Synthesis & Identification of Series from New Ligands derived from 5,6-diformyl-4-Chloro methoxy benzene and Complexation of One of Them with (Zn^{2+} ,Cd^{2+})

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Abstract

In this study, four ligands were synthesized from reaction of 2,6-diformyl-4-chloro methoxy benzene with different amino compounds such as(2-amino furan ,2-amino thiophene ,2-amino thiazole , 2-amino sulphadiazine) to produce ligands [1-4] ,the synthesized ligands is named {N,N-(5-Chloro-2-Methoxy-1,3-phenylene)bis (Methan-1-yl-ylidene)dithiophen-2-amine(FCM),N,N-(5-Chloro-2-Methoxy-1,3-phenylene)bis(Methan-1-yl-ylidene)difuran-2-amine (TCM),N,N- (5-Chloro-2-Methoxy-1,3-phenylene)bis (Methan-1-yl-ylidene)dithiazol-2-amine (ZCM),N,N-(5-Chloro-2-Methoxy-1,3-phenylene) bis(Methan-1-yl-ylidene) (SCM)} respectively.The ligand (ZCM) is used as a ligand with (Zn^{2+} ,Cd^{2+}) to formation of complexes and study of optimal conditions of complexes (stoichiometric study ,pH ,concentration of metals and ligand ,molar conductance) .All ligands with complexes were studied for antibacterial and antifungi activity.All ligands with complexes were characterized by (H.NMR–spectra ,FT.IR–spectra (C.H.N)-analysis, UV-Vib-spectra) , melting points.

Keyword :complexes of(Zn^{2+} ,Cd^{2+}) ,schiff ligand.

الخلاصة

تضمنت الدراسة تحضير أربع ليكاندات من تفاعل 6,2-ثنائي فورميل –4–كلورو –ميثوكسي بنزين مع مركبات أمين مختلفة تمثلت ب (2–أمينوفيوران , 2–أمينوثايوفين ,2–أمينو ثيازول , 2–أمينو سلفاديازين) لينتج ليكاندات [1-4] ,سُميت الليكاندات المحضرة بـ

{N,N-(5-Chloro-2-Methoxy-1,3-phenylene) bis(Methan-1-yl- ylidene)dithiophen-2-amine (FCM),N,N-(5-Chloro-2-Methoxy-1,3- phenylene) bis(Methan-1-yl-ylidene) difuran-2-amine(TCM), N,N- (5-Chloro-2-Methoxy-1,3-phenylene) bis (Methan-1-yl -ylidene) dithiazol-2-amine(ZCM),N,N-(5-Chloro-2-Methoxy-1,3-phenylene) bis (Methan-1-yl-ylidene) (SCM)}

على التوالي .المركب (ZCM) أُستُخدم كليكاند مع أيوني (Zn^{2+} ,Cd^{2+}). لتكوين معقدات ودراسةالظروف المثلى لتعقيدها (تكافؤية المعقدات , الدالة الحامضية ,تركيز الليكاند والأيونين ,التوصيلية المولارية , النسب

المولية) جميع الليكاندات المحضرة والمعقدات دُرست فعاليتها البكتيرية والفطرية وكذلك ,شُخصت بتقنيات (طيف الاشعة تحت الحمراء, طيف الرنين النووي المغناطيسي ,التحليل الدقيق للعناصر , الاشعة فوق البنفسجية والمرئية) ودرجات الانصهار.

الكلمات المفتاحية : التعقيد مع ايون الكادميوم (II) و ايون الخارصين (II) , قواعد شيف .

Introduction

The synthesized aniles in the present study are containing two imine groups which linked with aromatic heterocycles such as furan ,thiophene ,thiazole sulphadiazine ,these imine compounds were clinically known and have a wide range of bio activities such as antibacterial [1,2]drugs [3,4],in the biological engineering ,in synthesis of heterocyclic compounds [5,6]another applied fields [7-10]in due to several methods for preparing aniles were described in literature , but the famous method for synthesis is carried out through condensation reaction of carbonyl compounds with imine compounds of schiff bases are most used are chelating ligands in coordination chemistry ,they are also useful in catalysis and in medicine , the utility of schiff bases lay in their usefullness as synthons in the synthesis of bioactive molecules, schiff bases belongs to a widely used group of organic intermediates important for production compounds as a ligand with transition metals to formation complexes [11-13].

Experimental

All chemicals from Merk and Fluka companies . All measurments were carried out by : melting points in electrothermal 9300,LTD ,U.K .,FT.IR-spectra :in fourrier transform infrared shimadzu 8300,KBr-disc ., H.NMR- spectra in DMSO as a solvent in ppm unit , (C.H.N)-analysis in EA-Erek.

Synthesis of ligands [(FCM),(TCM),(ZCM),(SCM)]:

Acorrding to procedur[5,14] ,a mixture of (0.01 mole, 1.98g) from 2,6-diformyl-4-chloromethoxy benzene with one of [(0.02mole ,1.64g of 2-amino furan) , (0.02mole, 1.98g of 2-amino thiophene),(0.02mole ,o.20g of 2-amino thiazole),(0.02mole ,0.50gm of 2-amino sulphadiazine)] respectively in presence of absolute ethanol in refluxing for (4-6)hrs ,the precipitate was filtered and recrystallized to yield (84, 87,89 ,83)% ligands [(FCM), (TCM) ,(ZCM) ,(SCM)] respectively .

