



## Synthesis, Characterization of 2-azido-4-(azido (2-azido-2-( azido carbonyl)-1,3-dioxoian-4-yl)methyl)- 5-((R-azido (hydroxyl) methyl-1,3-dioxole-2-carbonyl azide. ethanol. hydrate (L-AZD) with Some Metal Complexes

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### Abstract

The reaction of (L- AsCl<sub>2</sub>) : Bis [O,O – 2,3, O,O – 5,6 – (chloro(carboxylic)methylidene) – L-ascorbic acid with sodium azide in ethanol with drops of distilled water has been given a new product (L-AZD), was isolated and characterized by elemental analysis (C,H,N) , <sup>1</sup>H-NMR, mass spectra and Fourier transform (Ft-IR). The reaction of the (L-AZD) with: [VO(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)], has been investigated and was isolated as tri nuclear cluster and characterized by: Ft-IR, U. v-Visible, electrical conductivity, magnetic susceptibilities at 25 Co, atomic absorption and molar ratio. Spectroscopic evidence showed that the binding of metal ions were through azide and carbonyl moieties resulting in a six- coordinating metal ions in [Cr (III), Mn (II), Co (II) and Ni (II)]. The Vo (II), Cu (II), Zn (II), Cd (II) and Hg (II) were coordinated through azide group only forming square pyramidal for VO (II), square planar geometry for Cu (II) and tetrahedral for Zn (II), Cd (II) and Hg (II), - for Ni (II), Cr (III) complexes were calculated, the ratio of (L-AZD) to metal ions was (3:1) confirmed by metal ratio and atomic absorption spectrophotometer, magnetic moment values at (298 K) of VO (II), Cr (III), Mn (II), Co (II), Ni (II) and Cu (II) are lower than the total spin-only indicate a dominate of anti-ferromagnetic coupling between them.

**Keywords:** *Synthesis, Tri nuclear cluster, Azide.*

### Introduction

L-ascorbic acid and derivatives which containing azide and carbonyl groups have been prepared and characterized by our group with their metal ions , multi nuclear clusters were forming [1-3]. A tri nuclear cluster containing the {Fe<sub>3</sub> (U<sub>3</sub>- O)}<sup>7+</sup> has been prepared through the reaction of basic iron benzoate with sodium azide [4]. The combined use of anion of phenyl (2-pyridyl) ketone oxime and azides (N<sub>3</sub><sup>-</sup>) in nickel (II) [5], and two new novel Cu (II) complexes with versatile azide or thiocyanate bridging derived from symmetrical azo-linked schiff base of 1- (5-chloro-2-hydroxyl-phenyl)-ethanone and propane 1,3-diamine have been reported too [6]. Continuing our interested is the synthesis a tri nuclear cluster containing ( M<sub>3</sub>, azide, and carbonyl), M = VO (II), Cr (III), Mn (II), Co (II), Ni (II),

Cu (II), Zn (II), Cd (II) and Hg (II) and characterized.

### Experimental

#### Materials and Reagents

All chemicals are purchased from BDH and used without further purification.

#### Instrumentation

Ft-IR spectra were recorded on a (shimadzu Ft-IR 8400S) in the rang (400-4000 cm<sup>-1</sup>). The electronic spectra were recorded on the U.v-Visible spectrophotometer type shimadzu U. v-160 A in wave length rang of (200-1000 nm) with match quartz cells (1 cm) using water as a solvent. Atomic absorption spectrophotometers were measured by using flame atomic absorption technique type Analytic Jena (A.A 350).

These measurements have been done in the laboratories of Ibn Sina Company and at the central service laboratory / college of Education for pure science, Ibn-Al Hathiam, University of Baghdad. Melting point was recorded on "Gallen Kamp" melting point Apparatus model SMP 30. The Conductance measurements were recorded at (25Co) for concentration rang (10-3- 10-5) mol. L-lin H<sub>2</sub>O by using Philips pw 5926 digital meter conductivity. Thin layer chromatography (TLC): for the ligand (L- AZD) was performed on aluminum plates coated with (0.25 nm) layer of silica gel F254 (Fluka) and were detected by iodine. These measurements have been done at chemistry department, college of Education of pure science, Ibn-Al-Hathiam, University of Baghdad.

Elemental analysis (C , H , N ) of the new ligand (L-AZD) was carried out by using Euro vector EA 3000 (Italy) 1H- NMR spectrum was recorded by using Bruner FRX (500-MHZ) spectrophotometer , chemical shift of 1H – NMR spectrum was recorded in (ppm) unit down field from internal reference tetramethylsilane (TMS) using D<sub>2</sub>O solvent. G.C.mass spectrometer Eager 300 for EA 1112. These measurements have been done at science Laboratory University, Teharan, Iran. Magnetic susceptibility values for the prepared complexes were obtained by using the Faradays method shore wood magnetic susceptibility Balance was performed at Al-Nahreen University.

## Synthesis

### Synthesis of (L-AZD) 2-azido-4-(azido(2-azido-2-(azido carbonyl)-1,3-dioxoian-4-

### yl) methyl)-5-((R-azido(hydroxyl)methyl)-1,3-dioxole-2-carbonyl azide. ethanol. hydrate

To a solution of (1g, m mole) of (L- AsCl<sub>2</sub>) (7) in (20ml ethanol + 7ml distilled water) were added a solution of (1.04 g, 6 m mole) sodium azide in (20ml ethanol + 3ml distilled water), drop wise. The mixture was refluxed for 3 hr. The resulting product was brown solution which was left to stand at room temperature, giving a brown solid and crystallized from distilled water and absolute ethanol in a ratio (1:1) yielding ( 0.844, 84.4%): Dc: 152-153, Rf=0.38.

