrow {}^6A_{1g}(G)$  and  ${}^4T_{1g} \rightarrow {}^6A_{1g}(D)$  transition for octahedral configuration. Another indication of this configuration is the magnetic moment of 4.88 B.M., which supports the suggestion of the octahedral geometry in which these dithiocarbamates ligands act as tridentate. This probably accommodates themselves around the manganese atoms with a stable coordinate ring with five and four-membered rings [19].

The electronic absorption spectra of divalent cobalt-complexes **Ic** and **Ic** were shown bands attributed to the presence of Co $\rightarrow$ MAC or Co $\rightarrow$ BAC of three absorption bands at 890-900 nm, 600-605 nm and 478480 nm assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(v1)$ ;  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(v2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)(v3)$  transitions respectively in an octahedral environment. These findings align with the data on magnetic susceptibility, which were estimated to be of value 3.66 B.M. [20].

The electronic spectra of the divalent nickel complexes **Id** or **Id**, which also were recorded in absolute ethanol, showed three absorption bands at 925-930 nm, 658-650 nm and 588-590 nm which were assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(v1)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(p)(v3)$  transitions respectively possessing an octahedral spatial arrangement. These complexes gave a magnetic

moment value of 3.08 B.M. because of two unpaired electrons, which may suggest a regular octahedral geometry ( $t_{2g}^6 e_g^2$ ) and hybridization  $sp^3d^2$  [21].

The magnetic susceptibility values for copper complexes **Ie** or **Ile** verify the existence of an individual electron (2.01 B.M.), and the electronic spectra of square planar copper(II) complexes intersect with the ligand. The most significant characteristic bands may be (270, 300, 370, 395 nm), which are caused by the transitions  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  ( $\nu_1$ ),  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  ( $\nu_2$ ) and  ${}^2B_{1g} \rightarrow {}^2E_g$  ( $\nu_3$ ) [22].

#### Conductivity measurement

The conductivity values of the novel complexes **I** and **II** were extended between (110-136)  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  in DMF at room temperature, as shown in Table 2, which were referred to that of all metal complexes were non-neutral and electrolyte and conductive species exist due to acceptations of the metal cations of the electron(s) from the dithiocarbamates ligands which decreased the novel complexes conductivity and these results came in agreement with literature [23-25].

Table 2. The conductivity measurements ( $\Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$ ) of the novel complexes **I** and **II** in DMF at 25 °C.

Complexes	Conductivity	Complexes	Conductivity
[Zn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(a)</b>	112	[Zn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(a)</b>	110
[Mn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(b)</b>	136	[Mn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(b)</b>	114
[Co(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(c)</b>	134	[Co(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(c)</b>	126
[Ni(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(d)</b>	126	[Ni(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(d)</b>	119
[Cu(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(e)</b>	128	[Cu(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(e)</b>	131

#### Infrared spectra

The importance of infrared bands of free organic ligands methyl or benzyl 4-minoantipyrinyl dithiocarbamates, respectively, and their complexes with Mn(II), Co(II), Ni(II), Zn(II), and Cu(II) ions are given in Table 3. After complexation, the strong band caused by  $\omega(\text{N-H})$  at  $3325 \text{ cm}^{-1}$  in the spectrum of free ligands did not change. The ligand spectrum showed two absorption bands (weak and medium) at  $2953 \text{ cm}^{-1}$  and  $3133 \text{ cm}^{-1}$ , respectively, because of the  $\omega(\text{C-H})$  aromatic and aliphatic groups. For both free ligand and metal complexes, the positions and intensities of these bands remained constant. The ligands showed their characteristic  $\nu(\text{C-N})$  band at  $1527 \text{ cm}^{-1}$ . In the bands of the metal complexes, these bands' positions stayed about the same frequency.

Table 3. The IR spectra of ligands and complexes

Compounds	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-S})$
(MAC)	3325	2954	1527	990	---	---	---
[Zn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(a)</b>	3301	2931	1494	1035	501	588	445
[Mn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(b)</b>	3132	2900	1495	980	512	548	475
[Co(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(c)</b>	3153	2925	1529	995	501	590	441
[Ni(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(d)</b>	3137	2925	1525	993	503	586	447
[Cu(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(e)</b>	3240	2925	1525	978	507	597	---
(BAC)	3322	2954	1522	990	---	---	---
[Zn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(a)</b>	3305	2923	1490	1016	501	590	435
[Mn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(b)</b>	3288	3101	1494	1014	507	595	428
[Co(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(c)</b>	3288	2925	1525	966	507	597	437
[Ni(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(d)</b>	3133	2922	1523	988	510	555	445
[Cu(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(e)</b>	3235	2945	1525	1008	522	535	---

*<sup>1</sup>H NMR spectroscopy*

Methyl-4-amino antipyrinyl dithiocarbamate ligand MAC showed the following chemical shifts (deuterated DMF). Three singlet peaks at 2.15, 2.41, and 3.10 ppm integrate for three protons assigned to the three methyl groups of thioester and methyl groups of the antipyrine ring. A multiplet at 7.35-7.52 ppm integrates five aromatic protons. Finally, a singlet at 8.36 ppm integrating for the NH proton, Figure 2.