Synthesis of complexes of ligands (ZCM)with (Zn^{+2},Cd^{+2}):

According to procedure[5] the hot ethanolic solution(5ml) of the metal chloride (Zn^{+2},Cd^{+2}) respectively with ethanolic solution of ligand (ZCM) in (1:1) (ligand: metal) molar ratios was mixed ,respectively after stirrings (2hrs) , precipitates formed , the solids were filtered ,dried , recrystallized from absolute ethanol to give complexes (Zn^{+2},Cd^{+2}) respectively .

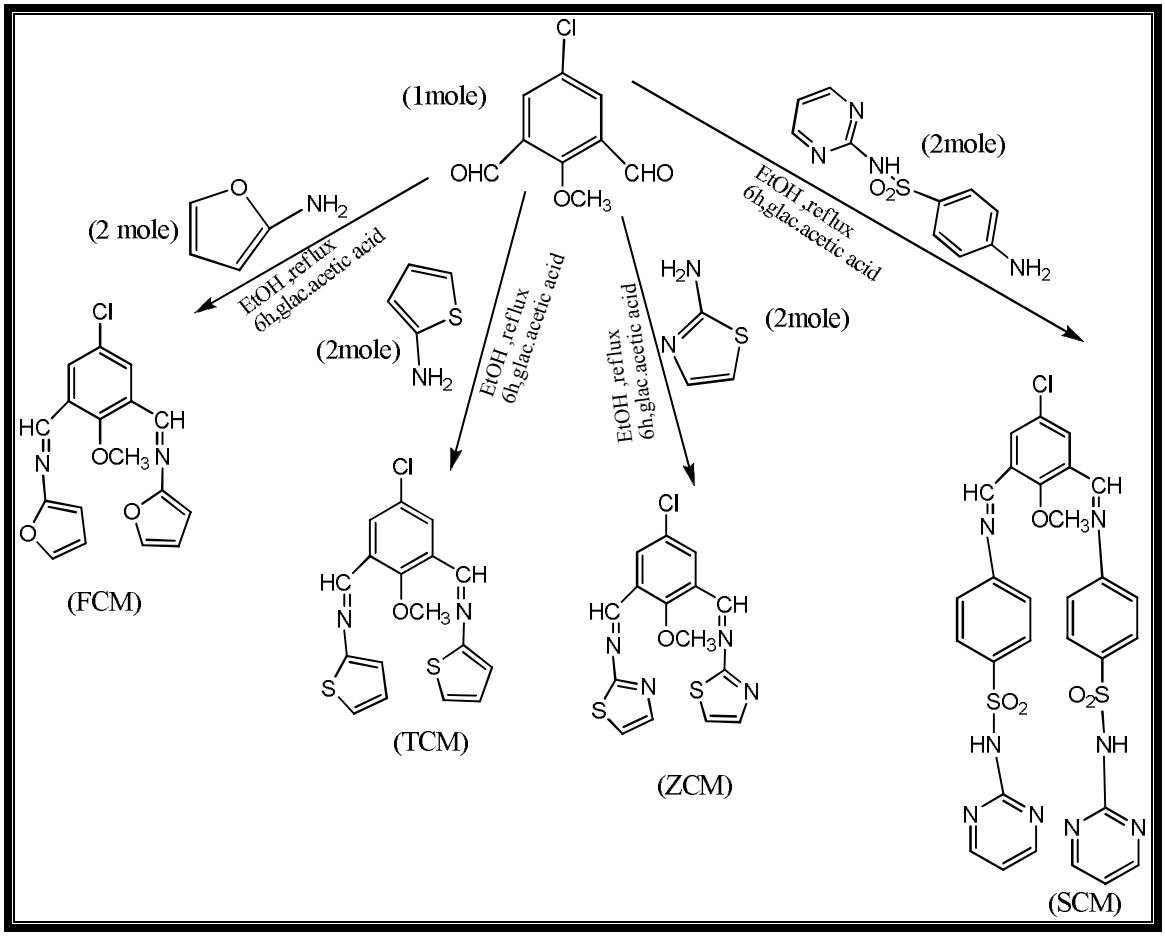


Fig (1)Reaction scheme: Synthesis & Identification of Series from new Ligands derived (2,6-diformyl-4-chloro methoxy benzene)

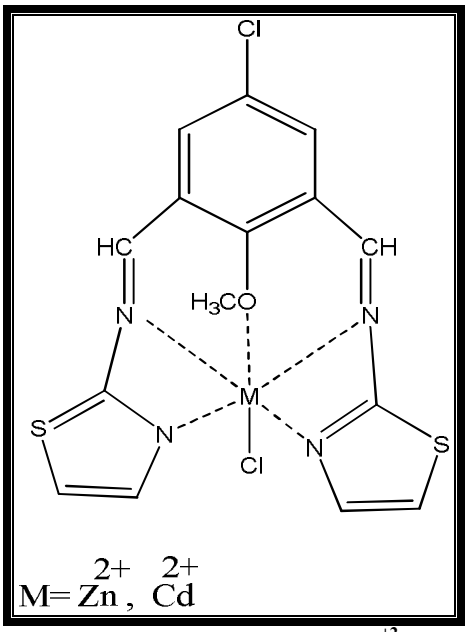


Fig (2) Complexation ZCM with Zn^{+2} and Cd^{+2}

Results and Discussion

All compounds were characterized by different methods :

