

## RESEARCH ARTICLE

# Synthesis, Characterization of Some Metal Complexes With 3-(Benzo[d]Thiazole-2-Yl)-9-Oxo-6,7,7a,9-Tetrahydro-2H-2,10:4,7-Diepoxyfuro [3,2-f][1,5,3] Dioxazonine-2,4 (3H)-Dicarboxylic Acid, Hydrochloride (L-as-am) and Study their Biological Activity

Yasamen A. Badeea,<sup>1</sup> Waleed K. Mahdi,<sup>1</sup> Yousif Ibrahim,<sup>1</sup> Falih H. Musa<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, College of Education of Pure Science, Ibn - Al Haitham, University of Baghdad, Baghdad, Iraq

<sup>2</sup>Head of Medical Laboratory Techniques Department, Ashur University College, Baghdad, Iraq

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## ABSTRACT

The reaction of 2-amino-benzothiazole with bis [O,O-2,3,O,O – 5,6 – (chloro(carboxylic) methylidene) ] – L – ascorbic acid (L-AsCl<sub>2</sub>) gave new product 3-(Benzo[d]Thiazole-2-Yl) – 9-Oxo-6,7,7a,9-Tetrahydro-2H-2,10:4,7-Diepoxyfuro [3,2-f][1,5,3] Dioxazonine – 2,4 (3H) – Dicarboxylic Acid, Hydro-chloride (L-as-am)), which has been insulated and identified by (C, H, N) elemental microanalysis fourier-transform infrared spectroscopy (FTIR), (UV-vis), mass spectroscopy and H-NMR techniques. The (L-as am) ligand complexes were obtained by the reaction of (L-as-am) with [M(II) = Co, Ni, Cu, and Zn] metal ions. The synthesized complexes are characterized by UV-visible (Ft – IR), mass spectroscopy molar ratio, molar conductivity, and Magnetic susceptibility techniques. (L-as-am) ligand analysis exhibited that metal ions coordinated with (L-as-am) thought the bidentate carboxylate, sulfur atom from one side and the other side with bidentate carboxylate and nitrogen atom forming binuclear six coordinated metal ions in an octahedral geometry. The purity of (L-as-am) ligand and their complexes were screened using thin-layer chromatography (TLC). Also, the study of the biological activity has been conducted for (L-as-am) ligand and its complexes, which showed diversity in its activity towards two types of pathogenic bacteria, (*Escherichia coli*, *Staphylococcus aureus*) and also against (*Candida albicans*) fungi.

**Keywords:** Biological activity, Characterization, Metal Complexes, Synthesis, (L-as-am).

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**Conflict of interest:** None

## INTRODUCTION

Ascorbic acid is the important source for the synthesis of many chemical compounds, representing the basic base used to prepare its derivatives required in the synthesis of coordination complexes. In terms of competence, collagen synthesis has various physiological and pharmacological functions,<sup>1,2</sup> anti-oxidation,<sup>3,4</sup> and antibacterial activity.<sup>5</sup> Another derivative of L-ascorbic acid has been synthesized, such as 5,6-O-isopropylidene-2,3-(2-X,1-carboxyl) deoxy-L-ascorbic acid, where X = I, Cl, 1,2-dihydroxyethyl-1-(2-mercaptophenyl)-5-(2-mercaptophenyl)-2,5-dihydro – 1H – pyrol – 3,4 – diol, 5,6 – O,2,3 – O – L-ascorbic acid were substituted by acetic acid. The thiol derivative of bis [ O, O – 2,3,O, O – 5,6 – (carboxylic) methylidene) ] – L-ascorbic acid has been prepared.<sup>5,6</sup> L – ascorbic derivatives of metal ions complexes were also synthesized and characterized, and their biological effect has

been noticed.<sup>5-7</sup> The research aims to synthesize new derivatives for L-ascorbic acid of (L-as-am) ligand with metal (II) ions complexes when, M<sup>(II)</sup> = (Zn, Cu, Ni, Co).

