Synthesis, Characterization, And Antibacterial activity Of Mn (II),Fe(II),Co(II),Ni(II),Cu(II),Zn(II),Cd(II),and Hg (II) Mixed- Ligand Complexes Containing Furan-2-carboxylic acid And (1,10-phenanthroline)

Taghreed, H. Al-Noor ; Faiza.H Ghanim and Aliea, S. kindeel Department of Chemistry, Ibn -Al-Haithem College of Education for pure science Baghdad University-IRAQ Corresponding author: e-mail- drtaghreed2@Gmail.com

Abstract

The research includes the synthesis and identification of type mixed ligand complexes of M^{+2} Ions using Furan-2-carboxylic acid($C_5H_4O_3$) (FCA H) as a primary ligand and 1,10-phenanthroline (phen)as secondary ligand. The resulting products were found to be solid crystalline complexes' which have been characterized by :Melting points, Solubility, Molar conductivity. determination the percentage of the metal in the complexes by flame(AAS), magnetic susceptibility, Spectroscopic Method [FT-IR and UV-Vis]. The proposed structure of the complexes using program , chem office 3D(2006) . The general formula have been given for the prepared mixed ligand complexes [M(FCA)_2(phen)_2]

M(II) - Mn (II) , Fe (II),Co(II) ,Ni(II),Cu (II), Zn(II) , Cd(II), and Hg (II).

Phen = 1,10-phenanthroline = $(C_{14}H_8N_2.H_2O)$ The results showed that the deprotonated ligand (Furan-2-carboxylic acid (FCA H) to (Furan-2-carboxylate ion (FCA⁻) by using (KOH) coordinated to metal ions as a monodendate ligand through the oxygen atom of the carboxylate group (-COO⁻), and the retention of v (C-O-C) band of the (FCA⁻) ring at 1224 cm⁻¹ oxygen atom of the ring cm⁻¹ indicates that is not taking part in coordination.

Keywords : Furan 2-carboxylic acid; 1,10-phenanthroline;mixed ligand complexes , heterocyclic aromatic compound.

1-INTRODUCTION :

Heterocycles can be conveniently classified as organic compounds in which one or more of the ring carbon atoms have been replaced by another element such as nitrogen, oxygen, and sulfur [1]. Heterocyclic compounds have a wide range of applications: they are used as optical brightening agents, as antioxidants, as corrosion inhibitors, and as additives with a variety of other functions [2].

Furan-2-carboxylic acid($C_5H_4O_3$) (FCAH) is a heterocyclic aromatic compound with five-membered ring structure consisting of four CH₂ groups, one oxygen atom and a carboxylic group. [3]. 4-amino-furan-2-carboxylic acid (proximicin) is an antibiotic which shows a weak antibacterial activity but a strong cytostatic effect to various human tumor cell lines.[4-7] .Naphtho [2,1- b] furan derivatives have antioxidant activities and can be used as a powerful source used for suppression of pimples.[8]

1, 10-phenanthroline(phen) and its derivatives such as 5,6-diamino-1,10-phenanthroline,1, 10-phenanthroline-5,6-dioxime play important roles as molecular scaffoldings for supramolecular assemblies, building blocks for the synthesis of metallo-dendrimers, thin films of luminescent complexes and ligands of synthesis of ringopening metathesis polymerization (ROMP) monomer [9]. 1,10- phenanthroline is a typical chelating ligand for transition metals and its metal complexes are useful as a photo- sensitizer, electroluminescent materials and catalysts for organic synthesis [10, 11]. Another importance of 1, 10- phenanthroline complexes is the capacity to absorb visible light and thereby to access to excited states by means of metal-to-ligand charge transfer (MLCT) process and are able to transform solar energy to a form of usable energy. [12-14].

In this paper we present the synthesis and study of { Mn Mn (II), Fe (II), Co(II), Ni(II), Cu (II), Zn(II), Cd(II), and Hg (II)} complexes with Furan-2-carboxylic acid as a primary ligand and (1,10-phenanthroline) as a secondary ligand have been used, respectively.

