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Synthesis and Characterization of some Metal Complexes with (3Z ,5Z, 8Z)-2-azido-8-[azido(3Z,5Z)-2-azido-2,6-bis(azidocarbonyl)-8,9-dihydro-2H-1,7-dioxa-3,4,5-triazonine-9-yl]methyl]-9-[(1-azido-1-hydroxy)methyl]-2H-1,7-dioxa-3,4,5-triazonine – 2,6 – dicarbonylazide(L-AZ) .

Thuraya A .Taher
Waleed K . Mahdi
Falih H . Musa
Dept. of Chemistry / College of Education of Pure Science (Ibn Al-Haitham) / University of Baghdad

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Abstract

The reaction of LAs-Cl_8 : [(2,2- (1-(3,4-bis(carboxylicdichloromethoxy)-5-oxo-2,5-dihydrofuran-2-yl)ethane – 1,2-diyl)bis(2,2-dichloroacetic acid)]with sodium azide in ethanol with drops of distilled water has been investigated . The new product L-AZ :(3Z ,5Z,8Z)-2-azido-8-[azido(3Z,5Z)-2-azido-2,6-bis(azidocarbonyl)-8,9-dihydro-2H-1,7-dioxa-3,4,5-triazonine-9-yl]methyl]-9-[(1-azido-1-hydroxy)methyl]-2H-1,7-dioxa-3,4,5-triazonine – 2,6 – dicarbonylazide was isolated and characterized by elemental analysis (C.H.N) , ^{1}H-NMR , Mass spectrum and Fourier transform infrared spectrophotometer (FT-IR) . The reaction of the L-AZ withM^{+n}: [(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 and characterized by FT- IR , UV-Visible ,electrical conductivity, magnetic susceptibilities at 22 C^o . Atomic absorption and molar ratio Spectroscopic evidence showed that the binding of metal ions were through the azide(μ-1,1-N_3) Triazonine(3,5 –N_3) and carboxyl moieties , resulting in a six – coordinating metal ions (Cr(III),Mn(II),Co(II),Ni(II) and Cu(II)) .The VO(II) , Zn(II) ,Cd(II), andHg(II) were coordinated through azido (μ-1,1-N_3) , triazonine(3,5-N_3) only forming square pyramidal for VO(II) and tetrahedral geometry for Zn(II) , Cd(II) ,and Hg(II)$\beta,\acute{B}$ for Ni(II) , Cr(III) complexes were calculated too . The molar ratio and metal estimation showed , the ratio of L-AZ to metal ions was (10:1) ; (M/L) .

Keywords: Synthesis, characterization, cluster, azide

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Introduction

Organic azides are considered flexible energy – rich functional molecules [1] , which have been widely used in a number of areas such as material science , synthetic chemistry and biomedicine .Apart from its potential applications in the development of explosive and superconducting materials [2] or as an intermediate in organic synthesis . The complexes with azide is interesting for the development of new molecule based magnetic through bridges to form compounds with varying topologies and in addition to promote the magnetic exchange interaction between the meta of azide centers .Cobalt(II) complex of azide anion with bis (pyrazol-1-yl) methane [3] and cobalt(II) complexes of azideanion with 1,10-phenanthroline and bis (2-pyridyl) amine have been reported [4] . Tetra nuclearCo(III) complexes [5] , tetra nuclear and octanuclear copper(II) complexes of 2,6-bis [(2-hydroxy-ethylimino)- methyl]-4-methyl phenol have been reported [6] . Continuing our interest is the synthesis of compounds derived from L-ascorbic acid [7-10].We report the synthesis and characterizing of new compound (L-AZ) (3Z ,5Z, 8Z)-2-azido-8-[azido(3Z,5Z)-2-azido-2,6-bis(azidocarbonyl)-8,9-dihydro-2H-1,7-dioxa-3,4,5-triazonine-9-yl]methyl]-9-[(1-azido-1-hydroxy)methyl]-2H-1,7-dioxa-3,4,5-triazonine – 2,6 – dicarbonylazide, contains many groups of terminal azides , acetylazide,andtriazonine complexes with VO(II), Cr(III) ,Mn(II), Co(II) ,Ni(II), Cu(II), Zn(II) , Cd(II) , and Hg(II) .

Experimental

Materials ,Instrumentation :All chemicals are purchased from BDH, and used without further purification.

1. Infra-red spectra between (400-4000cm^{-1}),Shimadzu (FT-IR)-8400 spectrophotometer at service laboratory in Chemistry Department , College of Education of Pure Science ,Ibn Al-Hathiam .

2.The electronic spectra were recorded on the UV-Visible spectrophotometer typeShimadzu UV-160A in the wave length range of(200-1000) nm, with match quartz cells (1cm) using water as a solvent at service laboratory in Chemistry Department , College of Education of Pure Science ,Ibn Al-Hathiam .

3. The melting point was recorded on "Gallen Kamp Melting point Apparatus model SMP30 atCollege of Education of Pure Science ,Ibn Al-Hathiam .

4. The conductance measurements were recorded on W.T.W. conductivity meter at Chemistry Department , College of Education of Pure Science ,Ibn Al-Hathiam .

5. The characterize of new ligand L-AZ is achieved by ;

A:Elemental analysis for carbon , hydrogen and nitrogen was using a Euro Vector EA 3000 A Elemental Analysis (Italy) ,at Al- Mustansiriya University .