## MATERIALS AND METHODS

### Experimental Chemicals

Metal salts (CoCl<sub>2</sub> · 6H<sub>2</sub>O, NiCl<sub>2</sub> · 6H<sub>2</sub>O, CuCl<sub>2</sub> · 2H<sub>2</sub>O, ZnCl<sub>2</sub> · 2H<sub>2</sub>O) have been acquired from fluka, Merck, L-ascorbic acid, 2-aminobenzothiazol (fluka) Tri chloro acetic acid (Riedel-de Haën).

### Instrumentations

1. The electronic spectra were measured on (UV-Vis) spectroscopy kind Shimadzu UV-160A at the wavelength range (200–1000) nm, using match quartz cells (1 cm) and water as a solvent at service laboratory in Chemistry Department, College of Education of Pure Science, Ibn

\*Author for Correspondence: falih.hassan@au.edu.iq

Al-Hathiam. The 2-Melting point was registered on "Gallen Kamp (mp) device model SMP30 at College of Education of Pure Science, Ibn Al-Hathiam. 3-conductivity measurements were registered using conductivity meter type W.T.W at Chemistry Department, College of Education of Pure Science, Ibn Al-Hathiam. The characterize of the new ligand (L-as-am) and its complexes is achieved by:

- A:** The elemental micro analysis of (C,H,N) measurements using Euro Vector EA type 3000 A (EA-Italy), at Al-Mustansiriya University.
- B:** G C M S spectrum was performed using mass spectrometer type 5975 quadrupole analyzer, at University of, Iran Tehran.
- C:** Infrared spectra are performed in the range (4000–400)  $\text{cm}^{-1}$  in KBr discs on (FT-IR) Shimadzu type-8400S. Spectra were recorded at Laboratories of the Jadriya College of Sciences, Baghdad.
- D:** Proton ( $^1\text{H-NMR}$  spectra) of the new ligand was registered by using (Bruner spectrophotometer – 500-MHz type DRX in (d  $^6$ -DMSO). The chemical shifts are in ppm relative to  $\text{Me}_4\text{Si}$  were performed at University Sharif Sainte, Iran, Tehran.
- E:** (TLC) Thin layer chromatography: for the ligand (L-as-am) was performed in aluminum plates coated by (0.25 mm) layer of silica gel Fluka type (F254) and detected in Iodine.
- F:** Magnetic susceptibility values were obtained at room temperature by using the Faradays method, Johnson Matthey catalytic system, at Al-Mustansiriya University.

#### Synthesis of Ligand (L-as-am):

Bis [ O,O – 2,3, O,O – 5,6 – (chloro (carboxylic methyldiene) ] – L ascorbic acid (L-As- $\text{Cl}_2$ ) (0.375 g, 1mmole) dissolved in mixture of (15 mL EtOH + 5 mL,  $\text{H}_2\text{O}$ ). 2-aminobenzothiazole (0.150 g, 1 mmole) in (5 mL EtOH) was added dropwise to that solution and used reflux for 3 hours. A yellow solution was formed, then its filtered and left for few days at room temperature to give the yellowish product. The precipitate was crystallized from (25 mL) mixture of ethanol and water (4:1) having yellow precipitate melting point =  $22^\circ\text{C}$ , yield (95%), Elemental analysis Found (Calc.) C % 43.94 (43.40), H % 3.51 (2.97), Rf = 0.43.

#### Synthesis of Complexes (M(II) = Co, Ni, Cu, and Zn)

To a solution of (L-as-am) (0.334 g, 1m mole) in a mixture of (15 ml EtOH + 5 mL  $\text{H}_2\text{O}$ ) a solution of (2 mmole of  $\text{MCl}_2 \cdot \text{XH}_2\text{O}$ ) in (20 ml ethanol) (0,475 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), ( $\text{NiCl}_2 \cdot$

$6\text{H}_2\text{O}$ , 0. 475 g), (0.340 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and (0.345 g,  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ ) were added. The (0.224 g, 4 mmole) of KOH solution was added to the mixture to form down the complexes. The secluded complexes are colored solids, insoluble in all organic solvent, but soluble in DMSO and stable in air. Table 1 showed Some physical properties of the synthesized (L-as-am) ligand and its complexes.

