ISSN : 0974 - 746X Volume 7 Issue 1

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 7(1), 2012 [1-8]

Antimicrobial activities of new transition metal complexes of furan-2-carboxaldehyde phenoxyacetyl hydrazone (HFCPA)

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Received: 20th September, 2011 ; Accepted: 20th October, 2011

ABSTRACT

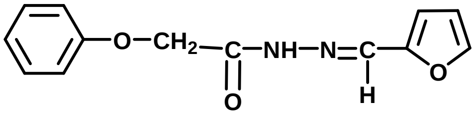
The synthesis and characterization of complexes of Co(II), Cu(II), Ni(II), Cd(II), Pd(II) and UO_2(VI) with furan-2-carboxaldhyde phenoxyacetyl hydrazone (HFCPA) (Structure 1) are reported. Elemental analyses, molar conductivities, magnetic measurements and spectral (IR and visible) studies have been used to elucidate their structure. The IR show that (HFCPA) behaves as neutral or mononegative bidentate ligand. Different stereochemistries are proposed for each of the Co(II), Cu(II) and Ni(II) complexes on the basis of spectral and magnetic studies.

KEYWORDS

Hydrazone;
NMR;
ESR;
Corrosion;
Antimicrobial activities.

INTRODUCTION

Interest in hydrazon chemistry has flourished for many years, largely as a result of its wide range of uses in numerous industrial and biological fields[1-14], besides having good complexing ability, and their activity increases on complexation with metal ions. Several works have been reported on hydrazone of transition metals complexes of 2-furaldhyde[15-20]. In this paper, we report the synthesis and spectroscopic characterizations of new complexes of Co(II), Cu(II), Ni(II), Cd(II), Pd(II) and UO_2(VI) with furan-2-carboxaldhyde phenoxyacetyl hydrazone (HFCPA, structure 1), studying the inhibition corrosion of the ligand and its antimicrobical activities of some metal complexes.



Structure (1)

EXPERIMENTAL

All chemicals used are BDH (British Drug LTD, England) quality.

Synthesis of the ligand

Furan-2-carboxaldhyde phenoxyacetylehydrazone (HFCPA) was prepared by refluxing an ethanolic solution (100 ml) of phenoxyacetylhydrazine (16.6 gm, 0.1 mol) and Furan-2-carboxaldehyde (9.6 ml, 0.1 mol) for 0.5 h. Upon cooling, a pale brown crystal separated out. The product was filtered off, washed with ethanol and diethylether, recrystllized from absolute ethanol and finally dried in a desicator over fused $CaCl_2$, yield ≈ 22.3gm, m.p 128 o C.

SYNTHESIS OF METAL CHELATES

The complexes, $[M(HFCPA)Cl_2(H_2O)_n]$, (M=

Co(II), Ni(II); n= 2 or Cd(II), n= 0) were prepared by adding an ethanolic solution (50 ml) of 1 mmole of HFCPA to a solution of 1 mmole of metal chloride in 25 ml absolute ethanol. The mixtures were heated under reflux for 1 h.

The complexes, $[M(FCPA)_2(H_2O)_n]$, (M=Co(II), Ni(II); n= 2 or M= Cu(II), Zn(II); n= o) were prepared by mixing an ethanolic solution (50 ml) 2 mmole of HFCPA in absolute to a solution of 1 mmole of the corresponding metal acetates in 25ml ethanol or water. The $[UO_2(FCPA)(OAc)(H_2O)_2)]$ complex was prepared by the same method using a solution of 1 mmole of HFCPA in 25 ml absolute ethanol. The reaction mixtures were heated under reflux for 1 h.

PHYSICAL MEASUREMENTS

The metal and chloride contents were analyzed by standard method (Vogel, 1989). IR spectra were recorded on a Mattson 5000 FTLR Spectrometer as KBr discs; electronic spectra in dimethylformamide (DMF) were obtained using an UV2-100 Unicam UV-visible spectrometer. Magnetic moments at 25° C were determined using a Gouy balance. H^1 NMR spectra were recorded on Prucker Ac 400 Spectrometer at King Abd El-Aziz University. Molar conductivities in DMSO at 25^o C were measured using a type CD6NGT Tacussel Conductivity Bridge.