### Synthesis of (L-AZD) - complexes [M = VO (II), Cr (III), Mn (II), Co (II), Ni (II), Zn (II), Cd (II) and Hg (II)

All complexes were prepared at follows: To a solution of (0.5g, 1mmole) (L-AZD) in a mixture of (15ml ethanol + 5ml distilled water). A solution of (3mmole of metal chloride and vanadyl sulfate) in (10ml absolute ethanol) [0.73g, 3mmole, CrCl<sub>3</sub>.6H<sub>2</sub>O], [0.53g, 3mmole, MnCl<sub>2</sub>.4H<sub>2</sub>O], [0.46g, 3mmole, CoCl<sub>2</sub>. 6H<sub>2</sub>O], [0.64g, 3mmole, NiCl<sub>2</sub>. 6H<sub>2</sub>O], [0.46g, 3mmole, CuCl<sub>2</sub>. 2H<sub>2</sub>O], [0.53g, 3mmole, ZnCl<sub>2</sub>. 2H<sub>2</sub>O], [0.51g, 3mmole, CdCl<sub>2</sub>. H<sub>2</sub>O], [0.73g, 3mmole, HgCl<sub>2</sub>] and [0.44g, 3mmole, VOSO<sub>4</sub>. H<sub>2</sub>O] respectively was added. The solution mixture was stirred for 3 hr and was left to evaporate slowly to bring down the complexes. The complexes were washed by hot ethanol. The physical properties for all synthesized ligand (L-AZD) and its complexes were shown in Table (1 and 2).

**Table 1: Some physical properties and analytical of (L-AZD) ligand**

Empirical formula	color	Dc	Yield %	Elemental Analysis % found (cal)		
				C	H	N
C <sub>12</sub> H <sub>14</sub> N <sub>18</sub> O <sub>9</sub> (L-AZD)	Pale yellow	152-153	84	29.08 (25.99)	2.24 (2.52)	44.07 (45.48)

**Table 2: Some physical properties and analytical for (L-AZD) complexes**

Empirical formula	Color	Mp°C Dc	Yield %	Metal% found(cal.)
[(VO) <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ]SO <sub>4</sub> .H <sub>2</sub> O	Dark Olive	126-128 Dc	75	14.95 (14.31)
[Cr <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>8</sub> ]Cl.2H <sub>2</sub> O.C <sub>2</sub> H <sub>5</sub> OH	Dark Olive	276-277Dc	81	14.46 (14.40)
[Mn <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>5</sub> Cl <sub>5</sub> ]Cl.4H <sub>2</sub> O.2C <sub>2</sub> H <sub>5</sub> OH	Pale Brown	292-293Dc	72	14.91 (14.70)
[Co <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>5</sub> Cl <sub>5</sub> ]Cl. H <sub>2</sub> O.2C <sub>2</sub> H <sub>5</sub> OH	Purple	284-285 Dc	57	16.39 (16.38)
[Ni <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>5</sub> Cl <sub>5</sub> ]Cl	Pale Green	234-235 Dc	73	19.64 (18.24)
[Cu <sub>3</sub> (L-AZD)(H <sub>2</sub> O) Cl <sub>5</sub> ]Cl. 4H <sub>2</sub> O	Olive	188°	67	19.84 (19.03)
[Zn <sub>3</sub> (L-AZD)Cl <sub>5</sub> ]Cl	White	215°	88	27.11 (21.81)

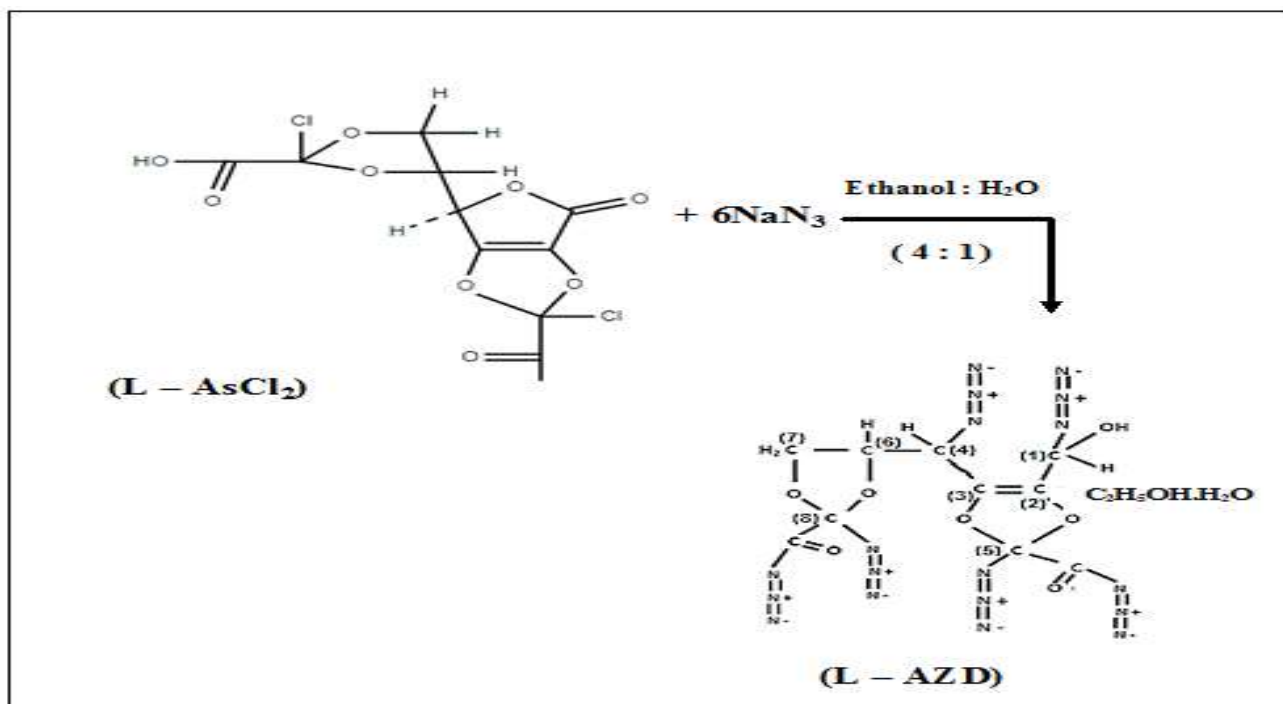
$[\text{Cd}_3(\text{L-AZD})(\text{H}_2\text{O})\text{Cl}_5]\text{Cl}$	White	225°	79	36.32 (31.79)
$[\text{Hg}_3(\text{LA-ZD})(\text{H}_2\text{O})\text{Cl}_5]\text{Cl}\cdot 2.5\text{H}_2\text{O}$	White	187°	68	34.00 (33.95)

Dc = Decomposition, mp = melting point

## Result and Discussion

In the present work of the ligand (L-AZD) was synthesized by reacting (1mole) of ligand

(L-AsCl<sub>2</sub>) [7], with (6mole) of sodium azide by using of mixture (4:1) (ethanol: distilled water) as solvent, Scheme (1).