Study of optimal condition :

The optimal conditions for formation of complexes were studied in this work ,from calibration curves(3) ,the optimal concentration of ligand (ZCM) is ($1*10^{-3}$) and concentration of metals (($0.95*10^{-4}$ m from Zn^{2+}) and ($0.8*10^{-4}$ m from Cd^{2+}) ,while optimal pH was (7) ,other studies such as stochiometric of complexes was (M:L) (1:1) By using mole ratoi method through taking of concentration from ligand and metal, this method gives ratio of (ligand: metal), figuer(5), while molar condaction indicated that the (Cl) atom participate hndicated in coordination for this reason, the suggestion figers of complexes are tetra hedral throng coordination from (four Nitrogen atom atom and one oxygen atom of methoxy group with Chloride ion. (UV-VIS)-Spectra shows red shift in complexes compared with ligand (in colour and λ_{Max}),figuer (3,4).All these measurments a (C.H.N)- analysis gave evidance of suggestion figurs of complexes (six-coordintion)

I.R - spectra :

The I.R- Spectra shows:

Band at (1164) cm^{-1} due to (C-O-C) in furan cycle in compound (FCM), band at (729)cm^{-1} due to (C-S) in Thiophene cycle in compound (TCM), bands at (729, 1537)cm^{-1} due to (C-S), C=N) endo cycle in Thiazol rang in compound (ZCM), bands to (SO_2-Sulphon, C=N) endo cycle in Sulphadazin in compound (SCM). I.R -spectra of four ligands shows bands at (1620-1645)cm^{-1} due to Imine[15] group (CH-N) in ligands ,but this band shifted at (1606) cm^{-1} in complexes of ligand (ZCM) with (Zn^{2+} ,Cd^{2+}) due to coordination of nitrogen atom from azomethine group (CH=N) with ions (Zn^{2+} , Cd^{2+})in the two complexes and appearance of other bands[15] at (470,499) cm^{-1} due to (M-N) and other bands[15] at (565 ,590) cm^{-1} due to (M-O) for formation of two complexes with (Zn^{2+} , cd^{2+}) .

UV-VIS-spectra:

Uv-vis-spectrum for FCM,TCM, ZCM, SCM, shows maximum absorbance at (λ_{Max}=348nm,352nm, 360nm, 375nm) respectively,but the spectrum of the complex between ZCM and Zinc(II) as [Zn(ZCM)Cl]giving maximum absorbance at λ_{max}= 410nm, but the complex with Cd(II) as [Cd(ZCM)Cl] was λ_{max}= 450.

H.NMR -spectra : Showes other signals at δ(5.27-5.74) due to protons of furan ring, signal at δ(6.93-7.07) due oin compound (FCM), signal at δ(6.53) due to protons thiophene ring, signal at δ(7.34-7.39) due to protons at δ(6.34-6.37) due to protons of Thiazol ring, signal at δ(7.26-7.81) due to phenyl group in compound (ZCM), signals at δ (5.95) due to proton of Sulphanamide, signals at δ(6.34-6.37) due to diazine cycle in compound (SCM) other signals δ (8.78 ,8.5 ,8.62 ,8.52) for proton of azomethine[5,14] group (CH-N) in all ligands ,other signals at δ (3.83 ,3.15, 3.41 ,3.8) respectively for protons of methoxy group (OCH_3) in all ligands ,but these signals shifted at coordination of ligands (ZCM) with (Zn^{2+} ,Cd^{2+}) in complexes .

Biological study :

The ligands with complexes were studied for their antimicrobial activity against bacteria (*staphyllococcus .aureus*) and fungi (Aspergillus *niger*) by using holes methods[15,16] ,the complexes of ligand (ZCM) with (Zn^{2+} ,Cd^{2+}) exhibited high activity and strong inhibitory action at ($1x10^{-3}$)M to wards bacteria than fungi and complexes have high active than ligands alone due to presence of metals in complexes to break wall of cell in bacteria

Table(1):melting point, M.F and Element. analysise

Compounds	M.p(c°)	$\Omega^{-1}.cm^{-1}.mol^{-1}$ " Molar conductance	λ_{max}	Calc ./ found			
				C%	H%	N%	M%
$C_{17}H_{13}O_3N_2Cl$ (FCM)	178	--	348	62.100 62.00	3.957 3.806	8.523 8.381	/
$C_{17}H_{13}ON_2S_2Cl$ (TCM)	190	--	352	56.588 56.347	3.606 3.418	7.766 7.507	/
$C_{15}H_{11}ON_4S_2Cl$ (ZCM)	197	--	360	49.655 49.381	3.034 3.00	15.448 15.209	/
$C_{29}H_{23}O_5N_8S_2Cl$ (SCM)	207	--	375	52.528 52.283	3.471 3.208	16.905 16.609	/
$C_{15}H_{11}ON_4S_2Cl_2Zn$ [Zn(ZCM)Cl]	238	18.23	410	38.850 38.711	2.374 2.215	12.086 12.100	14.117 14.02
$C_{15}H_{11}ON_4S_2Cl_2Cd$ [Cd(ZCM)Cl]	250	20.45	450	35.265 35.321	2.155 2.043	10.971 10.993	2.023 22.030