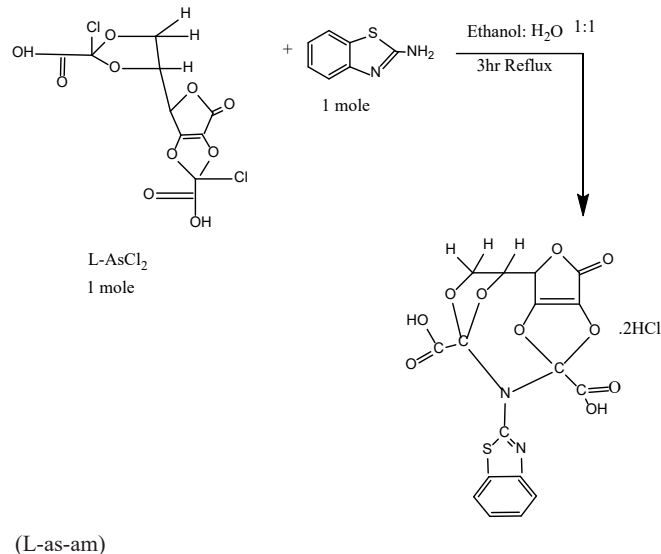
Dc = Decomposition, (L-as –am) = Ligand

## RESULTS AND DISCUSSION

The (L-as-am) Ligand: 3-(benzo[d] thiazol-2-yl)-9-oxo-6,7,7a,9-tetrahydro-2H-2,10:4,7-diepoxyfuro[3,2-f] $^{1,5,3}$  dioxazonine-2,4(3H)-dicarboxylic acid. hydrochloride. Is synthesized in a excellent yield according to the reaction of the precursor ligand (L- $\text{AsCl}_2$ ) with 2-amino benzothiazole (2-amb) as shown in Scheme-1.

### Fourier-transform infrared spectroscopy (FTIR) Spectral Studies

The I. R spectrum of (L- $\text{AsCl}_2$ ) as a precursor ligand is compared with the new (L-as-am) ligand spectrum, Table 2 are summarized these results the,(L- $\text{AsCl}_2$ ) ligand exhibited a new band at (833)  $\text{cm}^{-1}$  due to  $\nu(\text{C-Cl})$ , this band disappeared



Scheme 1: Represented the steps of preparation of (L-as-am) ligand

Table 1: Physical, analytical data of the ligand (L-as-am) and its complexes.

Compounds	M.Wt g/mol	Color	Dc	Molar Conductivity		Rf
				$\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	$\mu_{\text{eff}}^{\text{eff}}$ (BM)	
$\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_{10}\text{S}_2 \cdot 2\text{HCl}$ (L-as-am).2HCl	507	Yellow	220	—	—	0.43
$[\text{Co}_2(\text{L-as-am-H}^+)\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$	693	Violet deep	255	1.3	4.77	0.32
$[\text{Ni}_2(\text{L-as-am-H}^+)\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$	692	Bright green	290	2.3	3.43	0.34
$[\text{Cu}_2(\text{L-as-am-H}^+)\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$	702	Greenish blue	190	3	1.82	0.45
$[\text{Zn}_2(\text{L-as-am-H}^+)\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$	706	White	260	5.2	-----	0.3

