Preparation, Characterization and Antibacterial Studies of New 2-(naphthalene-2-yl)-2-(naphthalene-2ylamino) Acetonitrile Ligand with Some Metal Ions

Mohammed H. A. Al-Amery

Department of Chemistry, College of Science, Baghdad University, Iraq. E-mail: dr.al_amery1954@yahoo.com.

Abstract

In the present work, the synthesized of a series of metal ions complexes of [Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)] from new bidentate 2-(naphthalene-2-yl)-2-(naphthalene-2ylamino) acetonitrile ligand (L) which prepared from 2-naphthaldehyde and naphthalene-2-amine in the presence of KCN and alcoholic medium. These compounds were characterized by using several techniques FT-IR, UV-Visible spectrophotometer, magnetic susceptibility, thermal gravimetric analysis (TGA), elemental analysis, molar conductivity, ¹H-NMR, as well as atomic absorption. From the spectral studies, an octahedral monomer structure was proposed for all complexes. The nature of the complexes formed in ethanolic solution has been studied following the molar ratio method and the result recorded [1:2] [M:L] ratio. Some complexes were found to be non-electrolyte and others were found to be weak electrolyte in ethanol. Biological activities of the free ligand and its metal complexes have been tested against a number of microorganisms in order to assess their antimicrobial properties.

Keywords: Acetonitrile, bidentate ligand, 2-naphthaldehyde, naphthalene-2-amine.

Introduction

The reaction of primary or secondary amines and an aldehyde or ketone with the present of cyanide ion forms aminonitriles. a-Aminonitriles are important intermediates for the synthesis of a wide variety of amino acides. amides, diamines and nitrogencontaining hetrocyclles [1]. Ligands and its transition metal complexes have been of great interest to research workers since seventies of the last century. At that time it was found that pyridine complexes show activity against leukemia [2]. Three-component reaction of aldehydes, amines and cyanide, known as the Strecker reaction. The classical Strecker reaction provides one of the most efficient methods for the synthesis of α -aminonitriles since 1850 when Adolph Strecker interact an aldehyde, an amine and hydrogen cyanide [1]. The addition of cyanide to imines provides for route the synthesis direct of a α -aminonitriles. Some of the α -aminonitrile derivitives like 1-amino-4-phenylnaphthalene-2-carbonitrile have been postulated to have high fungistatic activity even stronger than the activity of the commercial fungicide - Kaptan [3]. α -aminonitriles are useful intermediates for the synthesis of amino acids [4,5] and nitrogen-containing heterocyclic such as thienopyrimidine derivatives which have antibacterial and antifungal activities higher

than the corresponding antibacterial ampicillin and antifungal nystatin [6-8]. Moreover, among many other applications, they are readily hydrolyzed to diamines, which are of interest as ligands for Platinum (II) complexes with potential antitumor properties [9, 10]. Several modifications of the Strecker reaction been have reported using а variety cyanating agent such of as α -trimethylsiloxynitriles and under various reaction conditions [11, 12]. Complexes with dinitrogen N2 ligand are of interest not only in theoretically but also from a practical point of view. They have found application as antitumor activity [13], antibacterial activity [14] and antiviral activity in agriculture field [15]. α -aminonitriles have often been used as chelating ligands through two nitrogen atoms in the field of amino coordination chemistry. This is one of a few studies to obtain a new coordination field of a-aminonitrile compounds as ligands and their interactions with transition metal ions.

Experimental

Chemical used

All the starting materials were commercially available. 2-naphthaldehyde, naphthalene-2-amine, metal salts CrCl₃.6H₂O, FeCl₃.6H₂O, CoCl₂.6H₂O, MnCl₂.4H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, ZnCl₂ CdCl₂.2H₂O, and HgCl₂ (BDH), Glacial acetic acid and potassium cyanide, (BDH), Ethanol, absolute ethanol, p-toluene sulphonic acid, ammonium hydroxide, sodium hydroxide sulfuric acid, chloroform, ethyl acetate, petroleum ether (30-60) and KBr (Fluka).

Instrumentation

The infrared spectra of the ligand and the complexes were recorded on SHIMADZU 8300 FTIR Spectrophotometer as KBr disk. Electronic absorption spectra were recorded on 1800-UV SHIMADZU. Atomic absorption technique was used to determine the metal contents of the complexes using Phoenix-986 Spectrophotometer. Molar conductivity was used to measure the conductivity of the complexes (10⁻³ M) at room temperature in freshly ethanol using (CDM 83) Digital conductivity meter. Elemental micro analysis for carbon, hydrogen and nitrogen elements were carried out at the Euro: (EA) Elemental analyzer. ¹H-NMR spectra of the ligand and Co (II) complex were recorded in DMSO using NMR Spectrometer 400 MHZ (Avance III Broker), Germany. Thermal gravimetric analyses (TGA) were recorded in SETARAM D350 analyzer. The magnetic properties were measured using Auto Magnetic susceptibility Balance (Sherwood Scientific). Melting points were measured using a Stuart SMP30 Digital Melting Point. The chlorine content determined gravimetrically.