Scheme 1:

### The Infrared Spectrum of (L-AZD)

Formation of the ligand (L-AZD), Figure (1), Table (3) was characterized by disappearance of bands at 3408cm<sup>-1</sup>, 3398cm<sup>-1</sup>, 1674cm<sup>-1</sup> and 827cm<sup>-1</sup> were due to hydroxyl group of  $\nu(\text{COOH})$ , and  $\nu(\text{C}=\text{O})$  stretching vibration of the non-ionized (COOH) and  $\nu(\text{C}-\text{Cl})$ , which were assigned in spectrum (L-AsCl<sub>2</sub>) [1-3]. A strong assignable to  $\nu(\text{OH}) + \nu(\text{H}_2\text{O})$  of

stretching vibration were appeared at 3390cm<sup>-1</sup>, and two bands were observed at 2129cm<sup>-1</sup>, 2048cm<sup>-1</sup> and (1240, 640) cm<sup>-1</sup> were due to the asymmetric, symmetric and deformation mode of azide group [1, 8-10]. The carbonyl azide group  $\nu(\text{CO}-\text{N}_3)$  appeared at 1640cm<sup>-1</sup>. (1,9-10) The (L-AZD) showed two bands at 1408cm<sup>-1</sup> and 1076cm<sup>-1</sup> which are attributed to  $\nu(\text{N}=\text{N})$  and  $\nu(\text{C}-\text{N})$  respectively [1, 10, 11].

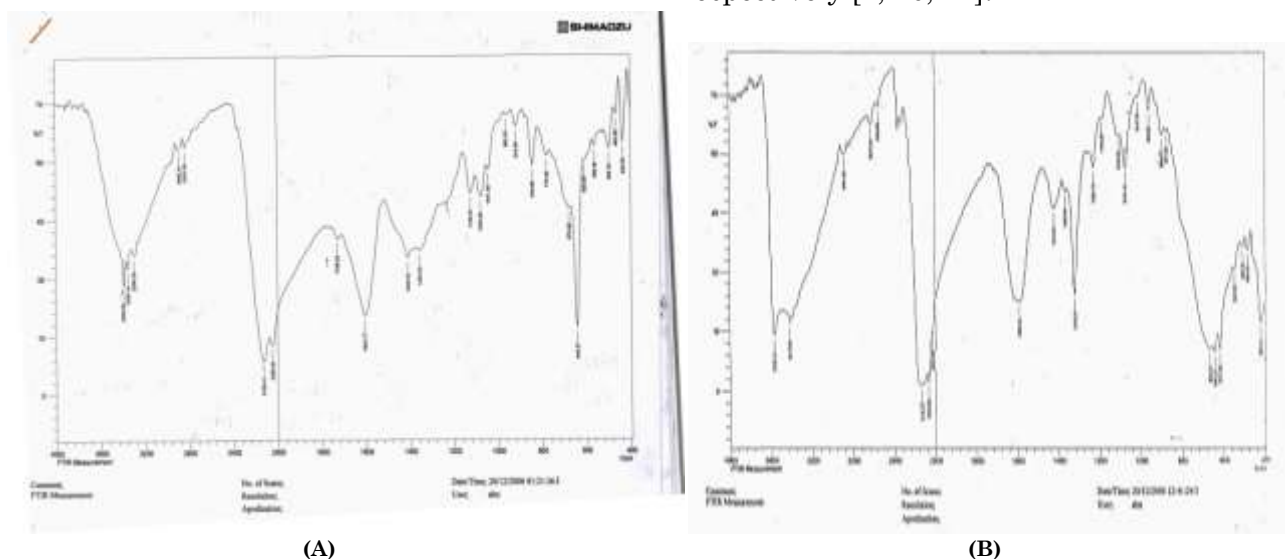


Figure 1: Ft - IR spectrum of: a - (L - AZD) ligand b - (L - AZD) - Mn (II) complex

**Table 3: Main characterization vibration frequency of (L-AsCl<sub>2</sub>) and (L-AZD) .**

Compound	(L-AZD) cm <sup>-1</sup>	(L-AsCl <sub>2</sub> ) cm <sup>-1</sup>
$\nu(\text{C-OH})$	3390 (S)	3481-3269 (br)
$\nu(\text{C-OOH})$	3298 (S)	3408 (w) , 3398 (w)
$\nu(\text{C-H})_{\text{aliph}}$	as 2885 (w) , s 2835 (w)	as 2991 (w) , s2937 (w)
$\nu(\text{C}=\text{O})$ Lactone	-----	1726 (m)
$\nu(\text{C}=\text{C})$ , $\nu(\text{C}=\text{O})$	1604 (Sh) , -----	1647 (Sh) , 1674 (Sh)
$\nu(\text{C-O})$ , $\delta(\text{C-O-H})$	1122 (m) , 1354 (w)	1122 (m) , 1330 (Sh)
$\nu(\text{C-Cl})$	-----	827 (Sh)
$\nu(\text{N}=\text{N}) + \nu(\text{C-N})$	1408 (m) + 1076 (m)	-----
$\nu(\text{N}_3)_{\text{as}}$	2129 (S) , 2048 (S)	-----
$\nu(\text{N}_3)_{\text{s}}$	1240 (w)	-----
$\nu(\text{N}_3)_{\text{def}}$	640 (Sh)	-----
$\nu(\text{CO-N}_3)$	1640 (Sh)	-----

Recorded as KBr disk, (Sh) = Sharp, (m) = medium, (w) = weak, (br) = board, As = asymmetric, s = symmetric, def = deformation.