in the FTIR spectrum of the new (L-as-am) ligand. The stretching vibration of carboxylic group  $\nu$  (COOH) was observed as a broad band at  $(3415) \text{ cm}^{-1}$ . The band at  $(1728) \text{ cm}^{-1}$  is due to the stretching vibration  $\nu$  (C=O) of lactone group; another band at  $(1658) \text{ cm}^{-1}$  are due to the  $\nu$  (C=O).<sup>8</sup> The band at  $3415 \text{ cm}^{-1}$  is due to  $\nu$  (OH–water) in all-metal complexes. Furthermore these modes of coordinated  $\nu$  ( $\text{H}_2\text{O}$ ) are due to the rocking vibration exhibited at the rang  $(833 - 846) \text{ cm}^{-1}$  in all complexes. The asy  $\nu$  (C=O) and sym  $\nu$  (COO) attributed to the stretching vibrations bands of the carboxylate are observed at  $(1689) \text{ cm}^{-1}$  for the (L-as-am) of free ligand, these bands are shifted in all complexes to Co(II) ( $1458$  asy,  $1394$  sym), Ni(II) ( $1485$  asy,  $1394$  sym), Cu(II) ( $1471$  asy,  $1392$  sym) and Zn(II) ( $1471$  asy  $1390$  sym)  $\text{cm}^{-1}$ . For all complexes,  $(64, 91, 79, \text{ and } 81) \text{ cm}^{-1}$  confirmed that the carboxylate coordinate as a bidentate<sup>9,10</sup> all the complexes showed a new band in the regions  $(480 - 528) \text{ cm}^{-1}$  and  $(422 - 472) \text{ cm}^{-1}$ , are assigned to  $\nu$  (M–O) and  $\nu$  (M–N)

band.<sup>11,12</sup> So its concluded from the IR spectra, that one side of the (L-as-am) ligand behave as anion tridentate bind to M(II) ion via the bidentate carboxylate and nitrogen atom and another side coordinated with bidentate carboxylate and side sulfur atom forming octahedral structure.

### <sup>1</sup>H-NMR Spectrum of the Ligand (L-as-am):

The <sup>1</sup>H-NMR spectrum of (L-as-am) ligand, Figure 1 in  $d^6$ -DMSO showed a signal at  $\delta = 2.53$  ppm due to protons of DMSO solvent another signals lies at  $\delta = 3.30, 3.34$  ppm were assigned to HDO. The CH – lactone signal at  $\delta = 3.45$  ppm, CH at  $\delta = (3.39)$  ppm and  $\text{CH}_2$  signal at  $\delta = 3.22, 3.31$  ppm. Signals at the range  $\delta = 6.96 - 7.66$  ppm are due to the benzothiazole protons. COOH signal is exhibited at  $\delta = 8.37$  ppm.<sup>13,14</sup>

### The Mass Spectrum of (L-as-am) Ligand

The mass spectrum of (L-as-am) ligand and its complexes showed a highest mass with single intensity (relative to the base peak at  $m/z$ ) as are summarized in Tables 3, 4 and, Figure 2.<sup>6,8</sup>

Table 2: The FTIR spectral data of (L-as-am) ligand and their complexes

Empirical formula for ligand and its complexes	$\nu$ (C-OH)		$\nu$ (C=O)	$\nu$ (C=O)	$\nu$ asy(COO <sup>-</sup> )	$\nu$ Δ		
	Carboxylic $\nu$ (O-H)	(H <sub>2</sub> O) aqua	Lactone	Carboxyl	$\nu$ sym(COO <sup>-</sup> )	COO	$\nu$ (M-O)	$\nu$ (M-N)
(L-as-am) $\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_{10}\cdot\text{S}\cdot\text{2HCl}$	3454, 3398 (m)	-----	1762 (m)	1689 (w)				
$[\text{Co}_2(\text{L-as-am-2H}^+) \text{Cl}_2\cdot 4\text{H}_2\text{O}]$	3490 – 3336 (br)	833 (s)	Overlap With C=N C=C	—	1458 (w) 1394 (m)	64	522 (m)	422 (w)
$[\text{Ni}_2(\text{L-as-am-2H}^+) \text{Cl}_2\cdot 4\text{H}_2\text{O}]$	3562-3377 (br)	846 (m)	1747 (w)	—	1485 (m) 1394 (w)	91	528 (w)	459 (w)
$[\text{Cu}_2(\text{L-as-am-2H}^+) \text{Cl}_2\cdot 4\text{H}_2\text{O}]$	3444(s) 3348(s)	844 (m)	Overlap With C=N C=C	—	1471 (m) 1392(m)	79	480 (m)	439 (s)
$[\text{Zn}_2(\text{L-as-am-2H}^+) \text{Cl}_2\cdot 4\text{H}_2\text{O}]$	3539-3411 (br)	833 (s)	1760 (vw)	—	1471 (w) 1390 (sh)	81	516(vw)	472 (s)

asy = asymmetric, sym = symmetric

(sh) = Sharp, (s) = strong, (br) = broad, (m) = medium, (w) = weak, (vw) = very weak.