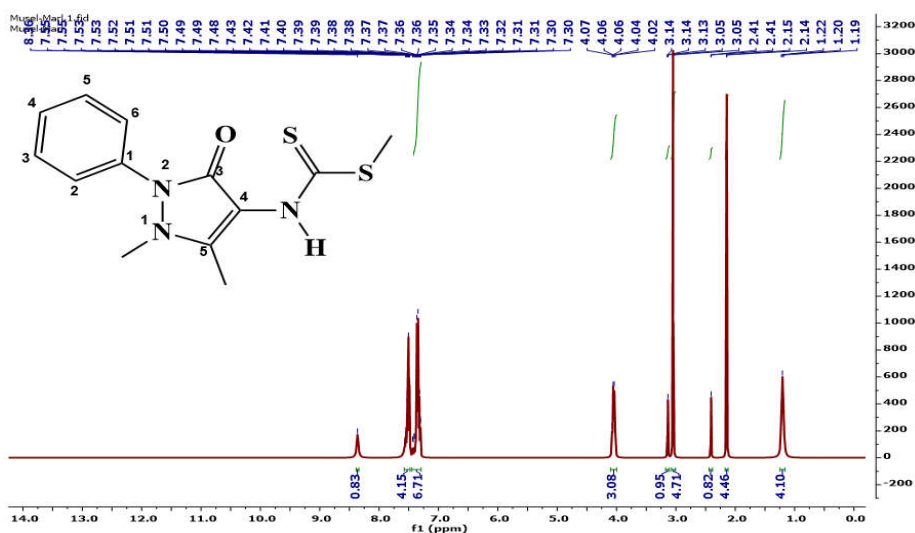


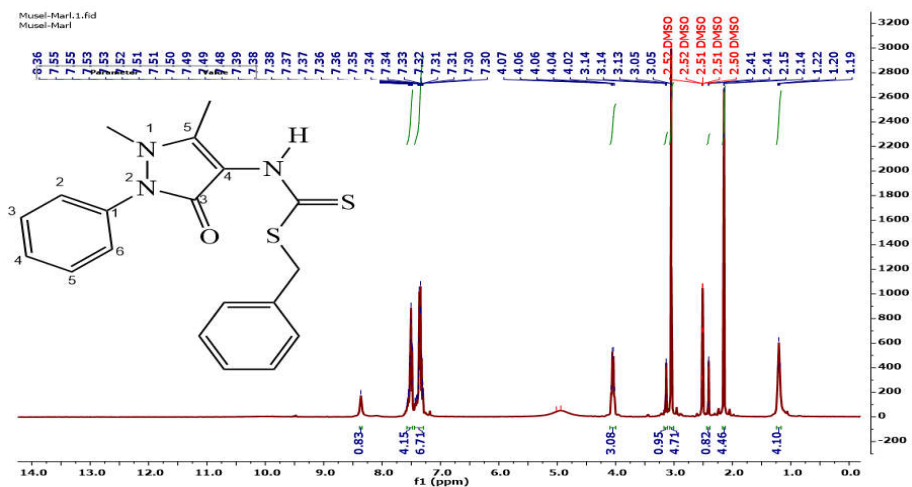
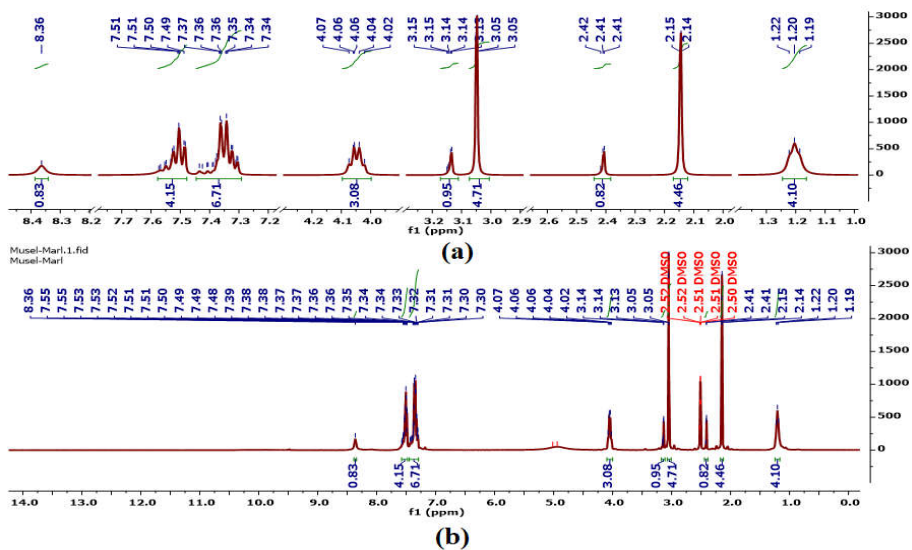
Figure 2. The <sup>1</sup>H-NMR of ligand MAC.