RESULTS AND DISCUSSION

The physical data of the complexes together with their elemental analyses and conductivities are listed in TABLE 1. The formation of complexes may be represented by the following equation.

$$\mathbf{MCl_2 + HFCPA \xrightarrow[\text{Reflux, 1 h}]{\text{EtOH}} [M(HFCPA)Cl_2(H_2O)_2]} \tag{1}$$

(M = Co(II) or Ni(II))

$$\mathbf{M(OAc)_2 + 2HFCPA \xrightarrow[\text{Reflux, 1 h}]{\text{Aqueous EtOH}} [M(FCPA)_2(H_2O)_n]+2AcOH} \tag{2}$$

(M=Co(II), Ni(II); n=2 or M=Cu(II), Zn(II); n=0)

$$\mathbf{UO_2(OAc)_2 + HFCPA \xrightarrow[\text{Reflux, 0.5 h}]{\text{EtOH}} [UO_2(FCPA)OAc(H_2O)_2]+AcOH} \tag{3}$$

$$\mathbf{CdCl_2 + HFCPA \xrightarrow[\text{Reflux, 1 h}]{\text{EtOH}} [Cd(HFCPA)Cl_2]} \tag{4}$$

TABLE 1 : Analytical and physical data of HFCPA and its metal complexes.

Compound	Empirical Formula	Yelid %	Color	M.P. ^oC	% calc (found)				Λ^a_m in DMSO
					C	H	M	Cl-	
HFCPA	$C_{13}H_{12}N_2O_3$	85	Piege	128	63.9 (63.7)	5.0 (5.0)	-	-	-
$[Co(HFCPA)Cl_2(H_2O)_2]$	$CoC_{13}H_{16}N_2O_5Cl_2$	80	Violet	212	38.1 (38.0)	3.9 (4.1)	14.4 (14.3)	17.3 (17.7)	12
$[Ni(HFCPA)Cl_2(H_2O)_2]$	$NiC_{13}H_{16}N_2O_5Cl_2$	75	Green	250	38.1 (38.4)	3.9 (4.0)	14.3 (14.2)	17.34 (17.6)	10
$[Co(FCPA)_2(H_2O)_2]$	$CoC_{26}H_{26}N_4O_8$	70	Brown	285	53.7 (53.4)	4.5 (4.6)	10.1 (10.0)	-	6
$[Ni(FCPA)_2(H_2O)_2]$	$NiC_{26}H_{26}N_4O_8$	75	Orange	222	53.7 (53.8)	4.5 (4.5)	10.1 (10.0)	-	9
$[Cu(FCPA)_2]$	$CuC_{26}H_{22}N_4O_6$	80	Brown	215	56.8 (56.6)	4.0 (4.2)	11.6 (11.7)	-	4
$[Zn(FCPA)_2]$	$ZnC_{26}H_{22}N_4O_6$	70	Grey	245	56.6 (56.4)	4.0 (3.8)	11.8 (11.6)	-	3
$[UO_2(FCPA)(OAc)(H_2O)_2]$	$UC_{15}H_{17}N_2O_9$	80	Brown	262	29.6 (29.7)	2.8 (2.6)	39.2 (39.4)	-	2
$[Cd(HFCPA)Cl_2]$	$CdC_{13}H_{12}N_2O_3Cl_2$	80	Grey	243	36.5 (36.6)	2.8 (2.5)	26.3 (26.2)	16.6 (16.5)	6

$(\Lambda^a_m) = \Omega^{-1}\ cm^2\ mol^{-1}$

The results indicates that all metal complexes are stable in air and insoluble in most organic solvent and most of them are completely soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO) the molar conductivities (□m) in DMSO at 25° C (TABLE 1) for all complexes are in the range 2 - 12 ohm^{-1} cm^2mol^{-1}, indicating their nonelectrolytic nature[21].

IR AND H^1NMR SPECTRAL STUDIES

The principal IR bands of (HFCPA) and its metal complexes are listed in TABLE 2. The IR spectrum of (HFCPA) (Figure 1) shows a very strong band at 1683 cm^{-1} attributed to υ(C=O)[22]. Two medium intensity band at 1645 and 1012 cm^{-1} are assigned to υ(C=N)[23] and υ(N-N)[24], respectively. The stretching vibration band of the NH group[25] lies at 3190 cm^{-1}. The breathing vibration band of the furan ring and the bending vibration of (C-O-C)[18] group appear at 1082 and 1293 cm^{-1}, respectively.

TABLE 2 : IR spectral data of HFCPA and its metal complexes.