B:^{1}H-NMR spectrum was recorded by using Bruner DRX (500-MHz) Spectrophotometer ,chemical shift of ^{1}H-NMR spectrum was recorded inδ (ppm) unit down field from internal reference tetramethylsilaine (TMS) , using DMSO – d^6 solvent .at Sharif Sainte , University of Tehran , Iran .

C: G C M S spectrum was performed agilent mass spectrometer 5975 quadrupole analyzer, at University of Tehran , Iran.

D : Thin layer chromatography (TLC) : for the ligand L-AZ : (TLC) was preformed on aluminum plates coated with (0.25mm) layer of silica gel F254 (Fluka) and were detected by iodine .

6. Atomic absorption spectrophotometer were measured by using flame atomic absorption technique type Analytic Jena (A.A350) ,in the laboratories of IbnSina Company .

7.Magnetic susceptibility values were obtained at room temperature ,by using the Faradays method , Johnson Mattey catalytic system ,at Al- Mustansiriya University .

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Synthesis

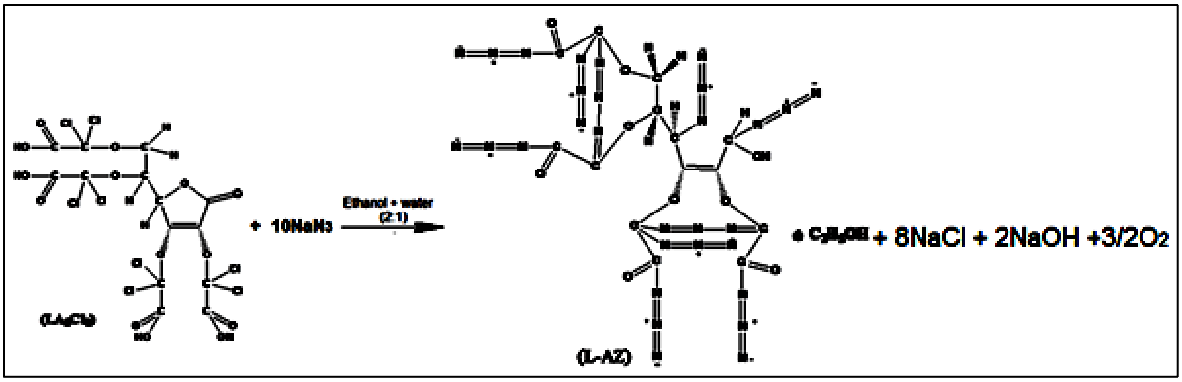
1-Synthesis of (L–AZ): (3Z ,5Z, 8Z)-2-azido-8-[azido(3Z,5Z)-2-azido-2,6-bis(azidocarbonyl)-8,9-dihydro-2H-1,7-dioxa-3,4,5-triazonine-9-yl]methyl]-9-[(1-azido-1-hydroxy)methyl]-2H-1,7-dioxa-3,4,5-triazonine – 2,6 – dicarbonylazide**.**

To a solution of (0.7g , 1mmole) of (L-AsCl$_8$) in (15mL ethanol +5mL distilled water) are added a solution of (0.7g , 10mmole) of sodium azide in (20mL ethanol) ,dropwise . The mixture was refluxed for 3h . The resulting product was brown solution , which was left to stand at room temperature for few days , giving a brown solid and recrystallized from absolute ethanol yielding (0.324g , 0.41mmole,62%) : mp 215-216^{o}C , Rf : 0.32.

2-Synthesis of (L-AZ) –complexes [M =VO(II) , Cr(III) , Mn(II) , Co(II) , Ni(II) , Cu(II) , Zn(II) , Cd(II) , and Hg(II) : All complexes are prepared at follows : To a solution of (1mmole) of (L-AZ) in a mixture of (15mL ethanol + 5mL distilled water) .A solution of [10mmole of metal chloride and vanadyl sulfate] in (10 mL absolute ethanol) .[3g , 10 mmole , $CrCl_3.6H_2O$] , [2g,10 mmole , $MnCl_2$.$4H_2O$] , [2.5g ,10 mmole $CoCl_2$. $6H_2O$] , [1.8g , 10 mmole, $NiCl_2$. $6H_2O$] , [1.8g , 10 mmole , $CuCl_2$. $2H_2O$] , [1.8g , 10 mmole , $ZnCl_2.2H_2O$] , [1.8g , 10mmole , $CdCl_2$] ,[3g ,10 mmole ,$HgCl_2.2H_2O$] and [1.7g , 10 mmole , $VOSO_4$. H_2O] respectively are added . The solution mixture is stirred for one hour and is left to evaporate slowly to bring down the complexes . The complexes are washed by mixture of (ethanol + distilled water) in the ratio (2:1) (Vol /Vol) . The physical properties for all synthesized ligand L-AZ and its complexes are shown in table (1) .

Results and Discussion

In the present work of the ligand (L-AZ) was synthesized by reacting (1mole) of ligand (L-AsCl$_8$).[11] with (10mole) of sodium azide by using of a mixture (2:1) (ethanol : water).as solvent , scheme (1) .