Preparation of ligand (L)

The ligand (L) was prepared as follows [17-19]: 2-naphthaldehyde (0.156 g, 1 mmol) was added to (20 ml) glacial acetic acid, p-toluene sulphonic acid was added in very small portion as catalyst, followed by addition of (0.143 g,1 mmol) of naphthalene-2-amine. The pH was adjusted to about 4 by addition of concentrated sulfuric acid drop wise to obtain Schiff base which stirred for 30 min. Potassium cyanide (2 mmol) was added to the mixture and kept under stirring for 4 days. The reaction mixture was poured into ice and then made slightly alkaline with ammonium hydroxide solution. The solid precipitate which formed was filtered, washed with water and air dried. The presence of nitrile group in the prepared α -aminonitrile was indicated by treating few amount of the sample with 10% sodium hydroxide solution, the liberation of ammonia after hydrolysis of nitrile group, which was detected by wet red litmus paper, indicating the presence of nitrile group. Purity of the obtained compound was checked by TLC, using chloroform and ethyl acetate (1:1) as eluent. The product color was dark brown and the yield percentage was (88.5%) and the was $(187-189^{0}C).$ melting point The condensation reaction to prepare the new ligand was clarified below:



Preparation of Complexes

All complexes were prepared by the reaction of (0.616 g, 2 mmol) of (L) with (1mmol) of metal chloride (0.267 g, 0.198 g, 0.270 g, 0.238 g, 0.238 g, 0.171 g, 0.136 g, 0.219 g and 0.272 g for CrCl_{3.6}H₂O,

FeCl_{3.6H₂O, MnCl_{2.4H₂O, CoCl_{2.6H₂O, NiCl_{2.6H₂O, CuCl_{2.2H₂O, ZnCl_{2.} CdCl_{2.2H₂O and HgCl₂, respectively) dissolved in (20 ml) absolute ethanol and refluxed with stirring under anhydrous conditions using Na₂SO₄ (anhydrous) for 24 hours. The obtained}}}}}}

complexes were collected after evaporation of ethanol and triturated with petroleum ether (30-60 0 C) then filtered and the products were left in the desiccators to be dried under silica gel. The yield percentage of the complexes were (79.6, 84.2, 75.7, 76.3, 86.6, 79.8, 77.3, 82.5 and 87.3) % respectively as shown in Table (1). The general reaction was clarified below:



Results and Discussion

The carbon, hydrogen, nitrogen and metal content data alongside the melting points, percentage and colors, of the ligand and the prepared complexes are shown in Table (1).

FT-IR spectra

In order to study the binding mode of the ligand to metal ion in the complexes, the IR spectrum of the free ligand was compared with those of the corresponding metal ion complexes. Selected vibrational bands of the ligand and its metal ion complexes and their assignments are listed in Table (2). The infrared spectrum of the ligand shows a band at 3328 cm⁻¹ which assigned to v(N-H)vibration. In the spectra of all the metal ion complexes this band shows shifts to high frequencies (3345-3379) cm⁻¹. These changes indicate that the (N-H) takes part in the coordination. The band related to $\delta(N-H)$ deformation of the ligand appeared at 1616 cm⁻¹, this band was shifted in the spectra of the complexes (1634, 1645, 1659, 1652, 1658, 1648, 1637 and 1655) cm⁻¹, respectively [20-21]. This gave further indication that the ligand was coordinated with metal ions through the nitrogen atom of α -amino group and thus supports the complexes formation.

The band at 2241 cm⁻¹ which was assigned to the $\upsilon(C\equiv N)$ stretching vibration of $(C\equiv N)$ group of the ligand [L] was shifted in the spectra of complexes towards to lower frequencies as shown in Table (2) which indicates the linkage of $(C\equiv N)$ group from nitrogen atom of the cyanide group. Other weak bands have been observed in the region (432-490) cm⁻¹ which are absent in the free ligand, can be assigned to $\upsilon(M-N)$ vibrations [20, 21].

¹H-NMR

The ¹H-NMR spectrum of the ligand [L] showed three peaks; The first one at $\delta(3.89 \text{ ppm})$, which corresponded to the (-N-<u>H</u>) proton, the second peak appeared at $\delta(5.36 \text{ ppm})$ which corresponded to the (-C<u>H</u>-C=N) proton and the last peak appeared at $\delta(6.52-7.69)$ ppm which corresponded to the aromatic protons [22]. The spectrum of the Zn (II) complex was also similar to that of the ligand. The signal of (N-<u>H</u>) of the ligand was shifted in this complex by 0.44 ppm and the signal of (-C<u>H</u>-C=N) was shifted in this complex by 0.14 ppm, this gave an indication for complex formation [22].