Compound	υ(C=O)	υ(C=N)	ν(>C=N-N=C<)	$\delta^{(C\text{-}O\text{-}C)}$	υ(N-N)	υ(C-O)	Furane breathing	υ(M-O)	υ(M-N)
HFCPA	1683	1645	-	1293	1012	-	1082	-	-
$[Co(HFCPA)Cl_2(H_2O)_2]$	1661	1624	-	1273	1025	-	1086	518	450
$[Ni(HFCPA)Cl_2(H_2O)_2]$	1661	1624	-	1272	1024	-	1087	521	456
$[Co(FCPA)_2(H_2O)_2]$	-	-	1620	1295	1046	1335	1085	480	445
$[Ni(FCPA)_2(H_2O)_2]$	-	-	1620	1296	1039	1334	1082	500	470
$[Cu(FCPA)_2]$	-	-	1618	1296	1051	1334	1081	485	440
$[Zn(FCPA)_2]$	-	-	1618	1289	1016	1344	1079	503	450
$[UO_2(FCPA)(OAc)(H_2O)_2]$	-	-	1630	1295	1026	1341	1083	480	430
$[Cd(HFCPA)Cl_2]$	1703	1620	-	1296	1014	-	1111	509	430

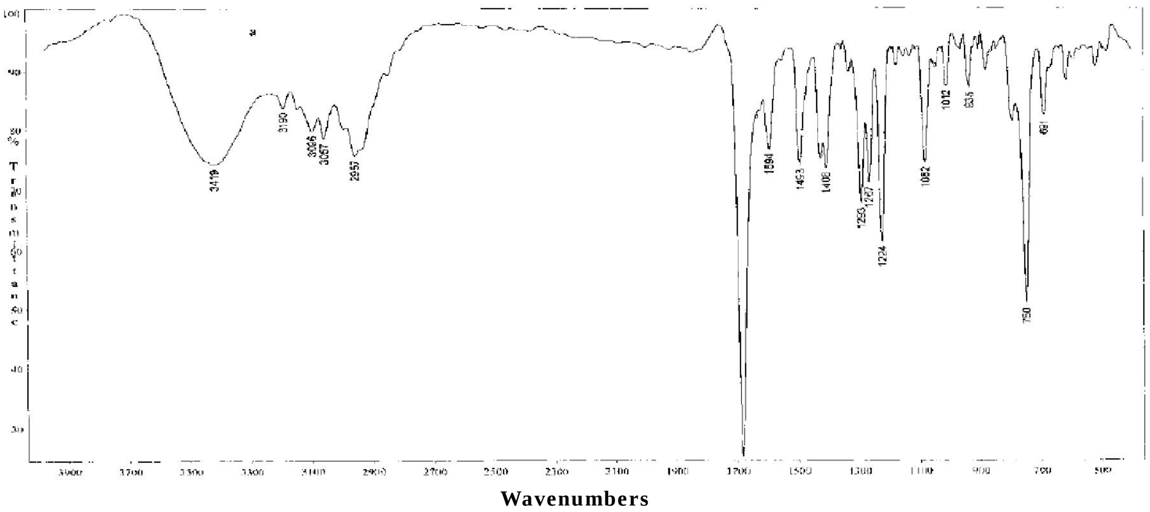


Figure 1 : IR spectra of: a- HFCPA

The ^{1}H NMR spectrum of HFCPA in DMSO-d6 (Figure 2) shows a signal at δ 11.5 ppm which disappears upon adding D_2O. This signal is assigned to the NH proton. The multisignal appear in the region δ 6.6-7.9 ppm are attributed to the protons of phenyl and furan rings. The singlet observed at δ 8.2 ppm is due to the azomethine proton. The sharp singlet appears at δ 2.5 ppm may be assigned to the protons of CH_2 group.

A comparison of the IR spectra of (HFCPA) with those of its metal complexes (TABLE 2) allows us to determine the coordinating atom in the different types of the isolated complexes.