Scheme (1)

The infrared spectrum of (L-AZ) formation of the ligand L-AZ , figure (1) ,table(2) was characterized by disappearance of bands at (3425) cm^{-1}due to hydroxyl group ν(COOH) , the band at (1670) cm^{-1} due to ν(C=0) stretching vibration of the non-ionized (COOH) [12] , the band at (1761) cm^{-1}was assigned to ν(C=0) lactone and finely , band at (829) cm^{-1}which was assigned to ν(C-Cl) in spectrum (LA_SCl_8).Instead a strong band assignable to ν(OH) stretching vibration of free hydroxyl group ν(C-OH) was appeared at (3383) cm^{-1}, and two bands were observed at (2110), (2042) cm^{-1} and (1228), (638) cm^{-1}are due to the asymmetric, symmetric and deformation mode of azide group [13] . The carbonyl ν(CO-N_3) group appeared at (1620)cm^{-1}[14] .The (L-AZ) showed bands at (1649) cm^{-1} (1433) cm^{-1} and (1033)cm^{-1} are attributed to triazonine group (C=N),(N=N) and (C-N) respectively[15].

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^{1}H-NMR spectrum of the ligand (L-AZ) :^{1}H-NMR spectrum of the in d_6-DMSO shows in table (4) , figure (3) . The ^{1}H- NMR spectrum of (L-AZ) appears signals atδ (1.10 , 3.57 , 4.78) ppm are due to protons in CH_3 , CH_2 , OH – ethanol . The signal at δ (2.5) ppm is due to water . The protons in N_3-CH can be obtained at (3.9) ppm as signal , also signals can be shown at δ (2.3 , 3.6 , 3.40) ppm are due to (CH-CH-CH_2) also a singlet can be appeared at δ (2.0) ppm is due to proton CH in (CH- OH) .Two signals are appeared at δ (8.2 , 8.4) ppm , assigned as hydrogen bond (NH , OH) . These results are compatible with the proposal molecular structure by using computer Chem .Office 2010 , 3DX program . [16] .

Mass spectrum of the ligand (L-AZ),showed abundant ion at (552 m/e) , with relative intensity 1.85 % , corresponding to loss of molecule ; (twelve) of nitrogen , hydroxyl , hydrogen (186 m/e) from the parent molecular ion , (738 m/e) . The fragmentation process was metastable loss of 14 mass units corresponding to loss of the nitrogen gave(538 m/e) followed by another loss of 14 mass corresponding to the nitrogen too obtained at (524 m/e)mass spectrum and the**.** fragmentation of the ligand (L-AZ) is shown in figure (4) and table (5) ,[10] .

The prepared complexes : Reaction of the ligand (L-AZ) with metal chloride(M= Cr(III) ,Mn(II) , Co(II) , Ni(II) ,Cu(II) , Cd(II) , Hg(II) and vanadyl sulfate . All the complexes were carried out in ethanol - distilled water under stirring for 3hours giving stable complexes , the analytical and physical data in table (1) and spectra data in table (3) . All complexes are dissolving in water ,DMSO , and DMF solvents.

IR Spectra data of the complexes.Table (3) ,usually provide a lot of valuable information on coordination mechanism .The ligand (L-AZ) which exhibits bands assignable to $\nu(\mathrm{C-OH})$ stretching vibration of free hydroxyl group . This band is almost appeared at the same position or cover with hydrate water in all complexes spectra . The ligand shows three bands at (2110) , (2042) cm^{-1}, (1228) $cm^{-1}$and (638) $cm^{-1}$are due to the asymmetric , symmetric and deformation mode of azide group [13] . In complexes , the asymmetric ,symmetric and deformation bond of N_3^-group are shifted corresponding to N_3^- coordination to metal ion through (μ-1,1-N_3) [17] .The ligand (L-AZ) shows band at (1649),(1433)$cm^{-1}$and (1033)cm^{-1}can be attributed to stretching (C=N) ,(N=N) bond and to aliphatic (C-N).These bands are characteristic of triazonine group [15].These bands are shifted upon coordination with metal ion through triazonine(3,,5-N_3) [18] .The band at (1620) $cm^{-1}$is confirmed to presence of carbonyl group in carbonyl azide in the ligand (L-AZ) . This band is shifted and broad in Cr(III) ,Mn(II) , Co(II) figure (2) , Ni(II) , and Cu(II) complexes indicating to (C=O) coordination to metal ion [19] , while inVO(II), Zn(II) , Cd(II) , and Hg(II) complexes , the (CO) stretching vibration didn't change ,due to uncoordinated (CO) withVO(II) , Zn(II) , Cd(II) and Hg(II) complexes[17]. In the IR spectra of complexes , the broad band appeared at range (3300 – 3577) $cm^{-1}$are due to hydrate water and the aqua is appeared at range (808-860) cm^{-1}. The weak bands appeared at (453-524) cm^{-1}region can be assigned to $\upsilon(\mathrm{M-N})$ vibration [20] .

Electronic SpectraStudies: The electronic spectral data of free ligand figure (5) and its complexes , are summarized in table (6) .The peak at 258nm (38760 cm^{-1}) in the electronic spectrum of free ligand (L-AZ) , is corresponding to the intralligand $\Pi \longrightarrow \Pi^*$.[21]

(L-AZ) – VO(II) Complex: The electronic spectrum of (VO)(II) complex , exhibits broad band at 906nm , (11038) cm^{-1}, which assigned to the spin allowed $^2B_2g \longrightarrow {}^2Eg$ and that confirmed the square pyramidal environment [22].