Table (2):FT.IR data (cm^{-1}) ofligands with complexes

Compounds	Name of compounds		Only (Importance groups)		
		(CH=N)schiff	(M-N)	C=N endocycle	(M-O)
(FCM)	N,N-di((2-furan)-2,6-diformyl amine)-4-chloro methoxy benzene	1645	--	- -	--
(TCM)	N,N-di((2-thiophene) -2,6-di formly amine -4-chloro methoxy benzene	1625	--	- -	--
(ZCM)	N,N-di((2-thiazole)-2,6-diformly amine)-4-chloro methoxy benzene .	1645	--	1537	--
(SCM)	N,N-di((2-sulphadiazine)-2,6-diformly amine)-4-chloro methoxy benzene	1620	--	1535	--
[Zn(ZCM) Cl]	complex	1606	470	1537	565
[Cd(ZCM) Cl]	Complex	1620	499	1539	590

Table (3): biological activity of ($1x10^{-3}$)M of ligands with complexes

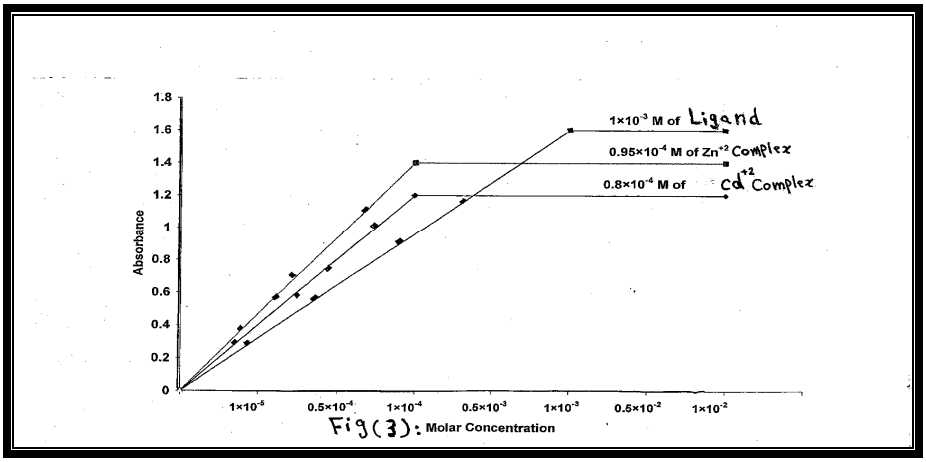
Compounds	Zone of Inhibition	
	Bacteria staphyllococus.aureus	Fungi Aspergillus
(FCM)	8	---
(TCM)	12	6
(ZCM)	13	6
(SCM)	19	11
[Zn(ZCM)Cl]	22	14
[Cd(ZCM)Cl]	23	14

Table(4): Solving ability of ligands and complexes

complex	Solvent(1)	Solvent(2)	Solvent(3)
FCM	Ethanol	DMSO	Methanol
TCM	Ethanol	DMSO	Methanol
ZCM	Ethanol	DMSO	Methanol
SCM	Ethanol	DMSO	Methanol
[Zn(ZCM)Cl]	Ethanol	DMSO	Methanol
[Cd(ZCM)Cl[	Ethanol	DMSO	Methanol

Table (5): Colour and λ_{Max} of ligands and complexes

compound	λ_{Max}	colour
(FCM)	348	Bill yellow
(TCM)	352	Yellow
(ZCM)	360	Yellow
(SCM)	375	Orang yellowish
[Zn(ZCM)Cl]	410	Orang
[Cd(ZCM)Cl]	450	Deep-orang



Fig(3):