Molar Conductance Data

The molar conductance of $(10^{-3}M)$ of all the prepared complexes was measured in absolute ethanol at room temperature. The values of the molar conductance of the complexes Co (II), Mn (II), Ni (II), Cu (II), Zn (II) Cd (II) and Hg (II) were relatively low, they were lie in the range of (13.7-17.2) Ω^{-1} .cm².mol⁻¹, these values indicated that these complexes were non electrolytes, this mean that all the chloride anions are coordinated to the metal ion (inside the coordination sphere) [23,24], while the molar conductance values of the complexes Cr (III) and Fe (III) were lie in the range of (33.8-38.3) Ω .cm².mol⁻¹, these values indicated that, these two complexes were weak electrolytes, so that for these two complexes two chloride anions were coordinated to the metal ion, leaving the other chloride anion outside the coordination sphere [25]. The values of molar conductance of the complexes are shown in Table (3).

Molar Ratio Method

The absorption spectra were measured for many mixed solutions containing (1 ml) of the metal ion salt in the optimum concentration, and variable volumes of the ligand solution in the same concentration. M:L ratio was obtained by plotting the relation between the mole ratio in the X-axis and absorbance in the Y-axis. The intercept of the two straight lines represent the M:L ratio, it was (1:2).

Magnetic Moment

The Cr (III) complex has a magnetic moment value of 3.88 B.M was in accordance with those having octahedral structure. The Fe (III) complex shows a magnetic moment value 5.54 B.M was in accordance with those having octahedral structure. The Cu (II) complex shows a normal magnetic moment of 1.71 B.M observed for a d^9 system with an unpaired electron [24]. The Ni (II) complex with a magnetic moment of 2.90 B.M reveals a spin free octahedral configuration [23]. The magnetic moment of 4.20 BM for the Co (II) complex suggested a high spin octahedral arrangement [23]. The Mn (II) complex has a magnetic moment 5.60 B.M, as expected for high spin octahedral geometry [23]. The Zn (II), Cd (II) and Hg (II) complexes are

diamagnetic as expected for a d^{10} configuration [23, 25].

Electronic Spectra

The electronic absorption spectra of the ligand and its metal in complexes were recorded at room temperature using absolute ethanol as the solvent. The solid state electronic spectra of the ligand and the complexes display the absorption bands listed in table 3. The ligand shows two bands, the first band at 39683 cm⁻¹ is due to intra ligand $\pi \rightarrow \pi^*$ and the second band located at 33333 cm⁻¹ is due to. On complexation, these bands are shifted to higher wavelengths, suggesting coordination of the uncharged dinitrogen N2 of the ligand to the metal ion. The spectra of the complex Cr (III) ion showed four bands observed at 9242, 13477, 17391 and 25773 cm⁻¹ respectively these bands may be assigned to the transitions ${}^{4}A_{2}g \rightarrow {}^{2}T_{2}g + {}^{2}Eg$, ${}^{4}A_{2}g \rightarrow$ ${}^{4}T_{1}(F)$ and ${}^{4}A_{2} g \rightarrow {}^{4}T_{1}(P)$ respectively[26]. The spectra of the complex Fe (III) ion showed two bands observed at 18820 and 22124 cm⁻¹, respectively, these bands may be assigned to the transitions ${}^{6}A_{1}g \rightarrow {}^{4}T_{2}g(G)$ and ${}^{6}A_{1}g \rightarrow$ ${}^{4}A_{1}g + {}^{4}Eg$. [27]. The Mn (II), Zn (II), Cd (II) and Hg (II) complexes do not show any d-d transitions but display charge transfer bands at 21459, 20576, 24390 and 25510 cm⁻¹, respectively. The cobalt (II) complex showed several electronic specta; some of them related to the ligand only, while the others related to the metal ion. These spectra may be characterized as follows: absorption at wavelength 245 nm is assigned to the $\pi \to \pi^*$ transition in the aromatic rings within the ligand. Absorption at 275 nm is assigned to the $n \rightarrow \pi^*$ transition from the (non-bonding electrons) which are available on the ligand nitrogens N2. The $d \rightarrow d$ transition which were confined to the d orbital of the metal ion are exhibited in three spectra; indicating in an octahedral geometry around the Co (II) ion, the first one did not show up due to its low energy and it will be calculated theoretically through the Tanabe-Sugano diagrams [28,29]. The second absorption occurs at 616 nm, and this is equivalent to the absorption band at 16223 cm⁻¹; and the third absorption occurs at 561 nm which is again equivalent to the band at 17835 cm⁻¹. All the above absorption are related to the following transitions; $v_1 = {}^4T_1g(F) \rightarrow {}^4T_2g(F), v_2 = {}^4T_1g(F) \rightarrow {}^4T_1g(P) \text{ and } v_3 = {}^4T_1g(F) \rightarrow {}^4A_2g(F).$