Meanwhile, benzyl-4-amino antipyrinyl dithiocarbamate ligand BAC showed the following chemical shifts (deuterated DMF). Three singlet peaks at 2.15, 2.41, and 3.14 ppm integrate for three protons assigned to the thioester CH<sub>2</sub> benzyl group and two methyl groups of methyl groups of the antipyrine ring. A multiplet at 7.30-7.55 ppm integrates ten aromatic protons. Finally, a singlet at 8.36 ppm integrating for the NH proton, Figure 3.

The <sup>1</sup>H NMR spectra of the complexes, which choose [Zn(MAC)<sub>2</sub>]Cl<sub>2</sub>, **I(a)** and [Zn(BAC)<sub>2</sub>]Cl<sub>2</sub>, **II(a)** as representatives for these series, the hydrogens environment of these complexes was confirmed. As can be seen from the two <sup>1</sup>H NMR, Figure 2 and Figure 3, the singlet at 8.36 ppm integrating for the NH proton of both MAC and BAC were deshielded the H atoms nuclei to the peaks downfield because of the effect of the metal (zinc) atom which pulling the electron density from the ligand's proton away from the methyl or benzyl groups of [Zn(MAC)<sub>2</sub>]Cl<sub>2</sub>, **I(a)** and [Zn(BAC)<sub>2</sub>]Cl<sub>2</sub>, **II(a)**, respectively, as shown in Figure 4a and b [26].

*Biological activity*

The antibacterial activity of these novel complexes was in vitro evaluated for their biological activities against Gram-negative bacteria (*Klebsiella*) and *Candida albicans* Bacteria (*Kleb*) *Klebsiella* and *Candida albicans*. Antibiotic discs: (NY) Nystatin 100 µg/mL = 16 mm (for *Candida*), Gentamicin 10 µg/mL = 15 mm (for *kleb*). The biological study showed that Co and Zn complexes have biological activity against bacteria *Klebsiella* at a concentration of 100 µg/mL, while the rest of the compounds did not affect any biological activity against bacteria.

Figure 3. The  $^1\text{H-NMR}$  of ligand BAC.Figure 4. The  $^1\text{H-NMR}$  of complexes (a)  $[\text{Zn}(\text{MAC})_2]\text{Cl}_2$ , **I(a)** and (b)  $[\text{Zn}(\text{BAC})_2]\text{Cl}_2$ , **II(a)**.

The complex of Co at a concentration of 100  $\mu\text{g/mL}$  and complex of Mn complexes at a concentration of 100, 50, and 25  $\mu\text{g/mL}$  showed biological activity against *Candida albicans*, while the rest of the relationships did not maintain any biological activity against *Candida albicans*. The data on biological activity is listed in Table 4 (where R mean resistance of bacteria).



Table 4. The data from the biological activity test

No.	Compound	Concentration $\mu\text{g/mL}$	Candida St = 16 mm	Kleb St = 15 mm
1	[Co(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(c)</b>	100	19.3	19.1
		50	13.5	16
		25	R	R
		12.5	R	R
2	[Zn(BAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>II(a)</b>	100	12.9	17.4
		50	R	13
		25	R	R
		12.5	R	R
3	[Zn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(a)</b>	100	14.7	15.1
		50	13.5	14.7
		25	13	11.2
		12.5	13	R
4	[Mn(MAC) <sub>2</sub> ]Cl <sub>2</sub> , <b>I(b)</b>	100	28.2	R
		50	25.2	R
		25	20.5	R
		12.5	15.1	R
5	(MAC)	100	14.7	R
		50	12.5	R
		25	R	R
		12.5	R	R

## CONCLUSIONS

Except for the copper complexes, which have a square planar structure, the data and outcomes from physical and spectral measurements demonstrated that the prepared complexes' spatial structure is octahedral. Figure 1A shows that the structures of all of these new complexes are octahedral, while Figure 1B shows that the structures of the copper complexes are square and planar. Additionally, it was observed that the prepared compounds, particularly the cobalt and zinc complexes, exhibited activity against the tested bacteria.

## ACKNOWLEDGMENTS

The authors sincerely thank the academics who are supervising them. We would also like to provide our sincere appreciation to all of our supporters, especially Al-Noor University, Mosul City, for their financial support and providing facilities that made this work possible.

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