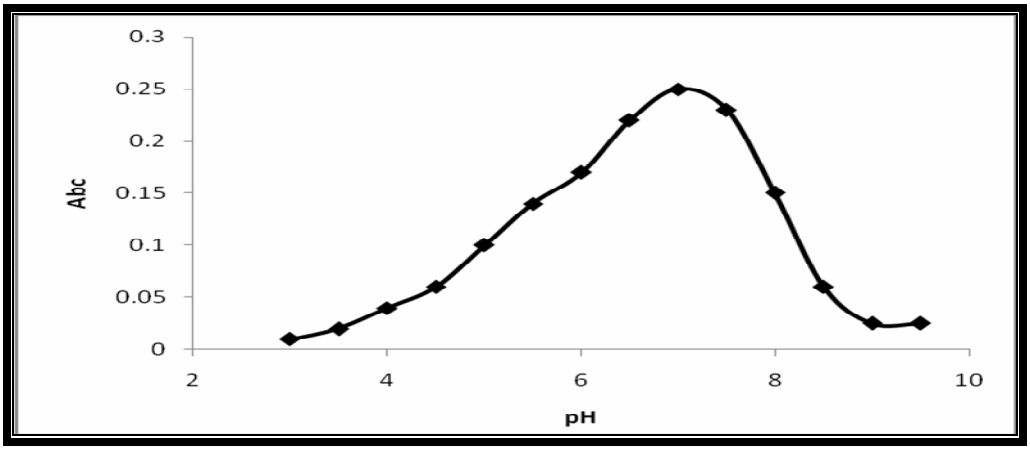


Fig (4) : Variation of pH with the absorbance of M (II)- Complexes

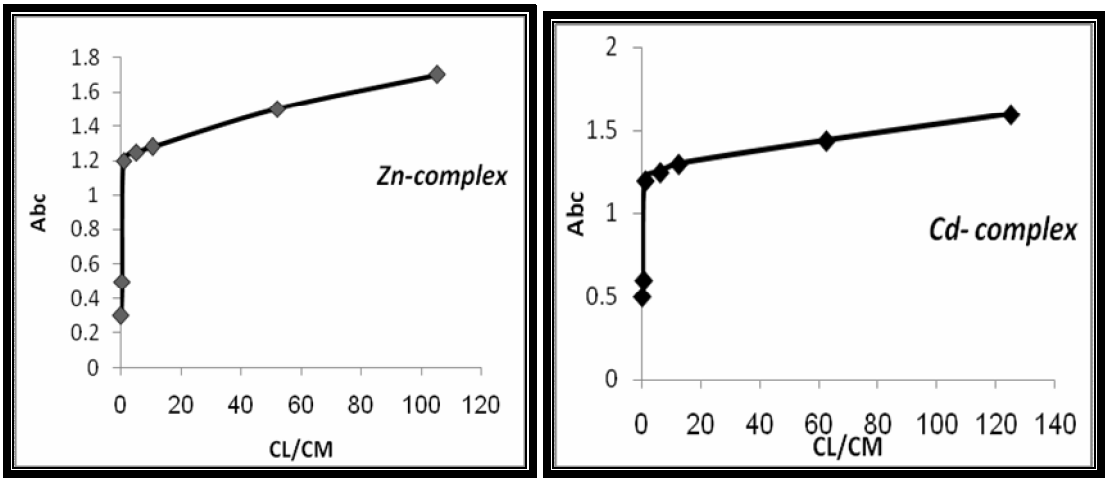
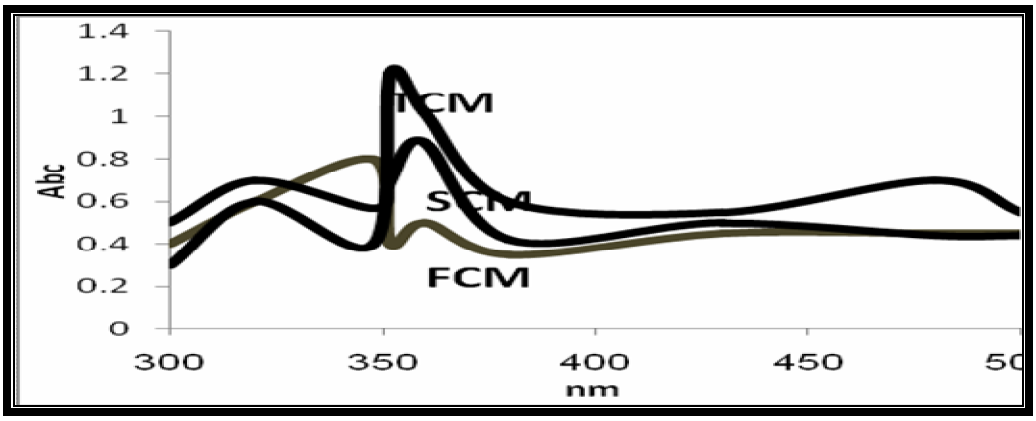


Fig (5) : ***Mole ratio method*** **of** ***M(II)- complex***



Fig(6): UV-VIS Spectrum of ligands(TCM,SCM,FCM)