The value of (v_1) has been calculated from Tanabe-Sugano diagrams [29]; where the value of Racah inter-electronic repulsion parameter (B'), needs to be obtained first, which was 580 cm⁻¹, and then using the following relationship $(15B = v_3 + v_2 - 3v_1)$ to determined the value of v_1 . The value of v_1 has been calculated accordingly and found to be 8453 cm⁻¹ which is equivalent to the wavelength 1183 nm; which is not in the visible area anymore. The electronic spectrum of Ni (II) complex exhibits two bands in the region 23095 and 16077cm⁻¹ which are assigned to the ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ (v₃), ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ (v₂) transitions, respectively, indicating in an octahedral geometry around the Ni (II) ion. The $(v_1)^{-3}A_2g(F) \rightarrow {}^{3}T_{2g}(F)$, transition is expected to appear at large wavelength, therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram [29]. The value of (v_1) has been calculated from Tanabe-Sugano diagrams; where the value of Racah interelectronic repulsion parameter (B'), needs to be obtained first, which was 630 cm⁻¹, and then using the following relationship $(15B = v_3)$ $+ v_2 - 3v_1$) to determined the value of v_1 . The value of v_1 has been calculated accordingly and found to be 9907 cm⁻¹ which is equivalent to the wavelength 1009 nm; which is not appear in the visible area. The spectrum of Ni (II) complex also exhibits a charge transfer band at 25400 cm⁻¹. The electronic spectrum of Cu (II) complex displays three bands at 14493, 22727 and 24991 cm⁻¹ corresponding to the following transitions: ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g} (d_{x}^{2}{}_{-y}^{2} \rightarrow d_{z}^{2}) , (v_{1}),$ $^{2}B_{1g} \rightarrow ^{2}B_{2g} (d_{x}^{2}-y^{2}\rightarrow d_{zy}), (v_{2}) \ ^{2}B_{1g} \rightarrow ^{2}E_{g}$ $(d_{x^{2}-y^{2}} \rightarrow d_{zy}d_{yz})$, (v₃), respectively. Therefore, the Cu (II) complex may be considered to possess a tetragonal geometry around the copper ion [30, 31]. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope [31]. The spectrum also exhibits a band at 25575 cm⁻¹, which is assigned to a charge transfer band.

Thermal Analysis

The data of thermal study of the prepared complexes are listed in Table (4). All the prepared complexes showed a similar thermal behavior as they showed that the thermal decomposition of the complexes passes through three stages; the first stage of mass loss was attributed to the loss of water of hydration which took place at a temperature range of (50–150) °C. It is hard at this point to differentiate between the coordinated water and the uncoordinated (lattice water) from the thermograms [33,34]. All the experimental mass losses were in good agreement with the calculated ones as it is shown in Table (4). The second stage is the dissociation and decomposition of the chloride at temperatures depending on bond energies, which results in a temperature range of (100-200) °C. The last mass loss recorded was between the range of (160 - 390) °C after that, a region of thermal stability was observed up to more than (800 °C) and was identified as the oxide of the corresponding metal ions which are known to be very stable even at very high temperatures [32-35].

Antibacterial Activity of the Prepared Compounds

The biological activity of the prepared ligand and the metal ion complexes were studied against selected types of micro organisms with include of Staphylococcus aureus, Bacillus subtilis (Gram positive), Escherichia Coli and Pseudomonas aerugin (Gram negative) in agar diffusion method, which is used (DMSO) as solvent. Agar diffusion method involves the exposure of the zone of inhibition toward the diffusion of micro organisms on agar plate. The plates were in cubated for (24) hrs. at (37 $^{\circ}$ C). The solvent (DMSO) showed no activity against the tested bacteria, while some of prepared complexes showed good results. Table (5) shows the inhibition zones of the ligand and the prepared complexes. The inhibition zones were measured in (mm) and compared to the inhibition zone of broad spectrum antibiotic. All the complexes and the ligand showed activity against the gram positive (Staphylococcus aureus). Some complexes showed no activity against the gram negative bacterium (Escherichia coli), which can cause disease. Some complexes showed activity the gram negative bacterium against (pseudomonas). This bacterium is known for its resistance to most of the developed antibiotics and is known to be the major case of many health issues and infections [36-38]. The Tetracycline (gram positive control) showed activity aginst the gram positive bacterium (Staphylococcus aureus). the inhibition zone is 16.8 mm. Some other Complexes showed activity against the gram positive bacterium (Staphylococcus aureus) which is a bacterium that causes staphylococcal food poisoning, found in the environment (soil, water and air) and is also found in the nose and on the skin of humans [149]. Complexes [Mn(II), Ni(II) Cu(II), Zn(II) and Cd(II) complexes as well as the ligand showed activity against the gram positive bacterium (Bacillus subtilis) which has been used for genetic and biochemical studies for several decades, and is regarded as paradigm of Gram-positive endospore-forming bacteria [38-40].

Conclusion

A series of complexes of [Cr (III), Fe (III), Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II)] with new bidentate 2-(naphthalene-2-yl)-2-(naphthalene-

2ylamino) acetonitrile ligand have been prepared and characterized. The bidentate ligand (N2) was forming octahedral structures as shown in Fig.(1 and 2).