**Table 4: Infrared spectra data for the ligand (L-AZD) and its metal complexes**

Empirical formula	$\nu(\text{N}_3)_{\text{as}}$ cm <sup>-1</sup>	$\nu(\text{N}_3)_{\text{s}}$ cm <sup>-1</sup>	$\nu(\text{N}_3)_{\text{def}}$ cm <sup>-1</sup>	$\nu(\text{CO-N}_3)$ cm <sup>-1</sup>	$\nu(\text{H}_2\text{O})_{\text{aquo}}$ , $\nu(\text{H}_2\text{O})_{\text{Hydrate}}$ cm <sup>-1</sup>	$\nu(\text{M-N})$ cm <sup>-1</sup>	$\nu(\text{M-O})$ cm <sup>-1</sup>
C <sub>12</sub> H <sub>14</sub> N <sub>8</sub> O <sub>9</sub> (L-AZD)	2129 (S) , 2048 (S)	1240 (w)	640 (Sh)	1640 (Sh)	----- ,3298(S)	-----	-----
[(VO) <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ]SO <sub>4</sub> .H <sub>2</sub> O	2110(m) ,2020 (w)	1200 (m)	621(Sh)	1640 (Sh)	810(m) ,3417(S)	450(S)	-----
[Cr <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>8</sub> ]Cl.2H <sub>2</sub> O.C <sub>2</sub> H <sub>5</sub> OH	2150(S),2040(w)	1288 (S)	640 (w)	1635(S) 1620(S)	810(w), 3471(w), 3441(S)	543(S)	451(S)
[Mn <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>5</sub> Cl <sub>5</sub> ]Cl.4H <sub>2</sub> O.2C <sub>2</sub> H <sub>5</sub> OH	2133(m),2063(S)	1226 (S)	663(m)	1630(Sh)	894(S), 3417(w)	505(w)	420(S)
[Co <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>5</sub> Cl <sub>5</sub> ]Cl.H <sub>2</sub> O.2C <sub>2</sub> H <sub>5</sub> OH	2121 (Sh)	1226 (S)	624(S)	1620(Sh)	837(w), 3398(br)	543(w)	447(S)
[Ni <sub>3</sub> (L-AZD)(H <sub>2</sub> O) <sub>5</sub> Cl <sub>5</sub> ]Cl	2155 (Sh) , 2102 (Sh)	1234 (S)	628(S)	1616(Sh)	898(w), -----	501(w)	455(S)
[Cu <sub>3</sub> (L-AZD)(H <sub>2</sub> O) Cl <sub>5</sub> ]Cl. 4H <sub>2</sub> O	2117 (Sh) , 2086 (Sh)	1265, 1300 (S)	686(S)	1640(S)	837(w), 3471(w) 3417(S)	540(S)	-----
[Zn <sub>3</sub> (L-AZD)Cl <sub>5</sub> ]Cl	2106 (Sh)	1242 (w)	624(w)	1640(S)	-----	501(w)	-----
[Cd <sub>3</sub> (L-AZD)(H <sub>2</sub> O) Cl <sub>5</sub> ]Cl	2125 (Sh), 2025 (Sh)	1284 (S)	644,624 (S)	1640(Sh)	763(m) -----	505(S)	-----
[Hg <sub>3</sub> (LA- ZD)(H <sub>2</sub> O)Cl <sub>5</sub> ]Cl.25H <sub>2</sub> O	2117 (Sh) , 2025 (Sh)	1257 (S)	640(S) , 680(S)	1640(Sh)	813(w), 3390(S) 3356(S)	597(m)	-----

(Sh) = Sharp, (S) = strong, (m) = medium, (w) = weak, (br) = board, as = asymmetric, s = symmetric, def = deformation.

$\nu_1(\text{SO}_4^{2-}) = 975\text{cm}^{-1}$  (sh),  $\nu_3(\text{SO}_4^{2-}) = 1111\text{cm}^{-1}$  (sh) (forbidentate coordinated),

$\nu_4(\text{SO}_4^{2-}) = 609\text{cm}^{-1}$  (w) (for free ionic),  $\nu(\text{VO}) = 1000\text{cm}^{-1}$ (sh)

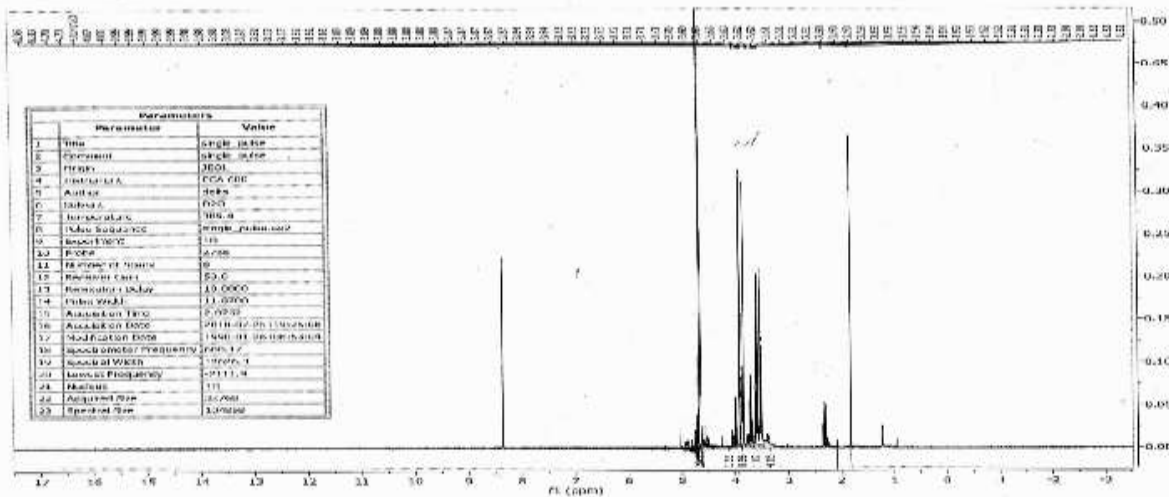
### **<sup>1</sup>H-NMR Spectrum of the Ligand (L-AZD)**