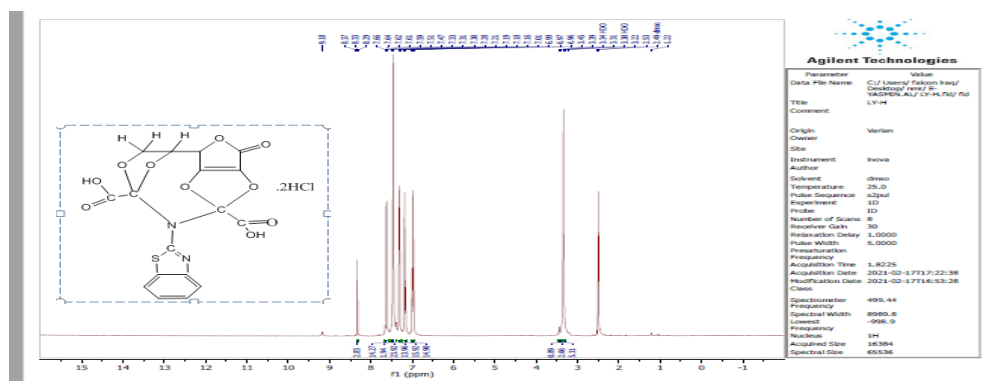


Figure 1: <sup>1</sup>H-NMR spectrum of (L-as-am) ligand

**Electronic Spectra Study and Magnetic Susceptibility Studies**

Table 5 explains that the electronic spectra of the Cobalt (II) complex is exhibited by several bands in the (visible-region) nigh to the region (516 nm, 19379 cm<sup>-1</sup>) ( $\epsilon_{\max} = 321361 \text{ mole}^{-1} \text{ cm}^{-1}$ ). These values are assigned to the transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)(v_3)$  in a mixture with another transition derived from the free ion  ${}^2G$  and  ${}^2H$  terms due to the spin has forbidden transition to doublet state which confirmed the high spin octahedral geometry. The measurement of the magnetic susceptibility of the cobalt (II) solid complex showed a value at (4.77) BM, which is due to the presence of three individual electrons, and this supports the octahedral geometrical coordination.<sup>15,16</sup> In Nickel(II) complex the electronic

spectrum exhibited bands located in the region (721nm, 13869 cm<sup>-1</sup>), ( $\epsilon_{\max} = 220542 \text{ mole}^{-1} \text{ cm}^{-1}$ ), (659nm, 15174 cm<sup>-1</sup>), ( $\epsilon_{\max} = 189036 \text{ mole}^{-1} \text{ cm}^{-1}$ ) and (398nm, 25125 cm<sup>-1</sup>), ( $\epsilon_{\max} = 441084 \text{ mole}^{-1} \text{ cm}^{-1}$ ) are assigned to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  ( $v_1$ ),  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(p)$  ( $v_3$ ) transition, consistent with its octahedral configuration, Ni(II) complex showed the magnetic moment value (3.43) BM, confirming octahedral structure.<sup>17,18</sup> The Copper (II) electronic spectrum showed a broadband center located at (773nm, 12937 cm<sup>-1</sup>), ( $\epsilon_{\max} = 114537 \text{ mole}^{-1} \text{ cm}^{-1}$ ) due to the  ${}^2E_g \rightarrow {}^2T_{2g}$  transition of octahedral structure The value of the magnetic susceptibility measurement of Copper (II) complex was (1.82) BM.<sup>19</sup> The Zn(II) complex spectra exhibited that the d-d transitions for the metal complexes are excluded.<sup>20</sup>

Table 3: The mass spectra data of the Ligand (L-as-am) and [Co<sub>2</sub>(L-as-am-2H<sup>+</sup>)Cl<sub>2</sub>.4H<sub>2</sub>O] complex.