2-EXPERIMENTAL:

2-1.Materials and Methods

a- All chemicals used were of reagent grade (supplied by either Merck or Fluka) and used as supplied. All the metal ions Mn (II), Fe (II), Co(II), Ni(II), Cu (II) and Zn (II) were of Analar grade (BDH). They were used in the form of chlorides without further purification.

b- Instruments: FTIR spectra were recorded as KBr discs using Fourier transform Infrared Spectrophotometer Shimadzu 24 FTI.R 8400s. Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10-3 M solutions in DMF at 25°C using shimadzu-U.V-160.A Ultra Violet Visible- Spectrophotometer with

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 1.000 ± 0.001 cm matched quartz cell. While metal contents of the complexes were determined by Atomic Absorption(A.A)Technique using Japan A.A-67G Shimadzu. Electrical conductivity measurements of the complexes were recorded at room temperature for 10-3 M solutions of the samples in DMF using pw9527 Digital conductivity meter (Philips). Melting points were recorded by using Stuart melting point apparatus .chloride ion content were also evolution by(Mohr method),Magnetic susceptibility measurements were measured using Bruker magnet BM6 instrument at 298°K following the Faraday's method. The proposed molecular structure of the complexes were determinated by using chem. office program, 3DX (2006).

2-2General synthesis of the mixed ligands metal complexes

A solution of Furan-2-carboxylic acid (0.224 gm,2 m mol) in 50% (v/v) ethanol –water (10 ml) containing potassium hydroxide (0.112, 2mmol) and A solution of 1,10-phenanthroline (0.396gm,2 m mol) in ethanol (10 ml) were added simultaneously to a solution of $MCl_2.nH_2O$ (1 m mol) in 50% (v/v) ethanol –water, (10 ml) in the stoichiometric ratio.[2 FCA-:M: 2phen].(Scheme 1)the above solution was stirred for 1-houre and allowed to stand for overnight .the product formed was filtered off ,washed several times with 50% (v/v) ethanol –water to remove any traces of the un reacted starting materials. and dried in air ,and analyzed employing standard method.General schem (1) of reaction as follow :



Scheme (1) : Schematic representation Preparation of the Complexes [M(FCA)₂(phen)₂]

2-3-Metal determination

A known amount of each metal complex was digested with 20 ml of concentrated HNO3 and then diluted to a volume of 100 ml with deionized water. Then, the metal content in the complex was determined using atomic absorption spectroscopy.

2-4-Chloride Test

A 10mg of each complex was digested in nitric acid and subjected to chloride identification using 0.1 M AgNO3 solution. A white precipitate formed confirms the presence of chloride in the sample.

2-5-Antimicrobial activity of compounds and their complexes

The two ligands and their complexes were analyzed for their antimicrobial activity against four test organisms namely *E.coli, Bacillus, Staphylococcu and Pseudomonas* at a concentration of 100 μ g/ml using DMSO as a solvent.

3. Results and Discussion:

All the complexes are colored ,non-hygroscopic and thermally stable solids (Table-1), indicating a strong metalligand bond.

3.1. Characterization of Mixed-Ligand Metal Complexes.

Generally, the Mixed- Ligand Metal complexes were prepared by reacting the respective metal salts with the ligands using 1:2:2 mole ratio, i.e. one mole of metal salt : two mole of 1,10-phenanthroline and two moles of potassium Furan-2-carboxylate. The synthesis of mixed ligand Metal complexes may be represented as follows: $2 \text{ FCA H} + 2 \text{ KOH} \rightarrow 2 \text{ FCAK} + \text{H}_2\text{O}$

2 FCA K + phen + MCl₂ \rightarrow [M(FCA)₂(phen)₂] + 4H₂O + 2KCl

(where phen is 1,10-phenanthroline and FCA H is Furan-2-carboxylic acid).

The formula weights and melting points, are given in (Table I).Based on the physicochemical characteristics, it was found that all the complexes were non-hygroscopic, stable at room temperature. The solubility of the complexes of ligands was studied in various solvents. The complexes are soluble in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) while insoluble in water and common solvents such as ether, chloroform, and. benzene.

The melting point of the complexes observed in (Table I). show the complexes exhibit higher activity than their parent ligands indicating formation of complexes.(14)

3.1.The molar conductance

The molar conductance values of the the ligands complexes in DMF at 10^{-3} M concentration are found to be (2.12. - 18.15) μ S.cm⁻¹, for complexes of composition [M(FCA)₂(phen)₂] indicating their virtually non-electrolytes nature [16].

3.2. The atomic absorption measurements and chloride ion content

The atomic absorption measurements and chloride ion content (Table-1) for all complexes gave approximated values for theoretical values. On the base of physico-chemical measurements we propose deformed octahedral stereochemistry for the complexes.