(L-AZ) – Cr(III) Complex: The Cr- Complex , showed three weak bands at 856,592, and428 nm , (11682,16892, and 23364) cm^{-1},these bands are attributed to $^4A_2g \longrightarrow {}^4T_2g(F)$ (υ_1) , $^4A_2g \longrightarrow {}^4T_1g(F)$ (υ_2) , and $^4A_2g \longrightarrow {}^4T_1g(P)$ (υ_3) , transitions respectively of octahedral geometry.By using Tanabe – Sugano for Cr (III) ,[23] .The value of $\beta,\acute{B}$were calculated $\frac{\upsilon2}{\upsilon1}$ = 1.44 ,∴ $\frac{E}{B}$ = 30 , $\acute{B}= \frac{16893}{30}$ = 563.07, β =$\frac{\acute{B}}{B} = \frac{563.07}{1030}$ = 0.547

(indicating some covalent bond character) .

(L-AZ) – Mn(II) Complex :The electronic spectrum of Mn(II) complex, showed no absorption bands in the visible region . The transition in octahedral – high spin (d^5) complexes are spin forbidden , and also the pale (pale brown) is due to forbidden transitions occur such as :

${}^6A_1g \longrightarrow {}^4Eg(G){}^4A_1g$ (G) , ${}^6A_1g \longrightarrow {}^4Eg(D)$ ${}^6A_1g$, ${}^6A_1g \longrightarrow {}^4T_1g(G)$, ${}^4T_2g(G)$.Thus doubly forbidden transitions are extremely weak [23] .

(L-AZ) – Co (II) Complex : The Co – Complex , figure (6) exhibited two bands appeared at 482nm (20747)cm^{-1}, and 508nm (19685) cm^{-1} in the visible region center at 495nm (20216) cm^{-1}, this may be attributed to the ${}^4T_1g \longrightarrow {}^4T_1g(P)$ transition in a mixture with spin forbidden to doubled states derived principally from the free ion ${}^2G$ and ${}^2H$ according with octahedral geometry [24] .

(L-AZ) – Ni (II) Complex : The electronic spectrum of Ni(II) complex ,exhibits multiple bands at 718nm , 660nm (13928 , 15152) cm^{-1} .The mean of them is (14540) cm^{-1},is due transition to ,${}^3A_2g \longrightarrow {}^3T_1g$ (F) (υ_2) .The other spin allowed transition is due to the ${}^3A_2g \longrightarrow {}^3T_1g(p)$ (, υ_3) assigned at 398nm , (25126) cm^{-1}. This is suggesting octahedral geometry[23] . The ($_1$) ,and Racha parameter are calculated by Tanaba – Sugano diagram for Ni(II) .

$$\frac{\upsilon_3}{\upsilon_2} = \frac{25126}{14540} = 1.73 ,E/\acute{B} = 20 = \frac{14540}{B} , \acute{B} = \frac{14540}{20} = 727\ cm^{-1},\beta = \frac{\acute{B}}{B_{Ni}} = \frac{727}{1030} = 0.71 ,$$

$$\frac{\Delta_\circ}{\acute{B}} = 11.5 ,\frac{\Delta_\circ}{727} = 11.5 , \qquad \Delta_\circ = 727 \times 11.5 = 8360.5\ cm^{-1} = \upsilon_1$$

(L-AZ) – Cu(II) Complex: The electronic spectrum of Cu(II) complex, showed a broad band at 814nm (12285) cm^{-1} which can be tentatively assigned to the transition ${}^2Eg \longrightarrow {}^2T_2g$, characteristic of octahedral [25] .

(L-AZ) - Zn(II) , Cd(II) , and Hg(II) Complexes : The U.v – Visible spectra of the free ligand (L-AZ) and Zn(II) , Cd(II) , and Hg(II) complexes in water . The band appeared at 258nm with absorption 0.48 in the U.V -Visible spectrum of L-AZ attributed to $\Pi \longrightarrow \Pi^*$, transition. This band and absorption is observed in [Zn(II) ,Cd(II) , and Hg(II)] complexes at (254nm , 0.102) , (258nm , 0.215) , (262nm , 0.026) . All complexes showed tail started (400-450nm) . From data above , table (4) , conforms the tetrahedral geometry of the complexes [26].

Solution chemistry

Molar conductivity for the complexes of ligand (L-AZ): The molar conductance of the complexes in DMSO as a solvent at 1×10^{-4}M concentration (C) , table (7) , lie in the (32.25 - 2.89) ($S.cm^2.mol^{-1}$) range indicating their non electrolytic nature except ionic nature for the complex VO(II) , gave 56 ($S.cm^2.mol^{-1}$) , indicating its electrolytic nature [27].

Molar ratio for the Ligand (L-AZ) and complexes : Molar ratio is a common way and simplicity to identify the complexity ratio between the metal ion and the ligand in complex. It's a measure absorbance of a series from the solutions containing a fixed amount of one component ligand at ($1x10^{-3}$ M) concentration with a variable amount of other component metal ion salts when wave length constant (£max),which the complex gave the highest

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absorbency with disappearance of any absorption of both ligand and metal ion in that region which is at the complex absorbance the complexes of the ligand(L-AZ) with metal ions M^{+2} [Co(II), Cu(II) figure (7), Cd(II) and Hg(II)] are studied in solution by using water as a solvent .In ordor to determine(ML) ratio in the prepared complexes ,it was determined from the relationship between the absorption of the observed light and mole ratio(M/L) found to be (10/1)the results of complexes formation in solution are shown in table(8).These data are compatible with the results obtained by atomic absorption for determination of metal analysis in the complexes.