In the complexes $[M(HFCPA)Cl_2(H_2O)_2]$ (M=Co(II) or Ni(II)), HFCPA acts as a neutral bidentate ligand coordinating through the carbonyl oxygen atom of (C=O) in the keto form and the nitrogen atom of the azomethine group (C=N), forming five

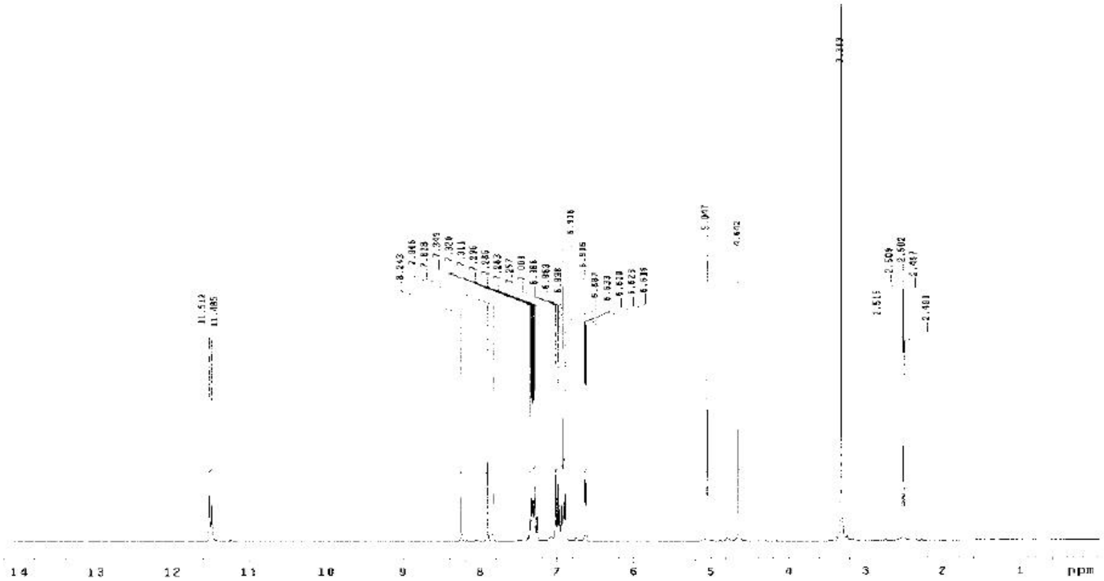
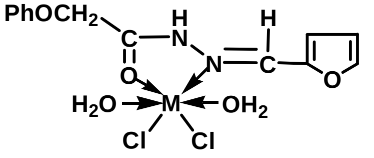


Figure 2 : ^{1}H NMR spectrum of HFCPA

member ring including the metal atom. This bonding mode (Structure 7) is supported by the following observations: (i) both υ(C=O) and υ(C=N) shifts to lower wave number, (ii) υ(N-N) shifts to higher wavenumber,(iii) the appearance of new bands in the regions 518-521 cm^{-1}and at ca. 450 cm^{-1} assigned to υ(M-O)[26] and υ(M-N)[27], respectively.



(M= Co(II) or Ni(II))

Structure (7)

In the complex [Cd(HFCPA)Cl$_2$] (Figure 3), HFCPA also acts as a neutral bidentate, but coordinating via the azomethine nitrogen (C=N) and the heterocyclic oxygen atom . This mode of complexation (Structure 8) is suggested on the basis of following observations :(i) υ(C=N) shifts to lower wavenumber, (ii) the ring breathing vibration shows a significant shift (29 cm^{-1}) to higher wavenumber[18], (iii) the appearance of new bands at 509 cm^{-1} and 430 cm^{-1} attributed to υ(Cd-O)[26] and υ(Cd-N)[27], respectively and (iv) υ(C=O) slightly shifts to higher wavenumbers (1703 cm^{-1}), indicating that the carbonyl oxygen (C=O) is not taking part in coordination.