C % H % N%M % Cl% Yield *M.P.* Formula Color Cal. Cal. Cal. Cal. Cal. M.wt. (gm/mol) % (**•***C*) (found) (found) (found) (found) (found) 85.71 5.19 9.09 $C_{22}H_{16}N_2$ Dark 88.5 187-189 308 Brown (84.89)(6..05)(9.44)[CrL₂Cl₂]Cl.3H₂O 63.73 4.59 6.76 6.28 12.85 79.6 Gray 218-220 828.5 (65.34)(4.52)(6.88)(6.18)(12.67)[FeL₂Cl₂]Cl.3H₂O Light 63.43 4.57 6.73 6.70 12.80 84.2 230-233 red (63.26)(4.60)(6.65)(7.3)(13.03)832.35 7.20 $[MnL_2Cl_2].2H_2O$ Yellow 68.49 4.63 7.06 9.13 75.7 192-195 777.94 Orange (67.72)(4.58)(6.89)(7.23)(9.35) $[CoL_2Cl_2].2H_2O$ Dark 66.01 4.75 7.00 7.37 8.88 219--221 76.3 (65.96) (4.80)(6.93) (7.45)(8.94)781.93 Brown [NiL₂Cl₂].2H₂O Chocolate 67.55 4.61 7.16 7.51 9.08 86.6 192-195 781.69 Brown (67.88)(4.54)(7.51)(7.72)(9.37)4.58 7.12 $[CuL_2Cl_2].2H_2O$ 67.13 8.08 9.03 79.8 Orange 210-212 786.55 (67.40)(4.62)(7.28)(8.34)(9.22) $[ZnL_2Cl_2].2H_2O$ 67.58 4.57 7.10 8.29 9.01 Light 77.3 223-225 788.38 Brown (67.37) (4.47)(7.02)(8.14)(8.96) $[CdL_2\overline{Cl_2}].2H_2\overline{O}$ Medium 63.78 4.31 6.70 13.46 8.50 82.5 226-229 835.41 Brown (63.90)(4.28)(6.58) (13.32)(8.41)[HgL₂Cl₂].2H₂O Brownish 87.3 187-189 57.69 3.90 6.06 21.72 7.69 923.59 Yellow

Table (1)Elemental analysis and some physical properties of the ligand (L) and the prepared complexes.

Table (2)
Characteristic infrared absorption bands of ligand (L) and the prepared complexes

Molecular Formula	υN-H cm ⁻¹	vC-H Aromatic cm ⁻¹	vC-H aliphatic cm ⁻¹	$ uC\equiv N $ cm^{-1}	$\delta N-H$ cm^{-1}	UC-N cm ⁻¹	<i>и</i> М-N ст ⁻¹
$C_{22}H_{16}N_2$	3328	3026	2981	2241	1616	1125	
[CrL ₂ Cl ₂]Cl.3H ₂ O	3368	3029	2940	2187	1634	1114	488
[FeL ₂ Cl ₂]Cl.3H ₂ O	3345	3031	2982	2189	1645	1110	490
[MnL ₂ Cl ₂].2H ₂ O	3357	3029	2965	2176	1659	1222	465
$[CoL_2Cl_2].2H_2O$	3348	3028	2988	2171	1652	1092	487
[Ni) ₂ Cl ₂].2H ₂ O	3224	3024	2980	2173	1658	1110	491
[CuL ₂ Cl ₂].2H ₂ O	3368	3025	2976	2193	1648	1098	484
$[ZnL_2Cl_2].2H_2O$	3355	3033	2991	2198	1637	1108	472
$[CdL_2Cl_2].2H_2O$	3361	3027	2979	2177	1655	1102	474
[HgL ₂ Cl ₂].2H ₂ O	3358	3026	2983	2179	1643	1107	432

Table (3)

Electronic spectra, spectra parameters, molar conductance, magnetic susceptibility and suggested stereo chemical of ligand (L) and the prepared complexes.

ctahedral		
ctahedral		
ctahedral		
geometry		
octahedral		
atab a dual		
octaneurai		
Distorted		
octahedral		
ctahedral		
ctahedral		
(1.1.1		
cianedrai		