<sup>1</sup>H-NMR spectrum of (L-AZD) in D<sub>2</sub>O shows in Table (5), Figure (2).The <sup>1</sup>H-NMR spectrum appeared signals at (1.30, 3.57 and 4.78) ppm were due to protons in CH<sub>3</sub>, CH<sub>2</sub> and OH-ethanol. The signal at (1.8) ppm was due to water. The protons in CH (6) could be obtained at (3.96) ppm as signal,

also signals showed at (2.3, 4.3 and 3.87) ppm were due to CH (4), CH (1) and CH<sub>2</sub> (7). A singlet signal could appear at (4.7) ppm was due to proton OH of (L-AZD) ligand. Another singlate was appeared at (8.4) ppm assigned as hydrogen bond (N-OH). These results are compatible with the proposal molecular structure by using computer chem. Office, 3DX program [1, 12, 13].

**Table 5: <sup>1</sup>H-NMR signals positions ( $\delta$ ) (ppm) for the ligand (L-AZD) .**

Ligand	(L-AZD)					Ethanol			
	N-OH	CH <sub>2</sub> (7)	CH(6)	CH(4)	CH(1)	H <sub>2</sub> O	OH	CH <sub>2</sub>	CH <sub>3</sub>
Found	8.4	3.87	3.96	2.3	4.3	1.8	4.7	3.57	1.30
Chem. office	8.4	3.87	3.95	2.3	4.3	-	4.7	3.59	1.37

Figure 2:  $^1\text{H}$  - NMR of ligand (L-AZD)

### Mass Spectrum of the Ligand (L-AZD)

Mass spectrum of the ligand (L-AZD) showed abundant ion at (554 m / e) with relative intensity (0.49%) corresponding to parent ion, then loss of (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>) molecular (-58 m / e) to form (496 m / e). The fragmentation process was meta stable loss six of nitrogen atoms

and two protons of mass units to gave (410 m / e) followed by another loss of 42 mass corresponding to three nitrogen to give (368 m / e) and then loss of-(NH) with 15 mass unit to gave (353 m / e) of mass fragment. Mass spectrum of the ligand (L-AZD) is shown in Figure (3) and Table (6) [1, 13].

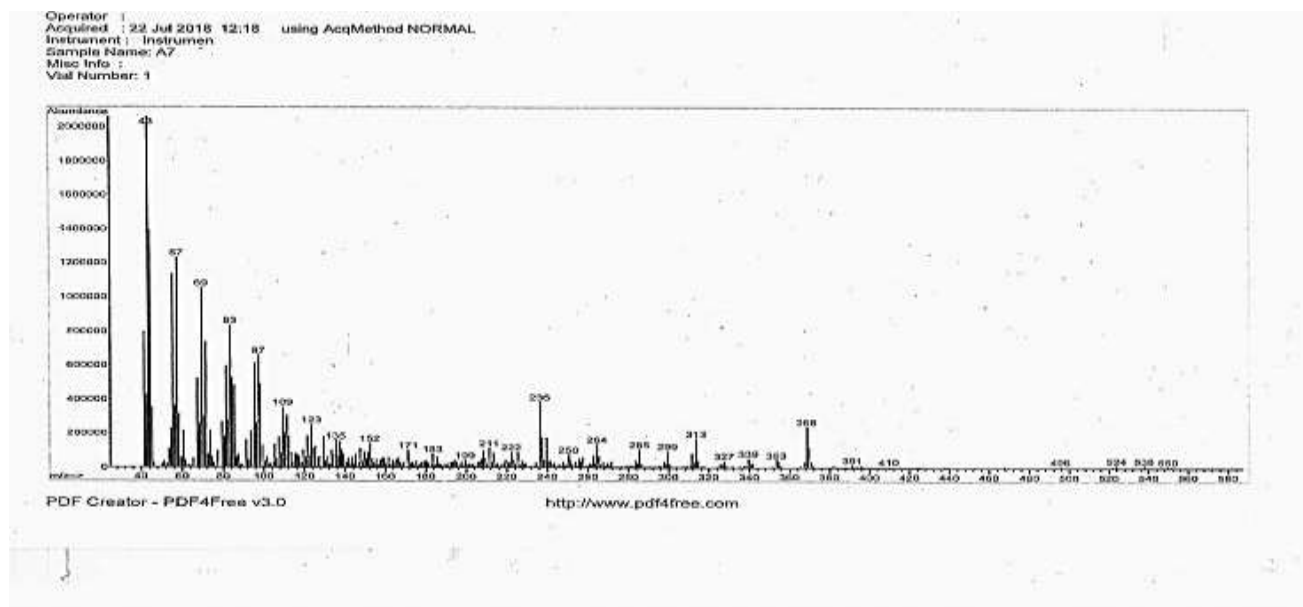


Figure 3: Mass spectrum of ligand (L-AZD)

Table 6: mass spectral of (L-AZD) ligand

Fragments	Formula weight g. mole <sup>-1</sup>	Relative abundance %
C <sub>12</sub> H <sub>14</sub> N <sub>18</sub> O <sub>9</sub>	554	0.49
C <sub>10</sub> H <sub>12</sub> N <sub>18</sub> O <sub>7</sub>	496	0.41
C <sub>10</sub> H <sub>10</sub> N <sub>12</sub> O <sub>7</sub>	410	0.20
C <sub>10</sub> H <sub>10</sub> N <sub>9</sub> O <sub>7</sub>	368	11.57
C <sub>10</sub> H <sub>9</sub> N <sub>8</sub> O <sub>7</sub>	353	2.47
C <sub>10</sub> H <sub>9</sub> N <sub>7</sub> O <sub>7</sub>	339	2.89
C <sub>9</sub> H <sub>9</sub> N <sub>7</sub> O <sub>7</sub>	327	1.65
C <sub>9</sub> H <sub>9</sub> N <sub>6</sub> O <sub>7</sub>	313	7.43
C <sub>9</sub> H <sub>9</sub> N <sub>5</sub> O <sub>7</sub>	299	4.13