Fragments	Relative	Relative
C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> SO <sub>10</sub> H <sup>+</sup>	435	45.94
C <sub>10</sub> H <sub>5</sub> O <sub>10</sub>	285	1.62
C <sub>10</sub> H <sub>4</sub> O <sub>7</sub>	236	3.78
C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> S	150	62.16
C <sub>7</sub> H <sub>5</sub> N <sub>2</sub>	117	41.35
C <sub>2</sub> H <sub>5</sub> O <sub>3</sub>	110	4.86
C <sub>4</sub> H <sub>2</sub> O <sub>2</sub>	82	19.72
C <sub>3</sub> H <sub>5</sub> N <sub>2</sub>	69	19.18
C <sub>4</sub> HN	63	10.27
CO <sub>2</sub>	44	100
[Co <sub>2</sub> (C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>14</sub> S)Cl <sub>2</sub> -2H <sup>+</sup> ]	691.7	76.21
[Co <sub>2</sub> (C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>13</sub> S)]	606	0.54
[Co <sub>2</sub> (C <sub>16</sub> H <sub>11</sub> N <sub>2</sub> O <sub>12</sub> S)]	577	0.81
[Co <sub>2</sub> (C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> S)]	266	1.08
(Co) <sub>2</sub>	118	2.70
(C <sub>4</sub> HO <sub>2</sub> )	81	6.48
(HN <sub>2</sub> CS)	73	2.16
(CS)	44	100
(CO <sub>2</sub> )	44	100

L.F=Ligand field, ILCT= Intra ligand charge transfer, C.T = Charge transfer

Table 4: Mass spectral data of [M<sub>2</sub>(L-as-am-2H<sup>+</sup>)Cl<sub>2</sub>.4H<sub>2</sub>O] complexes (M = Ni, Cu and Zn)

Fragments	m/z	Relative abundance %
[Ni <sub>2</sub> (C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>14</sub> S)Cl <sub>2</sub> ]	692	91.35
[Ni <sub>2</sub> (C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>13</sub> S)]	603	3.51
[Ni <sub>2</sub> (C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> S)]	264	11.89
(C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> )	83	49.72
(C <sub>6</sub> H <sub>4</sub> )	76	67.02
(NCS)	58	91.08
[Cu <sub>2</sub> (C <sub>17</sub> H <sub>16</sub> O <sub>14</sub> N <sub>2</sub> S)Cl <sub>2</sub> ]	702	
[Cu <sub>2</sub> (C <sub>17</sub> H <sub>8</sub> O <sub>12</sub> N <sub>2</sub> S)Cl <sub>2</sub> ]	662	87.33
(C <sub>17</sub> H <sub>8</sub> O <sub>12</sub> N <sub>2</sub> S)	464	85.33
[Zn <sub>2</sub> (C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>14</sub> S)Cl <sub>2</sub> ]	706	
[Zn <sub>2</sub> (C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>13</sub> S)Cl <sub>2</sub> ]	690	
[Zn <sub>2</sub> (C <sub>17</sub> H <sub>9</sub> N <sub>2</sub> O <sub>10</sub> S)Cl <sub>2</sub> ]	635	
(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> S)	150	2.70
(C <sub>6</sub> H <sub>3</sub> O <sub>3</sub> )	123	0.54
(C <sub>5</sub> H <sub>3</sub> O <sub>3</sub> )	111	0.43
(C <sub>4</sub> H <sub>3</sub> O <sub>2</sub> )	83	14.59