Magnetic moment measurements

The magnetic moment values at (295 K) of the Cr(III) , Mn(II) , Ni(II) and Cu(II) complexes , show in the range of (14-4.68)BM . Table (9),which are higher than the total spin-only , values indicating a high spin octahedral for Cr(III) , Mn(II) , Ni(II) and Cu(II) geometry . The higher of these magnetic moments indicates a dominant ferromagnetic interaction , in all four complexes with antiferromagnetic coupling between them . [28] The magnetic value of Co(II) and VO(II) complexes , showed values at (2.26 and 1.61) BM , which are lower than the total spin - only , value , indicating a high spin octahedral and square pyramidal around Co(II) and VO(II) complex . The lowering of this value indicates a dominant antiferromagnetic interaction through the nitrogen atoms of azido . The VO(II) complex , shows value at (1.61) BM near the spin only value . It indicates that the bridge groups may play a role in the enhancement of overlap between VO(II) and the antiferromagnetic interaction . The syn – syn conformation mediates the antiferromagnetic exchange pathway between the metal centers resulted in a low - dimensional feature , while the syn – anti favors the ferromagnetic exchange interaction . [28].

Conclusion

Spectroscopic evidence showed that the ligand (L-AZ) binding with the metal ions through the azide (μ-1,1-N_3) ,triazonine(3,5- N_3) and carboxyl moieties , resulting in a six – coordinating metal ions (Cr(III),Mn(II),Co(II),Ni(II) and Cu(II)) . The VO(II)Zn(II),Cd(II), and Hg(II) are coordinating through azido (μ-1,1-N_3) , triazonine(3,5-N_3) only forming, square pyramidal ,for VO(II) and tetrahedral geometry for Zn(II),Cd(II), and Hg(II) complexes .β, $\acute{B}$ for Ni(II) , Cr(III) complexes are calculated too.The molar ratio studies of ligand/ metal estimation gave (1:10) . (M/L) .Magnetic moment values at (295 K) of the Cr(III) , Mn(II) , Ni(II) and Cu(II) complexes ,are higher than the total spin-only, indicating dominant ferromagnetic interaction , in all four complexes with antiferromagnetic coupling between them .The magnetic value of Co(II) and VO(II) complexes , showed values are lower than the total spin - only, indicating dominant antiferromagnetic interaction .

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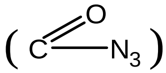
Table (1): Some physical properties and analytical data for the L-AZ and its metal complexes

Empirical formula	Color	C°m.p D°	Yield %	Element Analysis Found (cal.) %			Found (cal.) Metal %
				C	H	N	
$C_{14}H_6O_9N_{30}.C_2H_5OH$	Pale yellow	215-216 °C	62	26.66 (25.82)	0.96 (1.77)	54.7 (53.16)	——
$[VO_{10}LAZ(H_2O)_{20}](SO_4)_{10}.20H_2O.50C_2H_5OH$	Olive	274°D	64	------	------	--------	9.44 (9 .720)
$[Cr_{10}L\text{-}AZCL_{30}(H_2O)_7]\ 6H_2O.C_2H_5OH$	Dark green	228 °D	54	------	------	--------	19.971 (19.98)
$[Mn_{10}L\text{-}AZCl_{20}(H_2O)_4]\ 2H_2O.C_2H_5OH$	Pale brown	255°D	52	------	------	--------	25.651 (25.56)
$[Co_{10}L\text{-}AZCl_{20}(H_2O)_4]\ 26H_2O.C_2H_5OH$	Purple	108°D	61	------	-----	------	22.378 (22.48)
$[Ni_{10}L\text{-}AZCl_{20}(H_2O)_4]\ 11H_2O$	Green	260°D	56	------	------	--------	25.643 (25.46)
$[Cu_{10}L\text{-}AZ\ Cl_{20}(H_2O)_4]$	Green	115°D	96	------	------	--------	30.62 (29.62)
$[Zn_{10}L\text{-}AZCl_{20}]\ 35H_2O.C_2H_5OH$	White	224°D	67	————	————	-------	23.308 (23.41)
$[Cd_{10}L\text{-}AZCl_{20}]\ 30H_2O.C_2H_5OH$	White	239 °C	72	---	------	--------	35.585 (35.59)
$[Hg_{10}L\text{-}AZCl_{20}]\ nH_2O.mC_2H_5OH$	White	136 °C	-----	------	_----- ____	--------	---------

°D = Decomposition mp= melting point

Table (2): Main characteristic vibration frequencies of (L-As) ,(L-As-Cl$_8$) and (L-AZ) ligands

Compound	**(L-As)**	**(L-As-Cl$_8$)**	**(L-AZ)**
υ(O-H)	**3525(s), 3410(s)**	**3425(s)**	**(3383)(br)**
υ(COOH)	**3313(s), 3213(s)**	**OH (COOH)**	**C – OH**
υ(C-H) alph	**as2943 (w) s 2916 (w)**	**as 2980 (w) s 2883 (w)**	**as 2900 (w) s 2880 (w)**
υ(C=O) Lactone	**1751 (m)**	**1761 (sh)**	**-**
υ(C=C) υ(C=O)	**1647 (sh) 1678 (sh)**	**1654 (sh) 1670 (sh)**	**1599 (sh) -**
υ(C-O) S(C-O-H)	**-**	**1147 (s) 1344 (sh)**	**1120(s) 1334 (sh)**
υ(C-Cl)	**-**	**829 (sh)**	**-**
υ(C=N) υ(N=N) + υ(C-N)	**-**	**-**	**1649 (w) 1433 (w) + 1033 (s)**
υ $(N_3)_{as}$	**-**	**-**	**2110 (s) 2042 (sh)**
υ $(N_3^-)_s$	**-**	**-**	**1228 (w)**
$\delta(N_3^-)_{def}$	**-**	**-**	**638 (sh)**
	**-**	**-**	**1620 (sh)**