C <sub>9</sub> H <sub>9</sub> N <sub>4</sub> O <sub>7</sub>	285	4.95
C <sub>9</sub> H <sub>8</sub> N <sub>4</sub> O <sub>4</sub>	236	18.59
C <sub>9</sub> H <sub>8</sub> N <sub>3</sub> O <sub>4</sub>	222	4.10
C <sub>8</sub> H <sub>1</sub> N <sub>3</sub> O <sub>2</sub>	171	4.95
C <sub>4</sub> HN <sub>2</sub> O <sub>2</sub>	109	16.52
C <sub>3</sub> HN <sub>2</sub> O <sub>2</sub>	97	32.23
C <sub>3</sub> HNO <sub>2</sub>	83	40.49
C <sub>3</sub> HO <sub>2</sub>	69	51.23
C <sub>2</sub> O <sub>2</sub> H	57	60.33

### Properties of Prepared Complexes

Reaction of the ligand (L-AZD) with metal chloride (M = Cr (III), Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and vanadyl sulfate. All the complexes were carried out in ethanol distilled water under stirring for 3 hr giving stable complexes, the analytical and physical data in Table (1, 2) and spectra data in Table (3, 4) and Figures (1a, 1b). All complexes were dissolving in water only.

### IR spectra data of the (L-AZD) and its Complexes

The ligand (L-AZD) which could be exhibits bands assignable to  $\nu(\text{C-OH})$  stretching vibration of free hydroxyl group, but this band was covered with hydrate water in all complexes spectra. The (L-AZD) ligand shows three bands at (2129), (2048)  $\text{cm}^{-1}$ , (1240)  $\text{cm}^{-1}$  and (640)  $\text{cm}^{-1}$  were due to the asymmetric, symmetric and deformation mode of azide group [1, 8-10]. In complexes, the asymmetric, symmetric and deformation band of N<sub>3</sub>-group are shifted in the range (4-48  $\text{cm}^{-1}$ ) corresponding to N<sub>3</sub>-coordination to metal ion through N<sub>3</sub>- [1, 14]. The ligand (L-AZD) showed a bands at (1076)  $\text{cm}^{-1}$  which could be attributed to stretching  $\nu(\text{C-N})$ , this band has been shifted in the range (4-8  $\text{cm}^{-1}$ ) through formation of complexes [1, 15]. The band at (1640)  $\text{cm}^{-1}$  is confirmed to presence

of carbonyl group in carbonyl azide of (L-AZD) ligand. This band has been shifted in the range (5-24  $\text{cm}^{-1}$ ) to and broad in Cr (III), Mn (II), Co (II) and Ni (II) complexes indicating to (C=O) coordination to metal ion, [1, 15] while in VO (II), Cu (II), Zn (II), Cd (II) and Hg(II) complexes, the  $\nu(\text{C=O})$  stretching vibration didn't change, due to uncoordinated (C=O) with VO (II), Cu (II), Zn (II), Cd (II) and Hg (II) [14]. The SO<sub>4</sub>-2 ion in the VO (II) complex could coordinated to VO in two variety of ways.

According to Ft-IR,  $\nu_1$  (SO<sub>4</sub>-2) near at 975  $\text{cm}^{-1}$  (bidentate),  $\nu_3$  (1111),  $\nu_4$  (609) were due to free SO<sub>4</sub>-2 ionic. The  $\nu$  (VO) stretching band is observed at 1000  $\text{cm}^{-1}$  [16-18]. The spectra also demonstrated a broad band at rang (3583-3390)  $\text{cm}^{-1}$  are due to hydrate water and the aqua was appeared at rang (763-898)  $\text{cm}^{-1}$  and multiple bands at the rang (420-597)  $\text{cm}^{-1}$  region can be assigned to  $\nu$  (M-O) and  $\nu$  (M-N) vibrations [1, 3, 8].

### Electronic spectra of (L-AZD)-complexes

The electronic spectral data of the free ligand (L-AZD) Figure (4a) and its complexes are summarized in Table (7). The peak at 228 nm, (43860)  $\text{cm}^{-1}$  in the electronic spectrum of (L-AZD) is corresponding to the intra ligand,  $\pi \rightarrow \pi^*$  [1, 19].

Table 7: Electronic spectra of ligand (L-AZD) and its metal complexes, measurements of nephelauxetic parameter  $\beta$

Ligand and its complexes	Band(cal) position nm	Band(cal) position $\text{cm}^{-1}$	Assignment	B- $\text{cm}^{-1}$	$\beta$
Ligand (L-AZD)	228	43860	$\pi \rightarrow \pi^*$	-----	-----
VO(II)	920	13889	${}^2B_{2g} \rightarrow {}^2E_{2g}$	-----	-----
Cr (III)	774 580.5 421.5	12912(12858) 17227(17227) 23725(30575)	${}^4A_{2g} \rightarrow {}^4T_{2g}(F)(\nu_1)$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_2)$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_3)$	615.25	0.59
Mn(II)	-----	-----	Forbidden	-----	-----
Co(II)	510+470/2 490	20408	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$  ${}^2G, {}^2H$	-----	-----

<b>Ni(II)</b>	725+655.5/2	(8006.3)	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(v_1)$	678.5	0.65
	690.25	14488	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v_2)$		
	393	25445	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(v_3)$		
<b>Cu(II)</b>	377.5	26490	${}^2B_{1g} \rightarrow {}^2A_{1g}$	-----	-----
<b>Zn(II)</b>	325	30769	C . T	-----	-----
<b>Cd(II)</b>	325	30769	C . T	-----	-----
<b>Hg(II)</b>	325	30769	C . T	-----	-----