*Calculated value

Molecular Formula M.wt (gm/mol)	Step	Temp. range of decomposition •C	Suggested formula of resultant compound	Mass loss % Calculated Found	
[CrL ₂ Cl ₂]Cl.3H ₂ O 828.5	1 2 3	70-112 112-180 180-375	$[CrL_2Cl_2]Cl\\[CrL_2]\\Cr_2O_3$	6.52 12.85 74.35	6.44 12.72 74.09
[FeL ₂ Cl ₂]Cl.3H ₂ O 832.35	1 2 3	65-140 140-190 190-365	$[FeL_2Cl_2]Cl \\ [FeL_2] \\ Fe_2O_3$	6.49 12.80 74.01	6.33 12.68 73.89
[MnL ₂ Cl ₂].2H ₂ O 777.94	1 2 3	65-130 130-170 170-390	$[MnL_2Cl_2] \\ [MnL_2] \\ MnO_2$	4.63 9.13 79.18	4.59 9.02 78.95
[CoL ₂ Cl ₂].2H ₂ O 781.93	1 2 3	55-100 100-160 160-380	[CoL ₂ Cl ₂] [CoL ₂] Mix of CoO and Co ₃ O ₄	4.50 9.08 78.78	4.39 8.98 78.88
[NiL ₂ Cl ₂].2H ₂ O 781.69	1 2 3	50-105 105-175 175-380	[NiL ₂ Cl ₂] [NiL ₂] NiO	4.61 9.08 78.80	4.53 9.00 78.63
[CuL ₂ Cl ₂].2H ₂ O 786.55	1 2 3	50-115 115-200 200-385	[CuL ₂ Cl ₂] [CuL ₂] CuO	4.58 9.03 78.32	4.49 8.98 78.21
[ZnL ₂ Cl ₂].2H ₂ O 788.38	1 2 3	60-130 130-190 190-370	[ZnL ₂ Cl ₂] [ZnL ₂] ZnO	4.67 9.06 78.13	4.62 8.93 78.45
[CdL ₂ Cl ₂].2H ₂ O 835.41	1 2 3	60-140 140-195 195-360	[CdL ₂ Cl ₂] [CdL ₂] CdO	4.31 8.50 73.74	4.25 8.35 73.83
[HgL ₂ Cl ₂].2H ₂ O 923.59	1 2 3	50-150 150-190 190-380	[HgL ₂ Cl ₂] [HgL ₂] HgO	3.90 7.69 66.70	3.84 7.59 66.42

Table (4)Thermal decomposition data for the prepared complexes.

Table (5)

The antibacterial activity of the ligand and its metal ion complexes against the tested bacteria.

Compound	Inhibition zone zone (mm) Escherichia coli	Inhibition zone zone (mm) Pseudomonas aeruginosa	Inhibition zone zone (mm) Staphylococcus aureus	Inhibition zone zone (mm) Bacillus subtilis
DMSO				
Tetracycline	19.3	7.2	16.8	
$C_{22}H_{16}N_2$	9.3	10.9	13.7	9.6
[CrL ₂ Cl ₂]Cl.3H ₂ O	7.8	9.4	12.3	
[FeL ₂ Cl ₂]Cl.3H ₂ O		23.2	10.6	contaminated
[MnL ₂ Cl ₂].2H ₂ O	6.7		13.7	
[CoL ₂ Cl ₂].2H ₂ O		contaminated	11.2	11.4
[NiL ₂ Cl ₂].2H ₂ O	8.2		10.5	13.2
[CuL ₂ Cl ₂].2H ₂ O			7.4	12.3
$[ZnL_2Cl_2].2H_2O$	7.8	20.8	8.5	10.9
$[CdL_2Cl_2].2H_2O$			7.9	8.3
[HgL ₂ Cl ₂].2H ₂ O	contaminated		6.2	



[ML₂Cl₂]Cl.3H₂O [Di Chloro-bis {2-(naphthalene-2-yl)-2-(naphthalene-2ylamino) acetonitrile} Chrome or Iron (III)]Chloride (3) Hydrate Fig.(1) The proposed structure of the complexes, where M = Cr(III) or Fe(III).



$[ML_2Cl_2].2H_2O$

[Di Chloro-bis {2-(naphthalene-2-yl)-2-(naphthalene-2ylamino) acetonitrile} Manganese, Cobalt, Nickel, Copper, Zinc, Cadmium or Mercury (II)] (2) Hydrate Fig.(2) The proposed structure of the complexes, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

References

- Strecker, "Ueber die kunstiche Bildung der Milchsture und einen neuen dem glycocoll homologen"; Ann.Chem. pharm., 75, 27-45, 1850.
- [2] Ali M. A. and Livingstone S. E.; "Metal Complexes of Sulphur-Nitrogen Chelating Agents"; Coord. Chem. Rev. 13; 101-132, 1974.
- [3] Bartlomiej Kozik, Zbigniew J. Burgiel, Janusz J. Sepiol, Jarosaw Wilamowski, Michal K., Luczynski, Maciej Gora; "Synthesis and fungistatic activity of arylsubstituted naphthalene- and indene-2carbonitriles"; Enviromental biotechnology, 2 (1), 20-25, 2006.
- [4] Harada K.; "Asymmetric Synthesis of α– Amino Acids by the Strecker Synthesis", Nature, 200, 1201-1209, 1963.
- [5] Evans D.A. and Weber A.E.; "Asymmetric Glycine Enolate Aldol Reactions: Synthesis of Cyclosporine's Unusual Amino Acid MeBmt"; J. Am. Chem. Soc., 108, 6757, 1980.
- [6] Mosharef H. B., Mizanur R., Kamrul H. Kamrul H. and Mohammad A.; "Synthesis and antimicrobial evaluation of some new thienopyrimidine derivatives"; Acta Pharm., 56, 441–450, 2006.
- [7] Nitinkumar, S. S., R. and Imtiyaz, A. M.;
 "Synthesis and antimicrobial activity of some novel thienopyrimidines and triazolothienopyrimidines"; J. Chem. Sci., 121, (3), 301–307, 2009.
- [8] Mosharef H. B., Rahman M. M. and Imjamul I.; "Synthesis, Characterization and Antimicrobial Evaluation of Some Arylidenehydrazonofuropyrimidines and Thienopyrimidines"; Pak. J. Sci. Ind. Res., 52 (4), 180-185, 2009.
- [9] Guo Z. and Sadler P. J.; "metals in medicine", Angew. Chem. Int. Ed., 38, p.1512-1531, 1999.
- [10] Rafique S., Idrees M., Nasim A., Akbar H. and Athar A. "Transition metal complexes as potential therapeutic agents"; Biotechnol. Mol. Biol. Rev., 5, 2, 38-45 2010.
- [11] Saidi M. R. and Azizi N.; "A Novel and Efficient Method for the Synthesis of α-Aminonitriles by the Reaction of Aminals with Trimethylsilyl Cyanide Catalyzed by