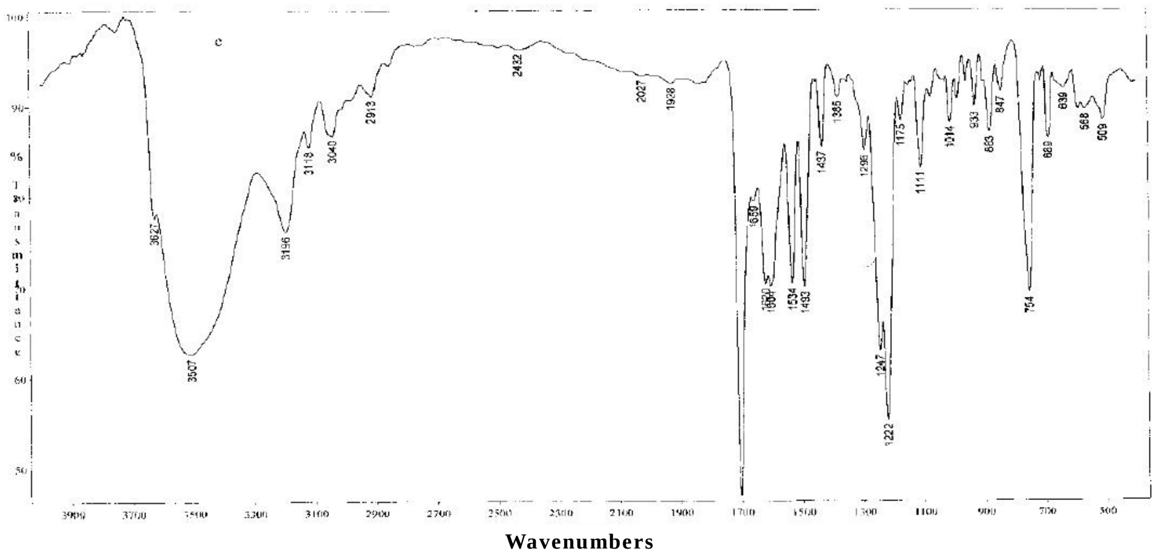
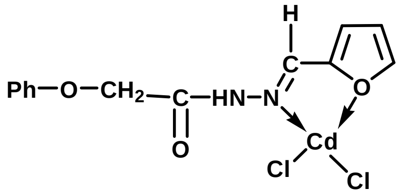


Figure 3 : IR spectra of [Cd(HFCPA)Cl$_2$



Structure (8)

Coordination of HFCPA in the [Cd(HFCPA)Cl_2] complex as a neutral ligand have been substantiated further by the ^{1}H NMR spectrum of the Cd(II) complex (Figure 4). The ^{1}H NMR spectrum shows no significant changes in the position of signals due to all protons.

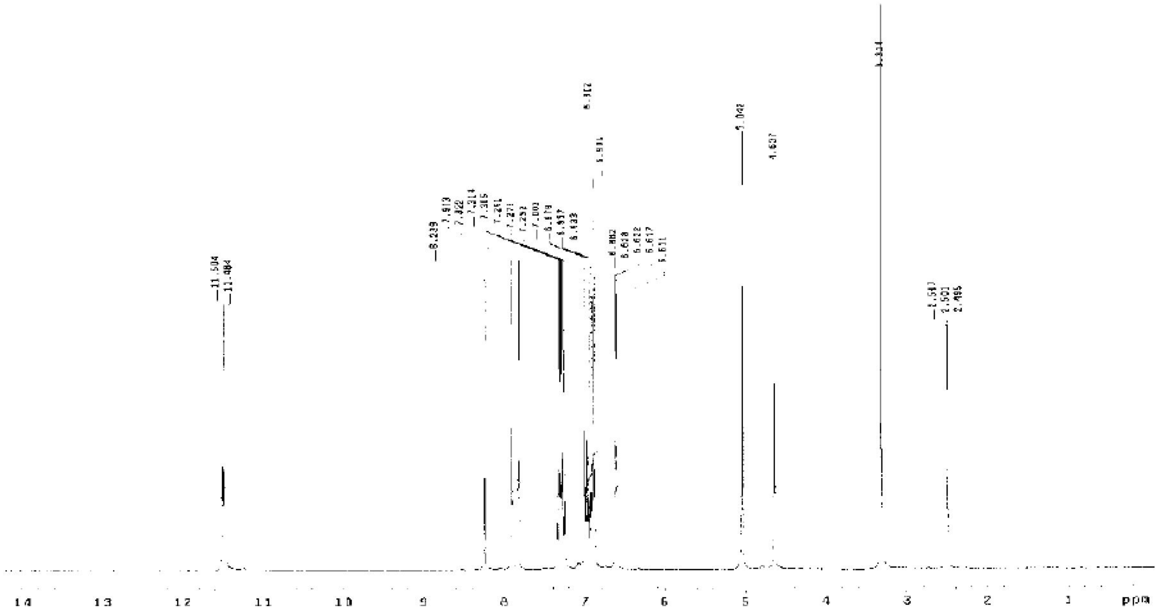
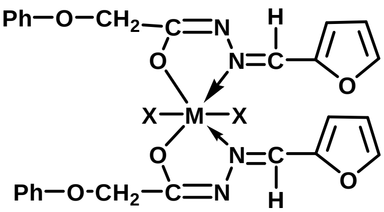


Figure 4 : ^{1}H NMR spectrum of [Cd(HFCPA)Cl_2]