3.3. FT-IR Spectra and the Mode of Bonding

The IR spectra of the complexes are compared with that of the free ligands to determine the changes that might have taken place during the complexation; The important infrared bands for the ligands and their complexes together with their assignments are listed in (Table -2). The IR spectra of the ligands show characteristic bands at 1622 and 1705 cm⁻¹ due to the v (C=O), v (C=N, pyridine ring nitrogen) functional groups, respectively. A strong band typical of C=C stretching frequency, v, are found in all the complexes in the region of 1633-1649 cm⁻¹ and 1627 cm⁻¹ in the free ligand uncoordinated 1,10- phenanthroline .

Inspection of IR spectra of complexes reveals that all the spectra are identical in all respects indicating that the bonding pattern must be the same in all the complexes. The observed shifts on the v(C=N) ring stretch regions after complexation to lower wave number by

18–61 cm⁻¹in the complexes indicates that these groups are involved in complexation [16,17] and indicate that they have been affected upon co-ordination to metal ion which also indicate the formation of M-N bonds whose IR stretching frequencies are all in the range of 459-525cm⁻¹.[18, 19]

The medium intensity band at 1224 cm⁻¹ \pm in the IR spectrum of the free (FACH) ligand assigned to furan ring v(C-O-C) stretching vibration was don't shifted suggesting the not involvement of the oxygen atom of furan ring moiety in coordination . The low frequency skeletal vibrations due to M–O and M–N stretching provide also direct evidence for the complexation. In the present investigation, bands in the (431-530) cm region of the complexes spectra have been assigned to v(M-O) vibration[18] The IR spectrum of the ligand (FACH) shows broad bands at 3142 - 3037cm⁻¹, which are attributed to the phenolic OH group. These bands are not found in all the complexes. The absence of the O-H stretching bonding vibrations from the spectra of the complexes indicates deprotonation of the O-H group. The results of IR spectral studies of complexes provide strong evidence for the complexation of the ligand with metal ion through carboxyl group (FACH). It is a simple rule that ionized and coordinated v(- COO⁻) stretching band occurs at 1595-1510 cm⁻¹ and 1363-1320cm⁻¹ which correspond to asymmetrical and symmetrical vibrations of the carboxyl group[16,17]. The IR spectra of the complexes show new bands at 501-687 and 412-478 cm⁻¹ assigned to ν (M-O) and ν (M-N), respectively. [18] Absorption assigned for v (-COO⁻⁾_{sym} was noticed at the range (1363-1320) cm⁻¹, shifted to lowered position by (62-19) cm⁻¹ while the band caused by $v(COO^{-})_{asym}$ appeared between (1595-1510) cm⁻¹ higher by (116-131) cm⁻¹ ¹, which indicates the coordination of the carboxylic group to the central metal ion (14,15) and the IR result shows that the all complexes coordinated via the N atoms from the 1,10-phenanthroline of the aromatic rings.

3.4. The UV-Visible Spectroscopy and Magnetic measurements:

The UV-Visible spectra of the free ligands Furan-2-carboxylic acid(FCA H) And

(1,10-phenanthroline.hydrate) and there metal complexes were carried out as DMF solutions (10^{-3} M) solutions. The values of band positions (nm) and molar absorptivity's

 $(\varepsilon_{max} L cm^{-1} mol^{-1})$ with the magnetic moment values for complexes are listed in Table 3 were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections. And together with the proposed assignments and suggested geometries. The results obtained are in good agreement with other spectra and the literature. [14-16]

A band at (270 nm) (37037 cm⁻¹), is assigned to $\pi \rightarrow \pi *$ for (FCA H), and a bands at 311 nm is assigned to $\pi \rightarrow \pi *$ π * transitions, while an intraligand band at (338 nm) is related to the $\pi \rightarrow n$ * transitions within the heterocyclic moieties [17] for (phen)ligand.

The Cu(II) complex exhibit normal magnetic moments (2.06 B.M.) indicating the distorted octahedral geometry, which is in agreement with data reported by several research workers [19-20]. These complex show broad asymmetric bands in the region 14144 cm⁻¹ and 33783 cm⁻¹ assignable to $2Eg \rightarrow 2T2g$ and charge transfer $L \rightarrow M$ (C. T) transition respectively [20]. These results reveal the distorted octahedral geometry for these complexes. The electronic spectrum of the Mn(II) exhibited two peaks, the first high intense peak at (286 nm) (34965 cm^{-1}) is due to the L \rightarrow M (C.T) while the second weak peaks at $(997nm)(10030 \text{ cm}^{-1})$, which assigned to $(6A1g \rightarrow 4Eg, 4T1g (4G), \text{ transition and } \mu \text{ eff} = 5.32B.M, \text{ which suggests octahedral geometry around the}$ central metal ion.