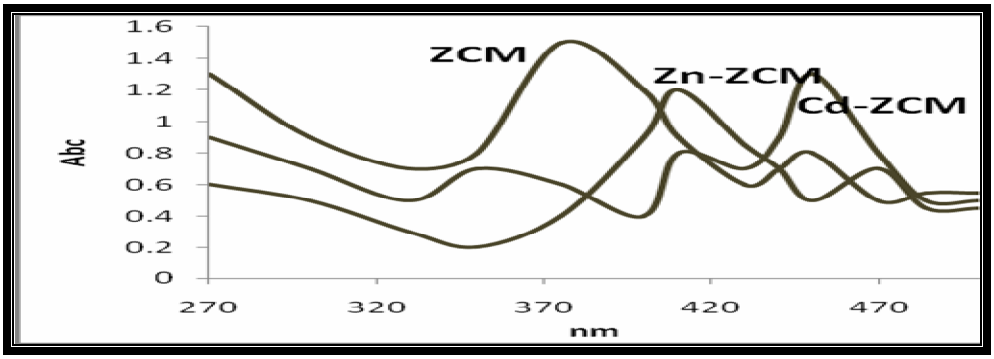


Fig (7): UV-VIS Spectrum of ligand (ZCM) and M(II)-complexes

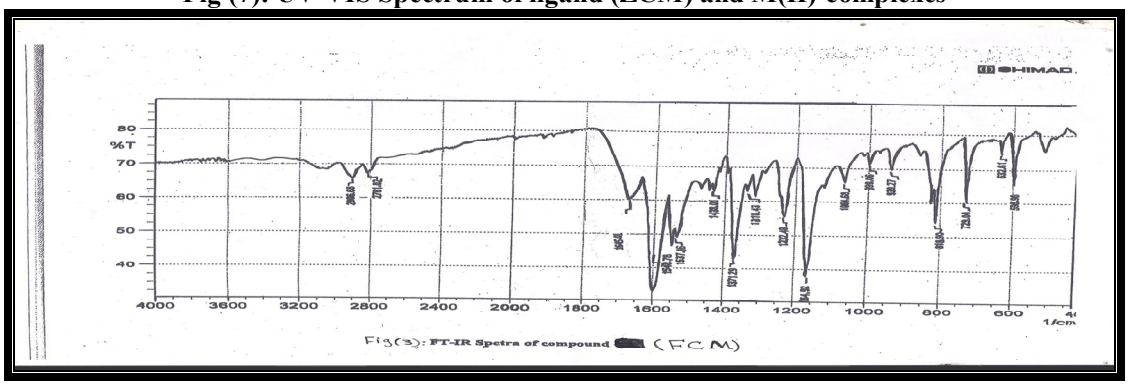


Fig (8); FT-IR Spectra of compound FCM

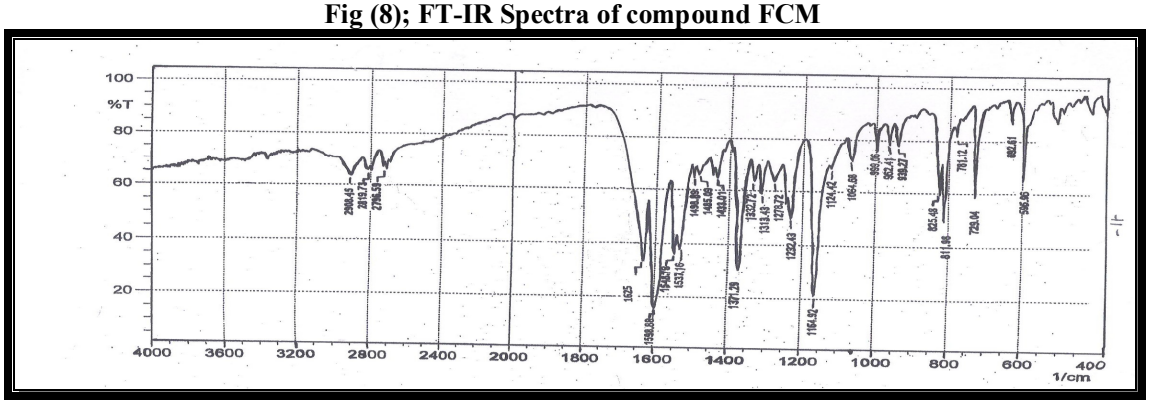


Fig (9); FT-IR Spectra of compound TCM

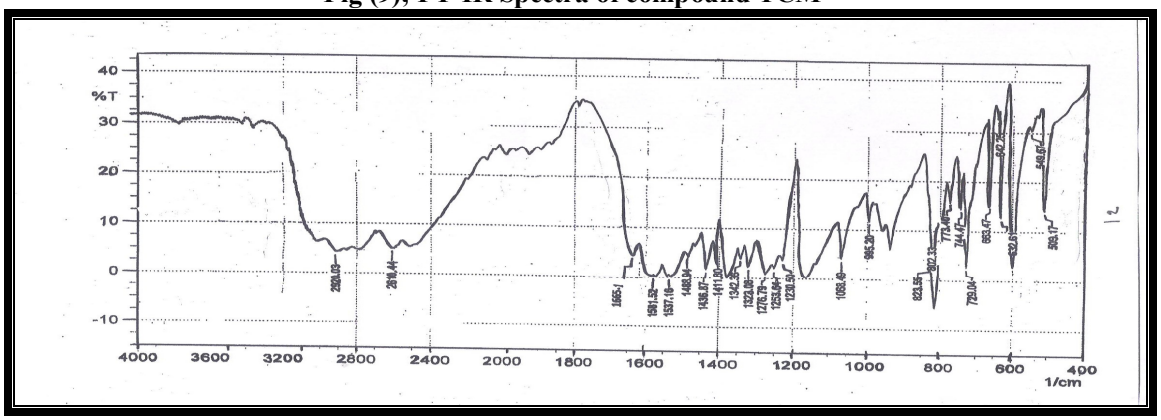