Recorded as KBrdisk(sh)=sharp,(s)=strong,(m)=medium,(w),weak, as=asymmetric,s=symmetric, def=deformation, alph=alphatic

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Table (3) :Infrared spectral data for the ligand (L-AZ) and its metal complexes

Empirical formula	υC-OH	υ(C-H) Aliphatic	$\upsilon(N_3)_{as}$	$\upsilon(N_3)_s$	$\delta(N_3)$ def	υ(CO - N_3)	υ(N=N) + υ(C -N)	$\upsilon(SO_4)^{-2}$	8H_2O aqua	H_2O υ Hydrate	υ(M-N)	υ(v=o)
Ligand (L – AZ) $C_{14}H_6O_9N_{30}.C_2H_5OH$	3383 (br)	as 2900 (w) 2880s (w)	2110 (s) 2042 (sh)	1228 (w)	638 (sh)	1620 (sh)	1433 (w) + 1033 (s)	-	-	-	-	-
$[(VO)_{10}(L\text{-}AZ)(H_2O)_{20}].(SO_4)_{10}.20H_2O.5OC_2H_5OH$	3390 (br)	as 2920 (w) s 2890 (w)	2125 (s) 2059 (s)	-	619 (s)	1620 (sh)	1417 (m) + (-)	1109 (sh) (1100-1200)	827(s)	3300 (br)	514(s)	948 (sh)
$[Cr_{10}(L\text{-}AZ)Cl_{30}(H_2O)_7].6H_2O.C_2H_5OH$	3566 (br)	as 2927 (w) s 2856 (w)	2158 (s) 2100 (s)	1280 (w)	636 (sh)	1625 (br)	1433 (w) + 1035 (w)	-	808 (s)	3348 (br)	516 (sh)	-
$[Mn_{10}(L\text{-}AZ)Cl_{20}(H_2O)_4].2H_2O.C_2H_5OH$	3440 (br)	as 2929 (w) s 2858 (w)	2167 (s) 2080 (w)	1226 (m)	669 (s)	1627 (m)	1460 (w) + 1053 (m)	-	812 (s)	3346 (br)	503 (s)	-
$[Co_{10}(L\text{-}AZ)Cl_{20}(H_2O)_4].26H_2O.C_2H_5OH$	3552 (br)	as 2908 (w) S 2866 (w)	2129 (br)	1226 (s)	621 (m)	1627 (m)	1446 (w) + 1080 (m)	-	837 (w)	3448 (br)	524 (s)	-
$[Ni_{10}(L\text{-}AZ)Cl_{20}(H_2O)_4].11H_2O$	3566 (br)	as 2940 (w) s 2880 (w)	2117	1236 (s)	692 (m)	1624 (br)	1440 (w) + 1033 (w)	-	860 (w)	3387-3440 (br)	453(m)	-
$[Cu_{10}(L\text{-}AZ)Cl_{20}(H_2O)_4]$	3448 (br)	as 2897 (w) s 2873 (w)	2080 – 2063 (s)	1346 (w)	632 (w)	1631 (br)	1454 (w) + 1072 (w)	-		3340 (br)	474 (m)	-
$[Zn_{10}(L\text{-}AZ)Cl_{20}].35H_2O.C_2H_5OH$	3440 (br)	as 2960 (w) s 2890 (w)	2160 (sh) 2102 (w)	1319 (m)	632 (w)	1620 (br)	1435 (w) + 1053 (m)	-	-	3525 (br)	493(s)	-
$[Cd_{10}(L\text{-}AZ)Cl_{20}(H_2O)_4].30H_2O.CH_5OH$	3456 (br)	as 2920 (w) s 2840 (w)	2090 (s) 2040 (w)	1325 (s)	628(m)	1620 (w)	1421 (m) + 1072 (m)	-	-	3566 – 3577 (br)	495(w)	-
$[Hg_{10}(L\text{-}AZ)Cl_{20}(H_2O)_4].nH_2O.mC_2H_5OH$	3437 (br)	as 2947 (w) s 2889 (w)	2113 (w) 2056 (sh)	1323 (s)	636 (s)	1620 (br)	1460 (w) + 1080 (s)	-	-	3540 (br)	489 (m)	-

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Table (4): ^{1}H-NMR signals position (δ)(ppm) for the ligand L-AZ

Ligand	CH_2-8	CH-9	CH-8N_3	CH-9-N_3	CH-9-OH	NH	OH	H2O	ETOH		
									OH	CH_2	CH_3
L-AZFound	3.6	3.40	2.3	3.9	2	8.2	8.4	2.5	4.78	3.57	1.10
L-AZChem.Office	3,54	3.0	2.5	3.9	2	—	—	—	4.78	3.57	1.10