The cobalt(II) complex show a magnetic moments value of 4.72 B.M. at room temperature. These high values of magnetic moments are due to orbital contribution. The stoichiometries suggest a coordination number of six for the central cobalt(II) ion and attaining an octahedral geometry [20] around the cobalt(II) ions .

The Ni (II) complex exhibit tow peaks, the first high peak at (279 nm)(35842 cm⁻¹ is due to (C.T), second peak $(279 \text{ nm})(35842 \text{ cm}^{-1})$ is due to (C.T) is of ligand origin assignable to the intra ligand transitions $(\pi \rightarrow \pi^*/n \rightarrow \pi^*)$ localized predominantly on the five-membered ring and on C=N fragments of the Furan-2carboxylic acid and (1,10-phenanthroline)-ligands, respectively. However, the d-d transition in the spectrum could not be resolved. In general, if the electronic transitions for M(II) systems are spin forbidden and hence weak, and are often marked by charge transfer bands.

The Zn(II), Cd(II) and Hg(II)complexes did not display any peak in the visible region, no ligand field absorptions band was observed, therefore the bands appeared in the spectra of three complexes could be attributed to [charge transfer transition (($\pi - \pi^*$), ($n - \pi^*$)] in fact this result is a good agreement with previous work of octahedral geometry and magnetic susceptibility measurements for Zn(II), Cd(II) and Hg(II) (d^o)(white complexes) showed diamagnetic as expected from their electronic configuration.[18,19]

Table 1-The physica	l properties of the complexes

	M. p °c			Metal			
Compound	M.wt	Color	(de) °c	Am µS.cm².Mol ⁻¹	theory	exp	Cl %
C ₅ H ₄ O ₃ (FCA)	112.08	off-white	128 - 130	1.06	-	-	-
C ₁₂ H ₈ O ₂ . (phen)	180.21	White	290	2.6	-	-	-
C34H22MnN4O6	637.09	yellow	260de	18.15	8.62	8.99	Nil
C ₃₄ H ₂₂ FeN ₄ O ₆	638.40	red	130de	14.34	8.75	10.0	Nil
C ₃₄ H ₂₂ CoN ₄ O ₆	641.08	Gray	de224	14.80	9.19	9.79	Nil
C ₃₄ H ₂₂ NiN ₄ O ₆	641.25	green	200 de	6.40	9.15	10.0	Nil
C ₃₄ H ₂₂ CuN ₄ O ₆	646.10	blue	158 de	8.36	9.84	10.04	Nil
$C_{34}H_{22}ZnN_4O_6$	647.97	white	256 de	10.16	10.09	11.00	Nil
$C_{34}H_{22}CdN_4O_6$	694.97	white	240 de	2.12	16.17	17.22	Nil
C ₃₄ H ₂₂ HgN ₄ O ₆	782.5	light yellow	268 de	2.32	25.61		Nil

Am = Molar Conductivity

de = decomposition

Compound	<i>v</i> ОН	v (CH) cyclic	v (C=O)	v >C=N- stretch	v (C-O-C) Furan ring	v (-COO ⁻) asym	v (-COO ⁻) sym	ν Μ-Ο	ν Μ-Ν
FCA	3142vs	2590	1622	-	1226 s	1479m	1382m	-	-
phen	-	2790	-	1588	-	-	-	-	-
[Mn (FCA) ₂ (phen) ₂]	3072m	2937m	-	15 27s	1222 m	1510	1358m	485 (w)	508 (w)
[Fe(FCA) ₂ (phen) ₂]	3311s	2930w	1658w	1560s	1222 m	1516s	1320m	490 (w)	517 (w)
[Co (FCA) ₂ (phen) ₂]	3477s	2993s	1658m	1568s	1222 m	1595vs	1359s	431 (w)	525 (w)
[Ni (FCA) ₂ (phen) ₂]	3344s	2924s	1656m	1560s	1227 m	1517vs	1363s	527 (w)	459 (w)
[Cu (FCA) ₂ (phen) ₂]	3435s	2883m	1618m	1560m	1220 m	1519s	1355s	530 (w)	467 (w)
[Zn(FCA) ₂ (phen) ₂]	3059s	3049s	1656w	1560m	1222 m	1517vs	1363s	527 (w)	460 (w)
[Cd(FCA) ₂ (phen) ₂]	3049s	3007s	1618w	1570m	1222 m	1510vs	1342s	638m	416m
[Hg (FCA) ₂ (phen) ₂]	3057s	1012s	1618w	1570m	1222 m	1490 s	1346 s	632 m	410w

Table (2) : Some selected FT-IR frequencies (KBr) cm ⁻¹ of the ligands and their mixed ligand complexes.