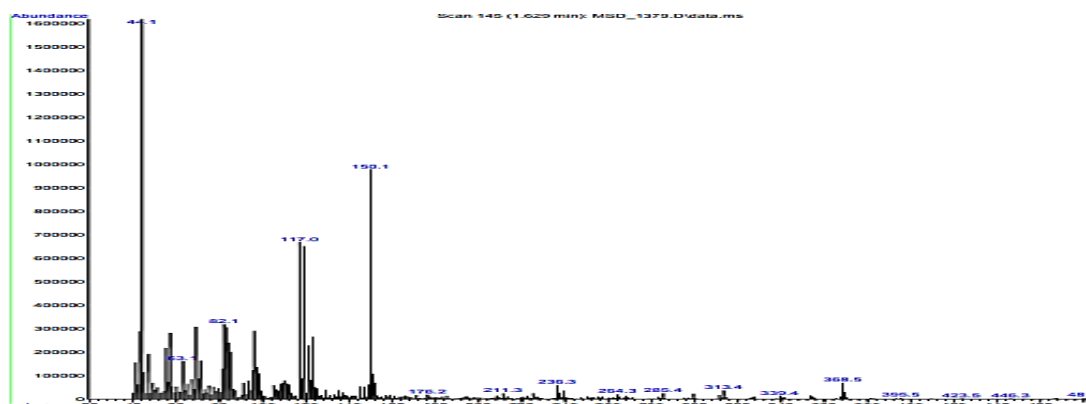


Figure 2: The (L-as-am) ligand mass spectrum

### TLC and Molar Ratio Studies

The purity of compounds in several components can be identified by using the (TLC) technique. (L-as-am) ligand and its complexes have been applied on plate aluminum oxide as a stationary phase, a solvent mixture (Hexane: Dichloromethane) in a ratio (2.5:2.5), known as the mobile phase was used. After the experiment, only one spots are visualized with different Rf as shown in Table 1), indicating the purity of the (L-as-am) ligand and its complexes.<sup>21,22</sup> The molar ratio methods for complexes of (L-as-am) with selected ions are studied in solution using (Ethanol:Water) in a ratio (1:1) as solvents, so from this method we can studying and determining the ratio of (metal:ligand) in the prepared complexes as shown in Table 6.<sup>23</sup>

### The Molar Conductivity Studies

In L-as-am ligand metal complexes study, Table 1 showed that the conductivity measurements complexes was performed in DMSO solvent, lie in the range (1.3–5.2) S. cm<sup>2</sup>. molar<sup>-1</sup> range, indicating its non-electrolytic nature.<sup>24</sup>

### The Biological Activity Studies

#### Study of Biological Activity of (L-as-am) Ligand and its Complexes

The biological activity study is done for the new L-as-am ligand with some synthetic metal ions complexes, which are examined with two types of pathological bacteria grown

in (nutrient agar) at a temperature of 37° C. The first type of bacteria is the bacteria with a positive strain, which is (gram-positive) like, *Staphylococcus epidermidis* and *Staphylococcus aureus*, the second type is the bacteria with a negative strain, which is (gram-negative) like *Klebsiella SP* and *Escherichia coli*. The study showed in Table 7 that the ligand (L-as-am) demonstrated the inhibition of these bacteria's growth, and also all prepared complexes showed different inhibition of the group of bacteria.<sup>25,26</sup>