In the complex [UO_2(FCPA)(OAc)$(H_2O)_2$] and [$M(FCPA)_2(H_2O)_n$] (M=Co(II), Ni(II), Cu(II) and Zn(II); n= 0 or 2), HFCPA behaves as a mononegative bidentate ligand coordinating via the azomethine nitrogen (C=N) and the deprotonated carbonyl oxygen (=C-O^-) group. This mode of chelation (Structure 9) is supported by the following evidences: (i) the disappearance of υ(C=O), υ(NH) and υ(C=N) with simultaneous appearance of new bands in the 1334-1344 and 1618-1630 cm^{-1} regions assigned to υ(C-O)[28] and the stretching vibration of the conjugation (C= N-N=C)[29], respectively, (ii) the appearance of new bands in the low frequency regions 480-503 and 430-470 cm^{-1} attributed to υ(M-O)[26] and υ(M-N)[27], respectively.

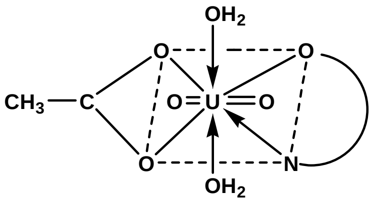


(M=Co(II) or Ni(II), X=H_2O and M=Cu(II) or Zn(II), X= nil)

Structure (9)

Strong evidence for the deprotonation of the enolized carbonyl (=C-OH) group comes from the ^{1}H NMR spectrum of the diamagnetic [$Zn(FCPA)_2$] complex (Figure 5) which show the disappearance of the signal at δ11.5 ppm due to the NH proton.

In the spectra of all the metal complexes except [Cd(HFCPA)Cl_2], the breathing vibration band of the furan ring and δ(C-O-C) remain more or less in the same position, indicating that the oxygen atom of the furan ring does not participate in coordination. The spectrum of uranyl acetate complex [UO_2(FCPA)(OAc)$(H_2O)_2$], shows two new bands at 1540 cm^{-1} and 1438 cm^{-1} assignable to υ_{as}(O-C-O) and υ_s(O-C-O), respectively of the acetate group, the difference between these two bands indicates bidentate coordination of acetate group[30] as shown in Structure 10.



Structure (10)

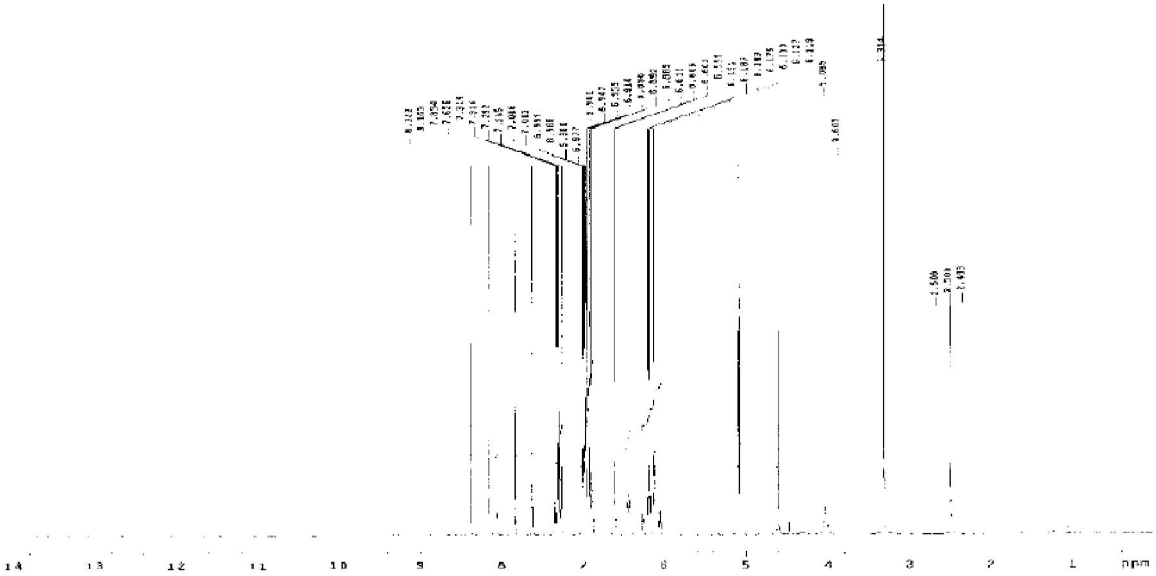


Figure 5 : ^{1}H NMR spectrum of $[Zn(FCPA)_2]$

The uranyl complex exhibits two bands at 925 and 805 cm^{-1} assigned to υ_3 and υ_1 vibrations, respectively, of the dioxouranium ions[31]. The υ_3 value is used for the calculation of the force constant (F) of the (O=U=O) bond by the method of McGlynn and Smith[32].