(vs) very strong (s) strong, (m) medium, (w) weak

Compounds	λ (nm)	v ' (cm ⁻¹)	Possible assignment	µeff (BM)
C ₅ H ₄ O ₃ (FCAH)	270	37037	π→π* (C=C)	-
1,10-phenanthroline	311 338	32154 29586	$\begin{array}{c} \pi \rightarrow \pi \ (C=C) \\ n \rightarrow \pi^* \ (C=N) \end{array}$	-
[Mn (FCA) ₂ (phen) ₂]	286 997	34965 10030	$LMCT \\ 6A1g \rightarrow 4Eg, 4T1g \\ (4G)$	5.32
[Fe(FCA) ₂ (phen) ₂]	299 512	33444 19531	$LMCT \\ 5T2g \rightarrow 5E2g$	
[Co (FCA) ₂ (phen) ₂]	299 997	19562 10030	LMCT 4T1g →4A2g	4.72
[Ni (FCA) ₂ (phen) ₂]	279 597	35842 16750	LMCT 3A2g →3T1g	3.17
[Cu (FCA) ₂ (phen) ₂]	296 707	33783 14144	LMCT 2Eg→2T2g	2.06
[Zn(FCA) ₂ (phen) ₂]	286	34965	СТ	0.0
[Cd(FCA) ₂ (phen) ₂]	286	34965	CT	0.0
[Hg (FCA) ₂ (phen) ₂]	279	35842	СТ	0.0

Table 3- Electronic S	pectral data, m	agnetic moment,	of the studied c	omplexes and	two ligands
	. /			1	

Proposed molecular structure :

Based on the chemical composition and physico-chemical studies, the schematic structures shown in Scheme (1), it is tentatively suggested that all of the complexes show an octahedral geometry, the existence of Hexa coordinated $[M(C_{14}H_8N_2)_2(C_5H_3O_3)_2]$, were M(II)=Mn (II), Fe(II), Co(II), Ni(II), Cu (II), Zn(II), Cd(II), and Hg (II). proposed models of the species were built with chem3D shows in Fig (1). These possibly accommodate themselves around the metal atom in such a way that a stable chelate ring is formed giving in turn, stability to the formed metal complexes.



Figure (1):The proposed General structure of (1,10-phenanthroline) -(Furan-2-carboxylic acid) with metal (II) chlorides. complexes

Antibacterial activity

Antibacterial activities of the Furan-2-carboxylic acid and 1,10-phenanthroline ligands and there complexes were studied against four types of bacteria (gram –ve) and

(gram +ve). compounds and complexes when tested for their antimicrobial activity against four micro-organisms at a temperature of 37^{0} C ,it is observed that antimicrobial studies conducted on four bacteria revealed highest antimicrobial activities by Mn (II), Fe (II), Ni (II) complexes against all complexes of the metals. most of the complex samples tested showed high microbial activity as compared to their ligands. Higher bactericidal activity exhibited by the complexes than ligand reveals positive impact of coordination of metals with the ligand in enhancing the activity [25-26]. These activities are due to presences of –COO group, the aromatic rings. and (C=N) groups. See Table 3 and Figure (2):

Compound	E-coli	Pseudomonas	Staphylococcus	Bacillus
			aureus	
Control(DMSO)	5	7	10	5
Furan-2-carboxylic acid	5	5	6	5
1,10-phenanthroline	16	14	13	0
$[Mn (FCA)_2(phen)_2]$	12	14	11	13
[Fe(FCA) ₂ (phen) ₂]	11	13	10	0
$[Co (FCA)_2(phen)_2]$	0	0	0	0
[Ni (FCA) ₂ (phen) ₂]	15	12	12	12

Table 3- The antibacterial activity data of the ligands and
Mn (II),Fe(II),Co(II)and Ni(II), mixed ligand complexes



Figure (2): Chart of biological effects of some of the studied complexes

Conclusion

In conclusion, the Mn (II),Fe(II),Co(II),Ni(II),Cu(II),Zn(II),Cd(II),and Hg (II)complexes of mixed furan-2carboxylic acid and 1,10-phenanthroline are reported. The resultant complexes are characterized by melting point, conductivity measurement, UV-Vis and Infra-red spectroscopy. Investigation of antimicrobial activities was carried out against the tested organisms. All the complexes are found to be in octahedral geometry.

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