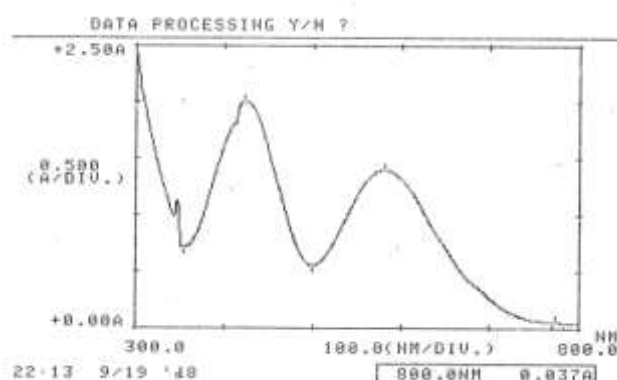
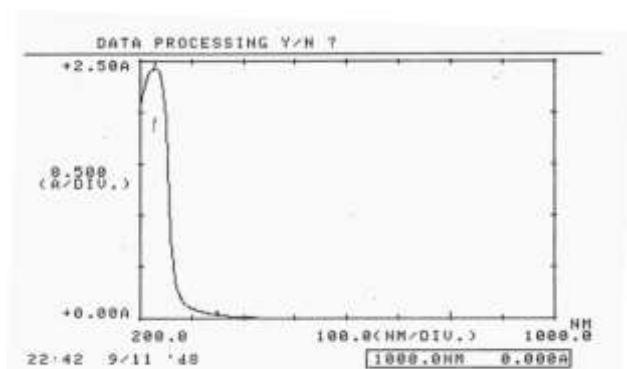


Figure 4: Electronic spectrum of: a - (L - AZD) ligand b - (L - AZD) - Cr (III) complex

### (L-AZD)-VO (II) complex

The electronic spectrum of olive green color for VO (II) complex, show the characteristic band at (920 nm, 13889  $\text{cm}^{-1}$ ), which assigned to the spin allowed  $2B_{2g} \rightarrow 2E_{2g}$  and that confirmed the square pyramidal environment [1, 20].

### (L-AZD)-Cr (III) complex

The electronic spectrum of dark olive color for Cr (III) complex Figure (4b) showed three characteristic bands at (774 nm, 12912  $\text{cm}^{-1}$ ), (580 nm, 17227  $\text{cm}^{-1}$ ) and (421.5 nm, 23725  $\text{cm}^{-1}$ ), these bands are attributed to  $4A_{2g} \rightarrow 4T_{2g}(F)(v_1)$ ,  $4A_{2g} \rightarrow 4T_{1g}(F)(v_2)$ , and  $4A_{2g} \rightarrow 4T_{1g}(P)(v_3)$ , transitions respectively of octahedral geometry, by using Tanabe-sugano for Cr (III) complex [1, 21]. The value of B and were calculated:  $B = 615,25 \text{ cm}^{-1}$ ,  $B = 0.597$  indicating some covalent characterization.

### (L-AZD)-Mn (II) complex

The electronic spectrum of pale brown color for Mn (II) complex, showed no absorption bands in the visible region. The transitions in octahedral-high spin ( $d^5$ ) complexes are spin forbidden [1].

### (L-AZD)-Co (II) complex

The electronic spectrum of purple color for Co (II) complex exhibited two bands appeared at (470 nm, 21277  $\text{cm}^{-1}$ ) and (510 nm, 20408  $\text{cm}^{-1}$ ) in the visible region center at (490 nm, 20433  $\text{cm}^{-1}$ ), this may be attributed to the  $4T_{1g} \rightarrow 4T_{1g}(P)$  transition in mixture with spin

forbidden to doublet states derived principally from the free ion  $2G$  and  $2H$  according with octahedral geometry [1, 22].

### (L-AZD)-Ni (II) complex

The electronic spectrum of pale green color for Ni (II) complex, exhibits three bands in the visible at (725.5 nm, 13784  $\text{cm}^{-1}$ ), (655.5 nm, 15256  $\text{cm}^{-1}$ ). The mean of them is (690 nm, 14488  $\text{cm}^{-1}$ ) is due to the transition  $3A_{2g} \rightarrow 3T_{1g}(F)(v_2)$ .

The other spin allowed transition is due to the  $3A_{1g} \rightarrow 3T_{1g}(P)(v_3)$  assigned at (393 nm, 25445  $\text{cm}^{-1}$ ). This is suggesting octahedral geometry [1, 21]. The ( $v_1$ ) and Racah parameter are calculated by Tanabe-Sugano diagram for nickel complex and found to be:  $B = 678,5 \text{ cm}^{-1}$ ,  $B = 0.65$  indicating some covalent characterization,  $v_1 = 8006.3 \text{ cm}^{-1}$ .

### (L-AZD)-Cu (II) complex

The electronic spectrum of the Cu complex shows band at (377, 5 nm, 26490  $\text{cm}^{-1}$ ) assigned to  $2B_{1g} \rightarrow 2A_{1g}$  transition suggesting square planar stereochemistry of the complex [23].

### (L-AZD) - Zn (II), Cd (II) and Hg (II) complexes

The U. v-Visible spectra for (L-AZD) complexes showed tail at (300 -350nm), center at (325nm, 30769  $\text{cm}^{-1}$ ) are due to the charge transfer (C.T). Therefore suggests the tetrahedral geometry for all complexes [1, 24].

## Solution Chemistry

### Molar Conductivity for the ligand (L-AZD) Complexes

The molar conductance of the complexes in

H<sub>2</sub>O as a solvent at 1 × 10<sup>-3</sup>M concentration (C), Table (8), lie in the rang (67.9-140.1) (s. cm<sup>2</sup>. mole<sup>-1</sup>) indicating its electrolytic nature for all complexes with ratio (1:1) [25].