### molar ratio co complexation

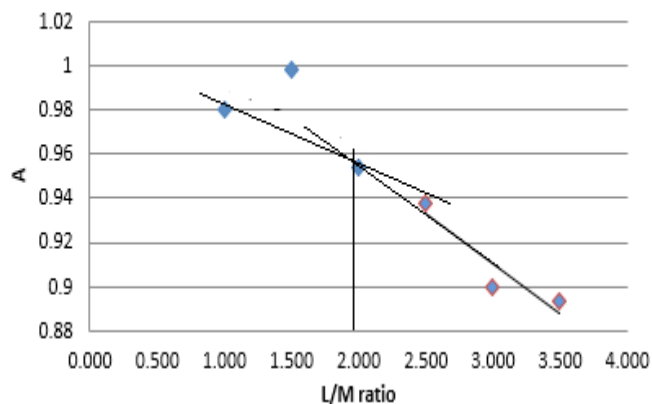


Table 5: The electronic spectra data of (L-as-am) Ligand and it's complexes

Ligand and complexes	Band ( $\lambda$ ) position (nm)	Band ( $\nu$ ) position (cm <sup>-1</sup> )	$\epsilon_{max}$ mole <sup>-1</sup> . cm <sup>-1</sup>	Assignment
(L-as-am)	221,252	45248,39682	—	$\pi \rightarrow \pi^*$
	283,313	35335,31948	—	$\pi \rightarrow \pi^*$
[Co <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] complex	221,252	45248,39682	—	L.F
	283	35335	—	L.F
	516	19379	321361	$^4T_{1g}(F) \rightarrow ^4T_{1g}(p)(\nu_3)$
[Ni <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] complex	221,236	45248,42372	—	L.F, ILCT
	254,283	39370,35335	—	L.F
	721	13869	220542	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)(\nu_1)$
	659	15174	189036	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)(\nu_2)$
	398	25125	441084	$^3A_{2g}(F) \rightarrow ^3T_{1g}(p)(\nu_3)$
[Cu <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] complex	283,315	35335,31948	-----	L.F
	773	12937	114537.4	$^2E_g \rightarrow ^2T_{2g}$
[Zn <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] complex	221,252	45248,39682	-----	L.F
	315	31948	298913	C.T

Table 6: The data of molar ratio method of (L-as-am) complexes and the curve of [Co<sub>2</sub>(L-as-am-2H<sup>+</sup>)Cl<sub>2</sub>.4H<sub>2</sub>O] complex.

V(mL) L × 10 <sup>-1</sup>	V(mL) M × 10 <sup>-1</sup>	[Co <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] $\lambda_{Max}=516 \text{ nm}\epsilon$	[Ni <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] $\lambda_{Max}=394 \text{ nm}\epsilon$	[Cu <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] $\lambda_{Max}=733 \text{ nm}\epsilon$	[Zn <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O] $\lambda_{Max}=320 \text{ nm}\epsilon$
1	1	0.98	1.315	2.006	0.436
1	1.5	0.998	1.1	2.137	0.420
1	2	0.954	1.035	2.201	0.414
1	2.5	0.938	0.959	2.319	0.410
1	3	0.9	0.922	2.337	0.414
1	3.5	0.893	0.884	2.398	0.413



**Table 7:** The inhibition zones in millimeter of the ligand (L-as-am) and its complexes with bacteria and fungi after 24 hours at 37°C

Compound	Zone of inhibition in millimeter				
	<i>Staphylococcus aureus</i>	<i>Staphylococcus epidermidis</i>	<i>Escherichia Coli</i>	<i>Klebsiella SP.</i>	<i>Candida albicans</i>
[Co <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O]	20	16	13	15	22
[Ni <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O]	13	12	11	15	14
[Cu <sup>2</sup> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O]	14	19	11	13	-
[Zn <sub>2</sub> (L-as-am-2H <sup>+</sup> )Cl <sub>2</sub> .4H <sub>2</sub> O]	14	34	14	13	14
(L-as-am)	9	11	18	14	15

### The (L-as-am) Ligand and Their Complexes' Biological Activities with Fungi

The (L-as-am) ligand and its complexes exhibited an important biological activity against (*Candida albicans*) fungi, it was found in the gastrointestinal and genitourinary tract. The test was performed by using the inhibition zone method, Table 7 shown the data of biological activities of both ligands and its complexes.<sup>27</sup> It was concluded from the data that the ligand (L-as-am) showed different inhibition activities with this group of fungi while Only the complex [Co<sub>2</sub>(L-as-am-2H<sup>+</sup>)Cl<sub>2</sub>.4H<sub>2</sub>O] did not show any inhibition.

### CONCLUSION

- The new (L-as-am) ligand and their metal (II) ions where coordinated by bidentate carboxylate and nitrogen from one side and another side, the second metal (II) ions coordinated with bidentate carboxylate and sulfur forming octahedral on each metal ion.
- All the Techniques are; Ft-IR, H-NMR, UV-ViS, Mass-Spectra, Molar ratio, Conductivity, Magnetic Susceptibility are Proved the structure of all complexes octahedral structure.
- The biological activity study results showed that (L-as-am) ligand and all complexes have a variety of antibacterial activities and antifungals.

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