Fig (10); FT-IR Spectra of compound ZCM

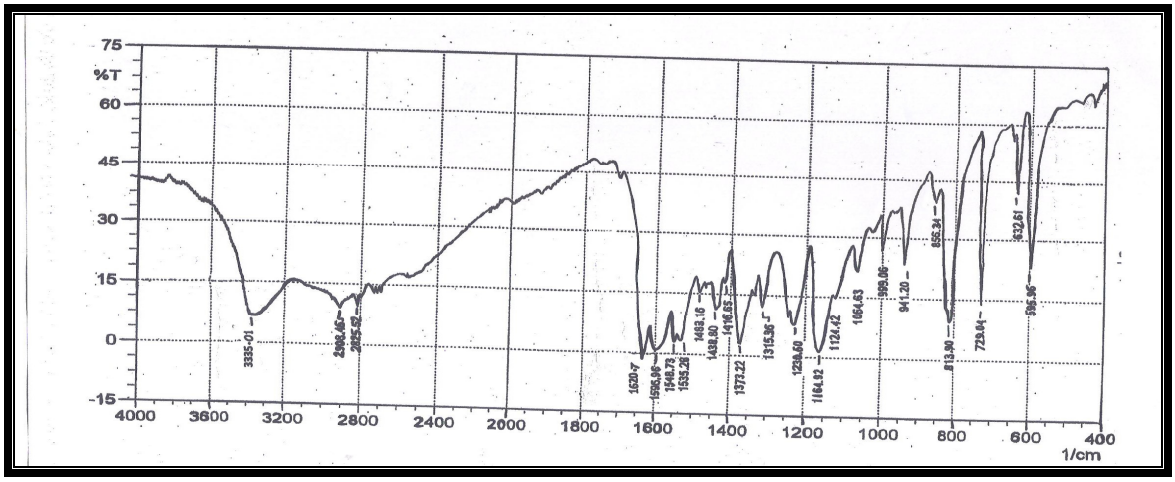


Fig (11); FT-IR Spectra of compound SCM

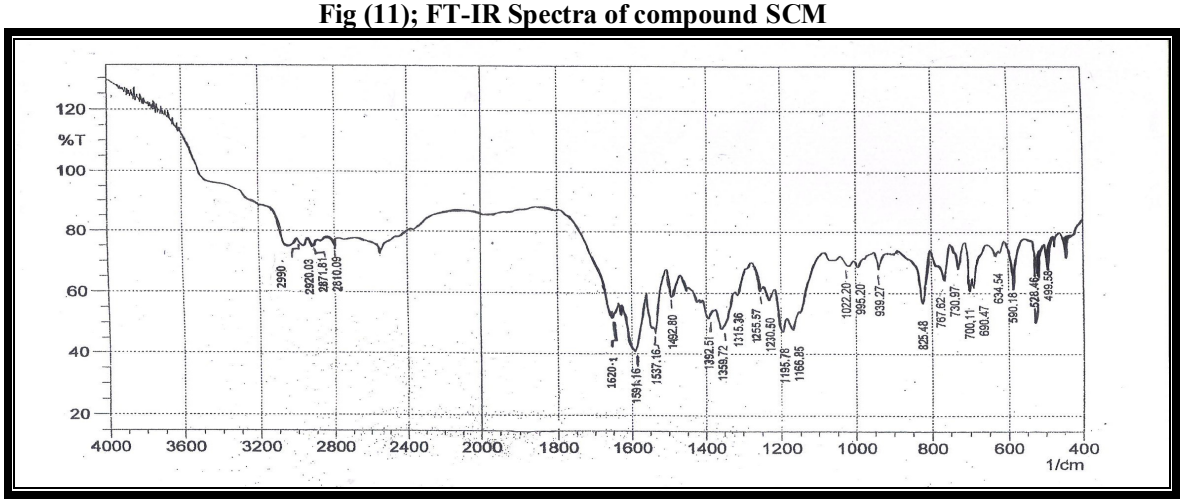


Fig (12); FT-IR Spectra of compound [Cd(ZCM)Cl]

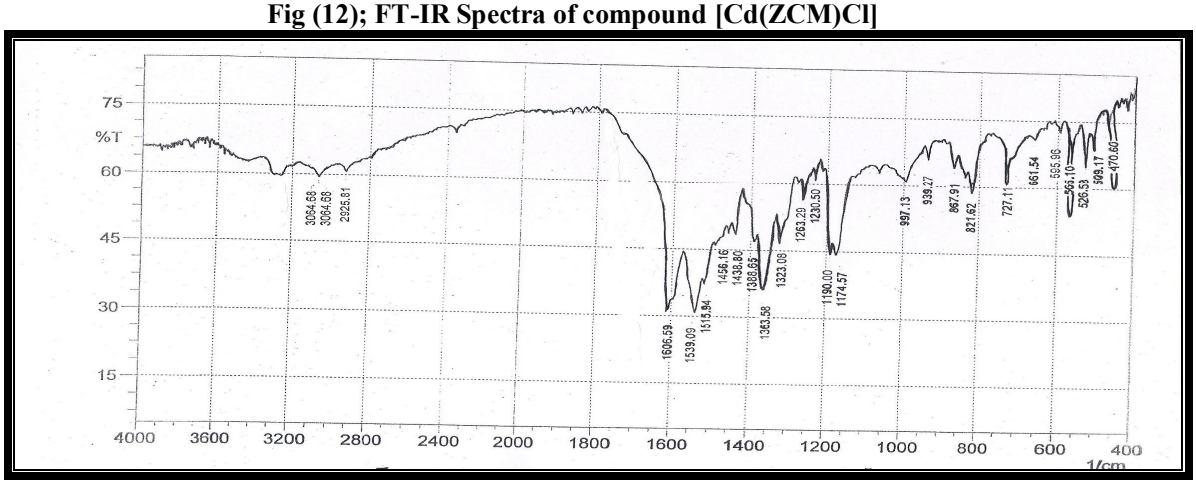


Fig (13); FT-IR Spectra of compound [Zn(ZCM)Cl]