**Table 8: Conductivity measurements of (L-AZD) complexes in water as solvent at 1 × 10<sup>-4</sup> concentration**

(L-AZD)Complexes	VO(II)	Cr(III)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)
$\Lambda_m$ (ohm <sup>-1</sup> . cm <sup>2</sup> . mol <sup>-1</sup> )	132	118.3	85.1	67.9	68.1	140.1	112.1	118.3	113.5

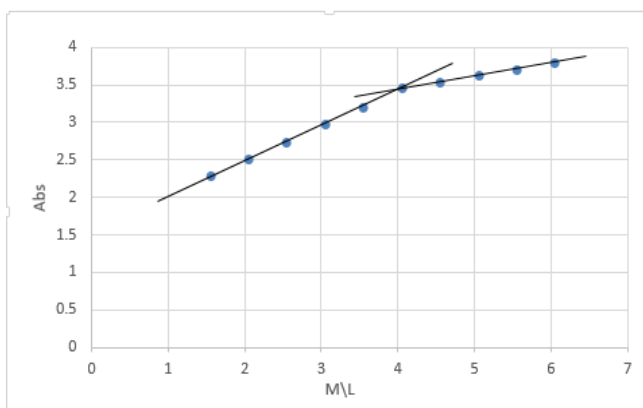
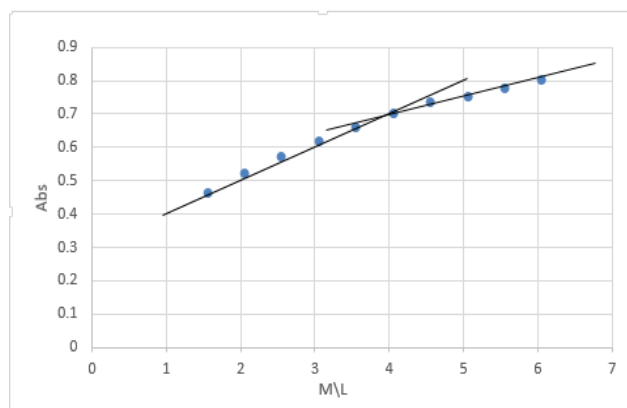
### Molar ratio for the (L-AZD) ligand complexes

The complexes of the ligand (L- AZD) with metal ions VO (II), Cr (III), Mn (II), Cu (II), Zn (II), Cd (II) and Hg (II) were studied in solution using water as solvent in order to determine (M:L) ratio in the prepared complexes, following molar ratio method (13). A series of solutions were prepared having a constant concentration (C) 10<sup>-3</sup>M of the hydrate metal chloride salt except VO (II)

with metal sulfate and the ligand (L-AZD), when wave length (max). The (M / L) ratio was determined from the relationship between the absorption of the observed light and molar ratio found to be (3 / 1)-(M / L). The results of complexes formation in solution are shown in Table (9) and Figures (5a, 5b); these data are compatible with the results obtained by atomic absorption for determination metal analysis in the complexes.

**Table 9: Molar ratio data for (L-AZD) – (VO) (II), Cr (III) , Mn (II), Cu (II), Zn (II), Cd (II) and Hg (II) metal complexes**

V (ml)	VO (Abs)	Cr (Abs)	Mn (Abs)	Cu (Abs)	Zn (Abs)	Cd (Abs)	Hg (Abs)
1.5	0.153	0.5	1.953	1.873	0.463	2.287	0.112
2	0.164	0.72	2.084	2.097	0.521	2.501	0.136
2.5	0.172	0.84	2.192	2.289	0.573	2.735	0.161
3	0.181	1.11	2.311	2.498	0.618	2.967	0.189
3.5	0.187	1.18	2.34	2.571	0.627	3.052	0.209
4	0.191	1.24	2.37	2.643	0.634	3.079	0.217
4.5	0.195	1.33	2.398	2.706	0.651	3.098	0.226
5	0.199	1.39	3.411	2.761	0.669	3.145	0.239
5.5	0.204	1.47	3.498	2.843	0.678	3.183	0.245
6	0.209	1.56	2.982	2.902	0.691	3.201	0.26



**Figure 5: Molar ratio curves of :- (L - AZD) – Zn (II) complex – (L - AZD) – Cd (II) complex**

### Magnetic studies

The magnetic moment valus at (298K) of the metal complexes of (L-AZD), M = [VO (II), Cr (III), Mn (II), Co (II), Ni (II) and Cu (II)]. Table (10), show in the range of (0.73-2.67)

BM respectively, which are lower than the total spin-only values indicating a high spin for all complexes. The lowering of these magnetic moments indicates a dominant of anti-ferromagnetic interaction. [1, 7, 26-27].

**Table 10: Data of magnetic moments and suggested structure for (L-AZD) – complexes**

(L-AZD) - complexes	$\mu_{\text{eff}}$ ( B . M )	Suggested structure
VO (II)	0.73	Square Pyramidal
Cr (III)	1.05	Octahedral
Mn (II)	1.24	Octahedral
Co (II)	2.67	Octahedral
Ni (II)	1.85	Octahedral
Cu (II)	1.12	Square Planar



## Conclusion

In this study, spectra data demonstrated that the prepared L- ascorbic derivative compound (L-AZD) behave as tridentate ligand binding to the tri nuclear cluster metal complexes of VO (II), Cr (III), Mn (II), Co (II) and Ni (II) through the nitrogen atoms of azido moiety and oxygen of VO (II) complex and oxygen atoms of carbonyl groups for other metal complexes except Cu (II), Zn (II), Cd (II) and Hg (II) complexes, the (L-AZD) ligand behave as bidentate ligand and binding to these tri nuclear metal ions through the nitrogen atoms of azide group only.

Moreover the analytical data of molar ratio method demonstrated that the ratio of (M / L) is (3 /1) in M = [VO (II), Cr (III), Mn (II), Cu (II), Zn (II), Cd (II) and Hg (II) complexes. There by, the suggested tri nuclear structure for all complexes will depend the result that obtained from FT-IR, UV-Visible spectra, atomic absorption, molar conductivity of complexes in water and magnetic moment at (298K). All complexes were electrolyte and have octahedral configuration except for VO (II) and Cu (II), Zn (II), Cd (II) and Hg (II) complexes which has square pyramidal for VO (II) and tetrahedral for Zn (II), Cd (II) and Hg (II), while is Cu complex gave square planar. All complexes showed anti ferromagnetic properties.

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