Iodine"; Journal of the Iranian Chemical Society, 1 (2), 136-140, 2004.

- [12] Fetterly B. M., Jana N. K., and Vercade J. G.; "An efficient homogeneous and solid – supported promoter for aza and thia – Michael reaction and for Strecker reactions"; Tetrahedron, 62, 440-456, 2006.
- [13] Abu-Surrah A. S. el al; "Palladium based chemotherapeutic agents: Routs toward complexes with good anti-tumor activity"; Cancer therapy, 6, 1-10, 2008.
- [14] Thoha S., Karki S. S. and Bhukya B. R.;
 "Sythesis, characterization and antibacterial activity of some novel mononuclear Ru(II) complexes"; Inter. J.Pharm. Pharmaceutical science, 1 (2), 62-70, 2009.
- [15] Thakur S. N., Yadav K. S., Singh N. P. and Yadav H. S. "Template synthesis and characterization of oxovanadium (IV) complexes with tetraaza macrocyclic ligands and their activity on potato virus X", J.Iran. Chem. Soc. 5 (2), 328-335, 2008.
- [16] Vogel A I, A.; "Text Book of Quantitative Inorganic Analysis"; 3rd Edn, Longman, London, p.266 and p. 324, 1989.
- [17] Ogata Y. and Kawasaki, A.; "Mechanistic aspects of the strecker aminonitrile synthesis"; J.Chem. Soc., (B), 325-329, 1971.
- [18] Stanley J. W., Beasleyand J. G., and Mathison I. W.; "Evidence for a cationic imine intermediate in N,N-disubstituted αaminonitrile formation"; J. Org. Chem., 37 (23), 3746-3748, 1972.
- [19] Heba A. A. "Synthesis of new hetrocyclic compounds via nitrile group"; M.SC., Thesis Al-Nahrain university, Baghdad, Iraq, 2005.
- [20] Stuart. B.; "Infrared spectroscopy, fundamental and application"; p 80, 2004.
- [21] Max. P. B., Charles. W. Baushlicher. J. and Scoot. A. S.; "The infrared spectrum of matrix isolated aminoacetonitrile, Advances in Spase Research"; 33, 40-43, 2003.
- [22] Raghu M. and Ch. Sanjeeva. R.; "ZrCl4 promoted efficient one pot synthesis of αaminonitriles"; Indian Journal of Chemistry, 48B, 295-300, 2008.

- [23] Sahbaa. A. Al-Sabaawi. "Synthesis and Characterization of some Mononuclear Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes containing Bis-(2thiophenelidene) thiosemicarbazone ligand"; Education Researchers Journal, 11(3), 765-776, 2011.
- [24] Kumar G., Deviand S. and Johari R.; "Synthesis and Spectral Characterization of Schiff Base Cr (III), Mn (III), and Fe (III) Novel macrocyclic complexes derived from thiocarbohydrazide and Dicarbonyl Compound"; E-Journal of Chemistry. 9(4), 2255-2260, 2012.
- [25] Pragathi M. Anupama P. J., B. and Gyanakumari C.; "Synthesis, spectral Characterization, Molecular Modeling, and Antimicrobial Studies of Cu(II), Ni(II), Co(II), Mn (II), and Zn (II) Complexes of ONO Schiff Base"; E-Journal of Chemistry, 4(9), 2145-2154, 2012.
- [26] Amirnasr M., Mahmoudkhani A., Gorji A., Dekghanpour S. and Bijaanzadeh H.; "Cobalt (II), Nickel (ll) and Zinc (II) complexes with bidentate N,N-bis (B-phenyl cinnamaldehyde)-1,2diiminoethane Schiff base; synthesis and structures"; polyhedron, 21, 2733-2742, 2002.
- [27] Joshua A. R., Johnson. F. A. and Matthew A.A.; "Synthesis and Biological Activities on Metal Complexes of 2,5-Diamino-1,3,4-thiadiazole Derived from Semicarbazide Hydrochloride"; Molecules, 16, 5861-5874, 2011.
- [28] Kalagouda B. G., Siddappa A. P., Ramesh S. V., Rashmi V. S. and Manjula S. P.; "Synthesis and spectral studies of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) complexes of a new macroacyclic ligand N,N'-bis(2-benzothiazolyl)-2,6pyridinedicarboxamide"; J. Serb. Chem. Soc. 71 (5), 529–542, 2006.
- [29] Miessler G. L. and Tarr, D. A;. "Inorganic Chemistry"; Third Edition, Person Prentice Hall, New Jersey, 2003.
- [30] Sunmez, M. and Sekerci, M.; "Synthesis and Cheracterization of Cu(II), Co(II), Ni(II) and Zn(II) Schiff Base Complexes from 1-amino-5-benzyl-4-phenyl-1-Hpyrimidine-2-one with Salicylaldehyde"; Polish J. chem., 76, 907-914, 2002.