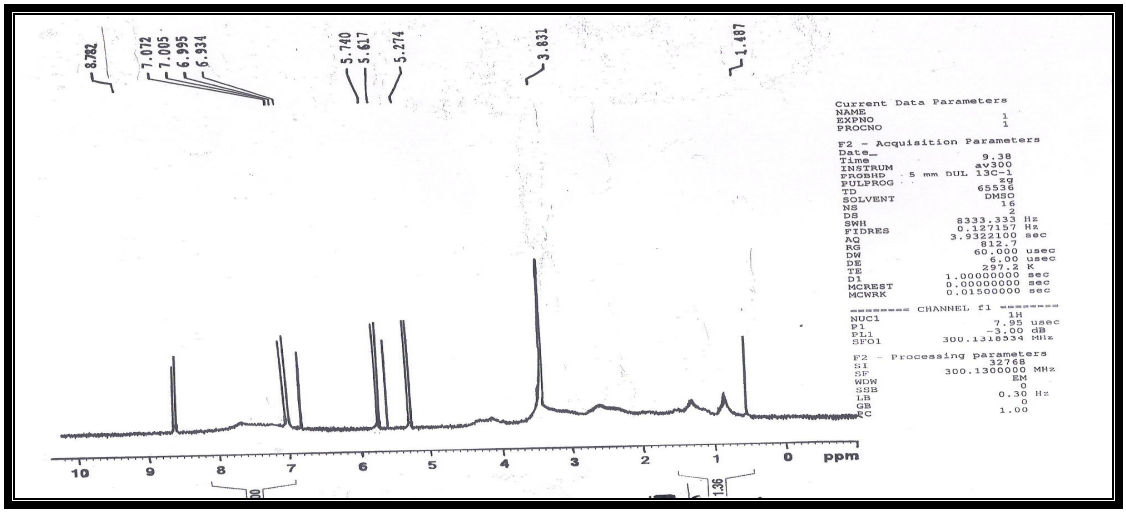


Fig (14) ; HNMR-Spectrum of compond FCM

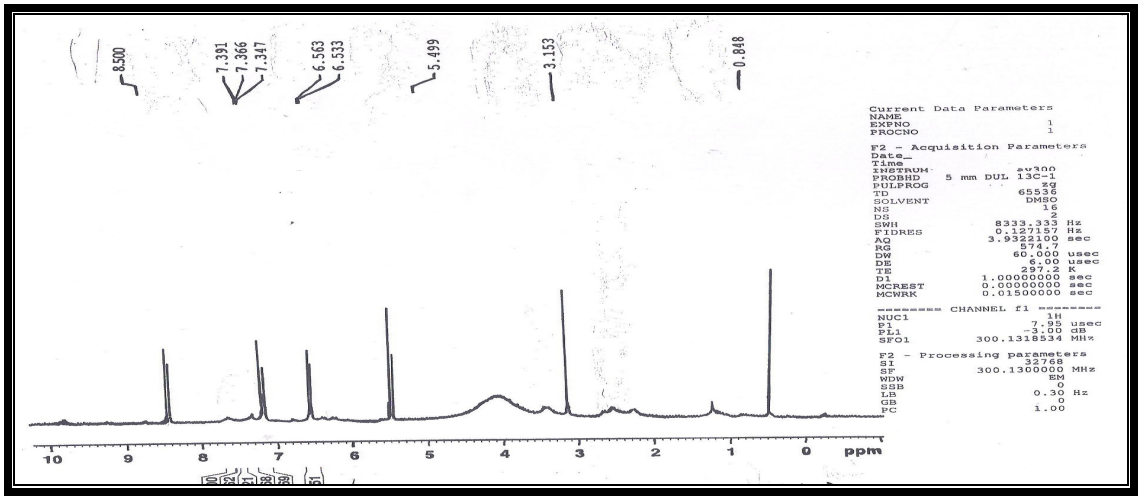


Fig (15) ; HNMR-Spectrum of compond TCM

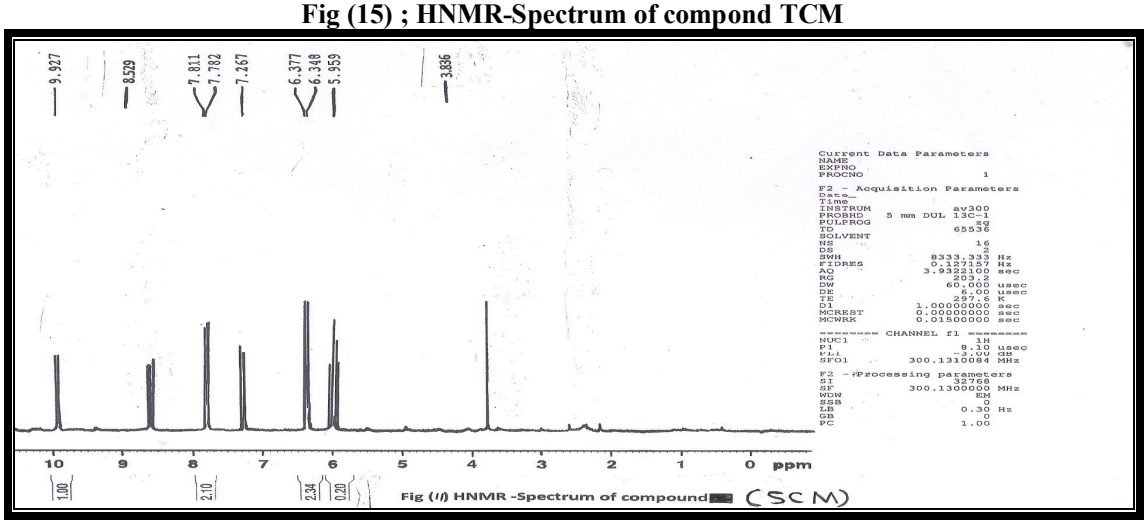


Fig (16) ; HNMR-Spectrum of compond SCM

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