Table (5): Mass spectral data of ligand L-AZ

Fragments	$C_{14}H_5N_{18}O_8$	$C_{14}H_4N_{17}O_8$	$C_{14}H_4N_{16}O_8$	$C_{10}H_4N_{13}O_4$.H	$C_{10}H_4N_9O_4$.H	$C_7H_4N_6O_4$	$C_3H_4N_3O_2$	$C_3H_3N_3O$	C_2H_3O
Formula weight g.mol	552	538	524	370	315	236	114	97	43
Relative abundance%	1.88	1.50	0.75	1.13	0.75	5.28	3.01	20	100

Table (6):Electronic spectra of ligand L-AZ and its metal complexes. Measurements of Racah B$^{/}$ and nephelauxetic parameterβ

Ligands and complexes	Band position nm	Band position cm-1	Assignments	B́ cm-1	β
Ligand (LAZ)	258	38760	$\pi \rightarrow \pi^*$	-	-
LAZ-VO(II)	906	11038	$^2B_{2g}\rightarrow{}^2E_g$	-	-
LAZ-Cr(III)	856 592 428	11682 (11712)(cal) 16892 (16892.1)(Cal) 23364 (26600)(cal)	$^4A_{2g}\rightarrow{}^4T_{2g}$ (F) (υ_1) $^4A_{2g}\rightarrow{}^4T_{1g}$ (F) (υ_2) $^4A_{2g}\rightarrow{}^4T_{1g}$ (P) (υ_3)	563	0.547
LAZ-Mn(II)	---------	-------------	$^6A_1g\rightarrow{}^4E$ g Forbidden		
LAZ-Co(II)	508+482 / 2 495	20216	$^4T_{1g}\rightarrow{}^4T_{1g\,(p)}$ ^2G , ^2H	-	-
LAZ-Ni(II)	660+718 / 2 689 398	(8360.5) (cal) 14540 25126	$^3A_{2g}\rightarrow{}^3T_{2g}$ (F) (υ_1) $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) (υ_2) $^3A_{2g}\rightarrow T_{1g}$ (P) (υ_3)	727	0.71 -
LAZ-Cu(II)	814	12285	$^2Eg\rightarrow{}^2T_2g$	-	-
LAZ-Zn(II)	254	39370	C.T	-	-
LAZ-Cd(II)	258	38760	C.T	-	-
LAZ-HgII)	262	39168	C.T	-	-

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Table (7): Conductivity measurements for the (L-AZ) complexes in DMSO as solvent at 1 x 10^{-4}M concentration .

(L-AZ)complexes	VO(II)	Cr(III)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)
Λ_m(S.cm^{2}mol^{-1})	56	2.89	19.42	7.32	32.1	15.17	21.8	5.95	32.25

Table (8): Molar ratio data of some L-AZ-complexes

V(ml)	L-AZ-Co(II),λ=508nm	L-AZ-Cu(II), λ=800nm	L-AZ-Cd(II), λ=258nm	L-AZ-Hg(II) , λ=260nm
1	1.1	1.21	1.73	1.2
3	1.23	1.4	2.01	1.7
5	1.44	1.61	2.26	2.1
7	1.57	1.92	2.67	2.5
10	1.8	2.3	2.98	3.2
12	1.89	2.47	3.11	3.2
14	1.97	2.58	3.23	3.5
16	2.12	2.76	3.42	3.7

Table (9): Data of magnetic moments and suggested structure for (L – AZ) complexes .

(L-AZ) complexes	μ_{eff}(B.M)	Suggested structure
VO (II)	1.6	Square pyramidal
Cr (III)	11.94	Octahedral
Mn (II)	14.44	Octahedral
Co (II)	2.26	Octahedral
Ni (II)	8.56	Octahedral
Cu (II)	4.68	Octahedral

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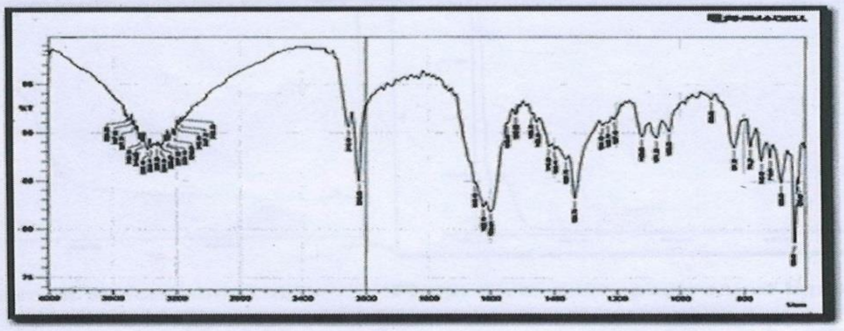
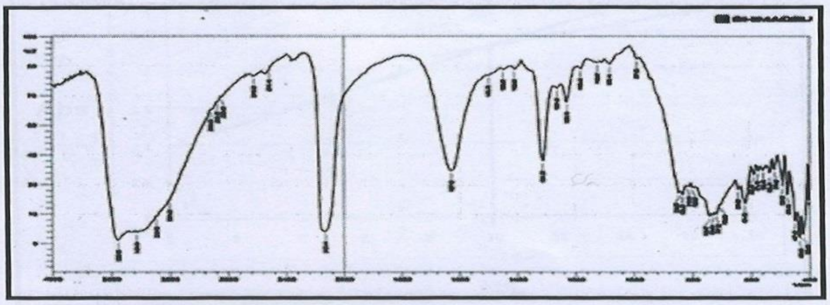
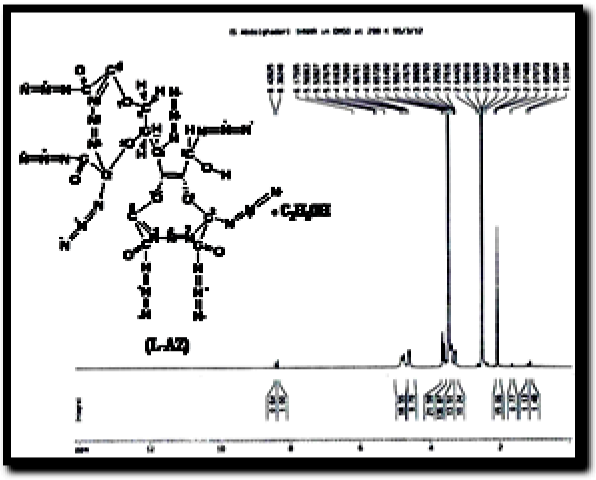