- [31] Lever A. B. P.; "Inorganic Electronic Spectroscopy, 2nd edn." Elsevier, Amsterdam; 1989.
- [32] C. M. Yin, Y. H. Kong, Z. R. Liu, C. Y. Wu, D. H. Ren, M. A. He and H. F. Xue., "Studies on the thermal behavior and decomposition mechanism of complexes of rare earth (III) nitrates", Journal of Analysis, vol. 35, 2471-2479, 1989.
- [33] L. Tongbu, G. Xinmin, T. Ning and T. Minyu. "Studies on rare earth complexes with crown ethers, synthesis and characterization of the complexes of lanthanide thiocyanates with dibenzo-24-crown-8", Polyhedron, vol.9:19, 2371-2374, 1990.
- [34] P. K. Das, S. C. Nayak and S. K. Khatua. "Synthesis and characterization of some iron (III) complexes containing heterocyclic nitrogen donor ligands", Ind. J. Sci. Res and Tech, vol.2:1, 9-15, 2014.
- [35] J. R. Allan and A. Rentos., Thermal studies on pyridine-3,4-dicarboxylic acid compound of cobalt, nickel and copper, Thermochimica Acta,vol.161, 111-118, 1990.
- [36] Ahmad A. and A. Z. Beg, "Antimicrobial and phytochemical studies on 45 Indian medicinal plants against multi-drug resistant human pathogens"; Journal of Ethnopharmacology, 74:2,113–123, 2001.
- [37] Taqui B. Khan, K. Najmuddin, S. Shamsuddin, K. A. and Bhatt, J.; "Synthesis, antimicrobial, and antitumor activity of a series of palladium (II) mixed ligand complexes"; Journal of Inorganic Biochemistry, 44(1), 55–63, 1991.
- [38] James. B. Kaper, James. P. Nataro and Harry. L. T. M.; "Pathogenic escherichia coli, microbiology"; 2, 123-140, 2004.
- [39] Banin, K. M. and Brady E. P. G.; "Chelator-induced dispersal and killing of pseudomonas aeruginosa cells in biofilm, Applied and Environmental Microbiology"; 72, 2064-2069, 2006.
- [40] Mutalik R.B. and Gaikar V. G.; "Cell permeabilization for extraction of penicillin asylase from Escherichia coli reverse micellar solution, Enzyme and Microbiological Technology" S; 32, 14-26, 2003.

الخلاصة

تضمنت هذه الدراسة تحضير وتشخيص مجموعة من معقدات بعض ايونت العناصر ثلاثية التكافؤ (Cr(III و Fe(III) وثنائية التكافؤ Mn(II) و Co(II) و Cu(II) و Cd(II) و Cd(II) و Cu(II) و Cu الليكاند ثنائي السن ٢-(نفثالين-٢)-٢-(نفثالين-٢] امينو) اسيتونتريل الذي حضر من تفاعل ٢-نفثاالديهايد مع ٢-امينو نفثالين بوجود سيانيد البوتاسيوم في محلول كحولي. حضرت المعقدات من خلال معاملة الليكاند مع املاح العناصر بنسبة مولية [[2:1] ملح: ليكاند] وشخصت المعقدات من خلال قياس درجة الانصبهار و التحليل الدقيق للعناصر و مطيافية الامتصاص الذري ومطيافية الاشعة تحت الحمراء و الاطياف الالكترونية و بروتون الرنين النووي المغناطيسي والتحليل الحراري والتوصيلية المولارية والقياسات المغناطيسية. طبقاً للبيانات التي تم الحصول عليها تم اقتراح الاشكال الهندسية المحتملة لهذه المعقدات على انها ثمانية السطوح. بعض المعقدات كانت غير الكتروليتية والبعض الآخر وجدت بشكل الكتروليت ضعيف. تمت دراسة الفعالية البايولوجية لليكاند و للجميع المعقدات المحضرة.