$$(\upsilon_3)^2 = (1307)^2(F_{U\text{-}O}) / 14.103$$

The calculated force constant is found to be 7.064 mdyne Å^{-1}. The value of the force constant for the uranyl complex was then substituted into the relation given by Jones[33] to calculate the bond distance ($R_{U\text{-}O}$):

$$R_{U\text{-}O} = 1.08(F_{U\text{-}O})^{-1/3} + 1.17$$

The value of the bond distance ($R_{U\text{-}O}$) =1.74 Å as well as the calculated value of the bond force, $F_{U\text{-}O}$, fall in the usual range for the uranyl complex[34].

The hydrated complexes were heated in an oven up to 120°C. No water molecules were removed indicating the presence of water molecule(s) in the inner coordination sphere.

MAGNETIC AND ELECTRONIC SPECTRAL STUDIES

The magnetic moments, electronic absorption bands in (DMSO) and ligand filed parameters of metal complexes are reported in TABLE 3.

The electronic spectra of $[Co(FCPA)_2(H_2O)_2]$ and $[Co(HFCPA)Cl_2(H_2O)_2]$ complexes exhibit two absorption bands in the 16667 – 16977 and 19230 – 20838 cm^{-1} regions, assignable to $^4T_{1g} \longrightarrow {}^4A_{2g}$ and

TABLE 3 : Magnetic moments, electronic bands and ligand filed parameters of HFCPA and its metal complexes.

Compound	Band Position	Assignment	B	β	D_q	M_{eff} (B.M)
$[Co(HFCPA)Cl_2(H_2O)_2]$	16.977 20.838	$^4T_{1g} \longrightarrow {}^4A_{2g}(f)$ $^4T_{1g} \longrightarrow {}^4T_{1g}(p)$	939	0.97	907	4.8
$[Co(FCPA)_2(H_2O)_2]$	16.667 19.230	$^4T_{1g} \longrightarrow {}^4A_{2g}(f)$ $^4T_{1g} \longrightarrow {}^4T_{1g}(p)$	836	0.88	888	5.4
$[Ni(HFCPA)Cl_2(H_2O)_2]$	16.806 28.121	$^3A_{2g} \longrightarrow {}^3T_{1g}(f)$ $^3A_{2g} \longrightarrow {}^3T_{1g}(p)$	928	0.89	1034	2.9
$[Ni(FCPA)_2(H_2O)_2]$	15.049 27.778	$^3A_{2g} \longrightarrow {}^3T_{1g}(f)$ $^3A_{2g} \longrightarrow {}^3T_{1g}(p)$	1059	1.02	898	2.8
$[Cu(FCPA)_2]$	18.242 37.037	$^2B_{1g} \longrightarrow {}^2A_{1g}$ CT	-	-	-	1.9
$[UO_2(FCPA)(OAc)(H_2O)_2]$	18.868 31.746	$^1?^+_g \longrightarrow {}^2\pi_u$ $n \longrightarrow \pi^*$	-	-	-	Diamagnetic

$^4T_{1g} \longrightarrow {}^4T_{1g}$ (P) transitions, respectively. The calculated D_q, B and β values (TABLE 3) lie in the range reported for octahedral structure[35]. The magnetic moment value (5.4- 4.8 BM) respectively, lie within the range of Co(II) ion in octahedral structure.

The electronic spectra of $[Ni(FCPA)_2(H_2O)_2]$ and $[Ni(HFCPA)Cl_2(H_2O)_2]$ complexes show two bands in the 15049 – 16806 and 27778 – 28121 cm^{-1}regions assignable to the $A_{2g} \longrightarrow {}^3T_{1g}(F)(\upsilon_2)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)(\upsilon_3)$ transitions, respectively in octahedral environments around nickel (II) ion[36]. The calculated values of the ligand filed parameters (TABLE 3) lie in the range reported for octahedral structure. Also, the magnetic moment values (2.8 – 2.9 BM) are consistent with those reported for octahedral geometry[37].