Figure (1)FT-IR spectrum of ligand (L-AZ)



Figure(2)FT-IR spectrum of L-AZ Co(II) complex



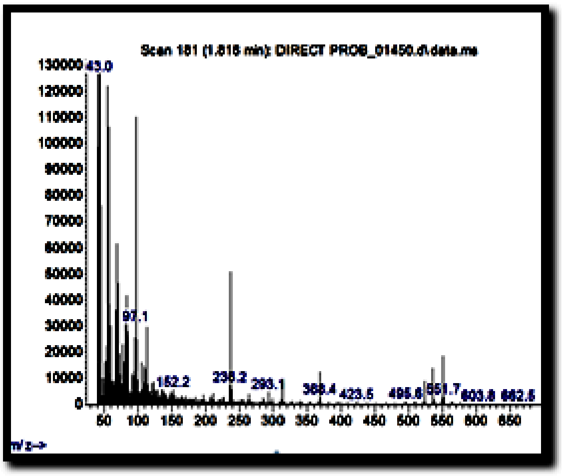


Figure (3): ^{1}H -NMR of ligand (L-AZ))

Figure (4): Mass spectrum of ligand (L-AZ)

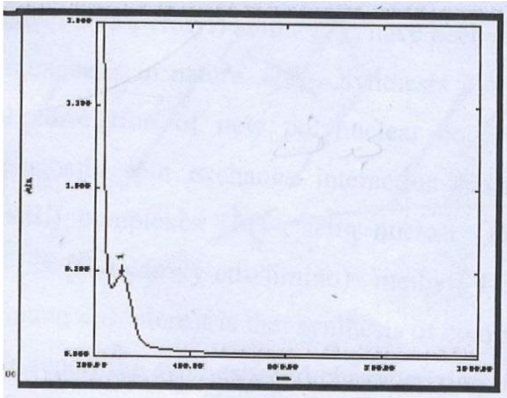


Figure (5) Electronic spectrum of ligand (L-AZ)

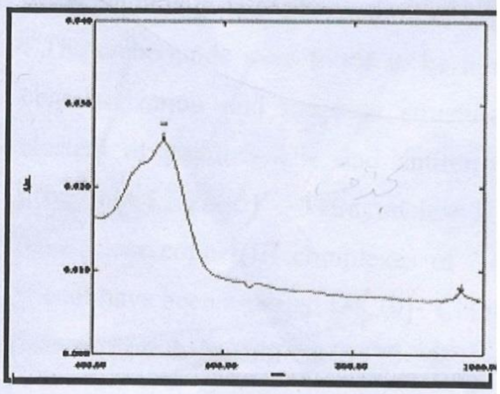


Figure (6) Electronic spectrumof LAZ-Co(II) complex

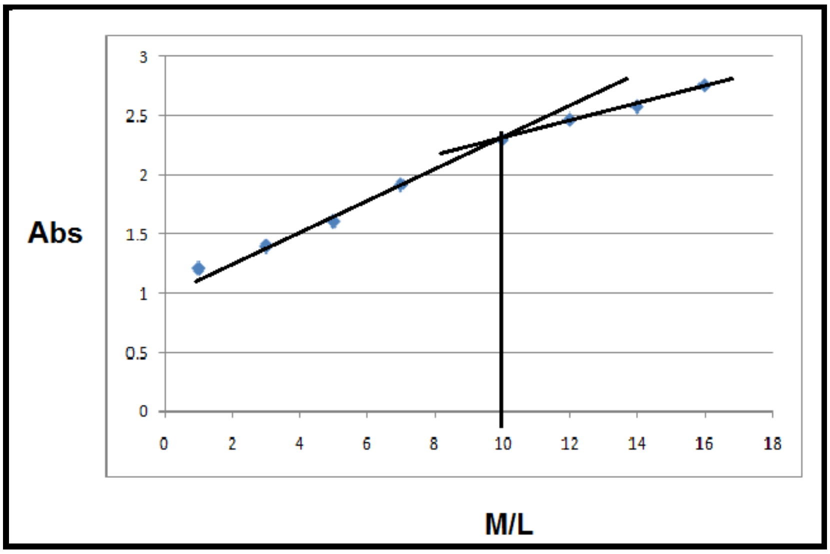


Figure (7): Molar ratio curve of L-Cu (II) complex

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