The electronic spectrum of $[Cu(FCPA)_2]$ complex shows a band at 18242 cm^{-1} assigned to $^2B_{1g} \longrightarrow {}^2A_{1g}$ transition in square planar geometry. The band at 37037 cm^{-1} may be due to charge transfer, respectively. Also, the value of magnetic moment (1.9 BM) lie within the range of Cu(II) ion[36,38]. ESR spectra, which is considered as an empirical index of square planar geometry for $[Cu(FCPA)_2]$ (TABLE 4) the $g_{\parallel}/A_{\parallel}$ quotient is 133[39].

TABLE 4 : ESR data of the copper(II) complexes at room temperature.

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (cm^{-1})	G	$g_{\parallel}/A_{\parallel}$	α^2	β^2	Symm.
$[Cu(FCPA)_2]$	2.41	2.08	180	4.3	133	0.97	0.89	D_{4h}

The UV spectrum of the $[UO_2(FCPA)OAc(H_2O)_2]$ complex shows two bands at 18868 and 31746 cm^{-1} assignable to $^1\Sigma^+_g \longrightarrow {}^2\pi_u$ transition of dioxuraium (VI) and charge transfer probably $n \longrightarrow \pi^*$ transition, respectively[40].

Studying the corrosion behavior of aluminum by the chemical technique

Figure 6 shows the weight loss- time curves for the corrosion of aluminum in 0.5 M hydrochloric acid in the absence and presence of different concentrations of the investigated compound at 30 °C. As shown in these figure, by increasing the concentration of these compounds, the weight loss of aluminum samples are decreased. This means that the presence of these compounds retards the corrosion. The decrease in corrosion rate of aluminum in 0.5M hydrochloric acid in the presence of theses investigated compounds indicates that these compounds act as inhibitors[41].

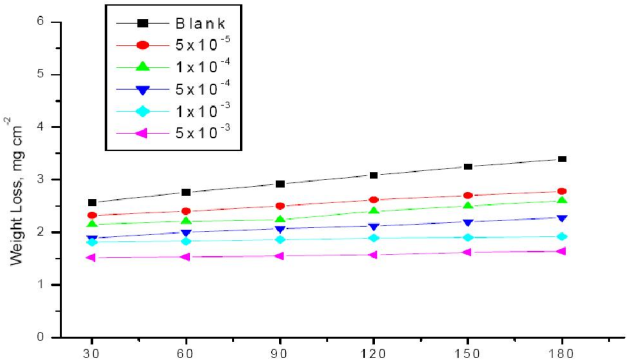


Figure 6 : Weight loss-time curves for the corrosion of aluminum in 0.5 M HCl in the absence and presences of different concentration of compound (HFCPA) at 30° C

The linear variation of weight loss with time in uninhibited and inhibited 0.5M hydrochloric acid indicated the absence of insoluble surface films during corrosion. In the absence of any surface filme, the inhibitors are first adsorbed onto the metal surface and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes. The percentage inhibition efficiency (% IE) of the investigated compounds (TABLE 5) was determined using the equation $\%\,IE = \dfrac{\Delta W - \Delta W_i}{\Delta W} \times 100$.

TABLE 5 : % Inhibition efficiency (% IE) at different concentrations of the investigated compounds for the corrosion of aluminum in 0.5 M HCL at 30°C.

Concentration M	HFCPA (%IE)
5×10^{-5}	33.3
1×10^{-4}	42.4
5×10^{-4}	63.6
1×10^{-3}	81.8
5×10^{-3}	87.9

Antimicrobial activity bioassay

The antimicrobial activities of ligand and complexes against Bacillus thuringiensis and pseudomonas aureginosa are summarized in TABLE 6. Growth inhibition zones are proportional to the antimicrobial activity of the tested compound . The data suggest that Gram-Positive and Gram-Negative bacteria were affected by the tested chemicals with strongest activity for $[Co(HFCPA)Cl_2(H_2O)_2]$ complex, also, $[Ni(HFCPA)Cl_2(H_2O)_2]$ for G.+ve bacteria[42].

TABLE 6 : Inhibition zones diameter (I.Z.D.) in mm as a criterion of antibacterial activity of the ligand and some complexes at concentration level of 2 mg ml^{-1}.

Compounds	Bacteria	
	Bacillus (G+ve) I.Z.D.(mm)	Pseudomonas (G–ve) I.Z.D.(mm)
HFCPA	0	0
$[Cu(FCPA)_2]$	0	0
$[Cd(HFCPA)Cl_2]$	0	0
$[Co(HFCPA)Cl_2(H_2O)_2]$	16	18
$[Ni(HFCPA)Cl_2(H_2O)_2]$	13	0

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