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Synthesis, antibacterial and corrosion activities of new thiopene-2-carboxaldehyde phenoxyacetyl hydrazone complexes (HTCPA)

Magdy M.Bekheit, Mohamed T.Gad Allah, Amira R.El-Shobaky*
Chemistry Department, Faculty of science, Mansoura University, Damietta Branch, (EGYPT)

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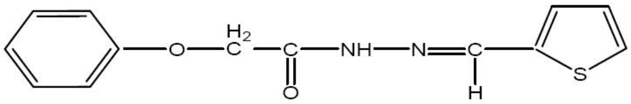
ABSTRACT

The synthesis and characterization of complexes of Co(II), Cu(II), Ni(II), Hg(II), Mn(II), Cd(II), Pd(II) and UO_2(VI) with thiophene-2-carboxaldhyde phenoxyacetyl hydrazone (HTCPA) (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 (HTCPA) behaves as neutral or mononegative bidentate ligand. Different stereochemistries are proposed for each of the Co(II), Cu(II), Ni(II) and Mn(II) complexes on the basis of spectral and magnetic studies.

KEYWORDS

Hydrazone complexes;
NMR;
Corrosion;
Biological activity.



Structure 1

INTRODUCTION

A large number of Schiff bases derived from 2-thiophene aldehydes or keton[1-3] have been studied for their interesting and important properties, e.g. catalytic activity, complexing ability and diverse biological activities, such as antibacterial and antitumor activities. Also, there have been few reports about the metal complexes of hydrazones derived from 2-thiophene aldehydes[4,5]. The present study was under taken to throw more light on the chelation behavior of hydrazone derived from thiophene -2 carboxaldehydes towards some transition metal elements, which may help in more understanding of the mode of chelation of HTCPA towards the metal.

EXPERIMENTAL

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

Synthesis of the ligand

Synthesis of the ligand was prepared by refluxing an ethanolic solution (100ml) of phenoxyacetylhydrazine (16.6 gm, 0.1 mol) and thiophene-2-carboxaldehyde (11.2 ml, 0.1 mol) for 0.5 h. Upon cooling, a pale yellow crystal separated out. The product was filtered off, washed with ethanol and diethylether, recrystllized from absolute ethanol and finally dried in a desiccator over fused $CaCl_2$, yieldH" 23.6 gm,m.p 164° C.

Synthesis of metal chelates

The complexes, $[M(HTCPA)Cl_2(H_2O)_n]$, (M= Mn(II), n=2; Cd(II) or Hg(II), n=0) and $[M(TCPA)Cl(H_2O)_3]$ (M= Ni(II) or Co(II)) were prepared by adding an ethanolic solution (25 ml) of HTCPA (0.26 gm, 1 mmole) to the corresponding metal chlorides (1 mmole) in the same solvent. The reaction mixtures were heated under reflux for 1 h. The $[Cu(TCPA)_2]$ complex was prepared by same method using ethanolic solution (50 ml) of HTCPA (0.52 gm, 2 mmole) and copper chloride (1 mmole).

The complexes, $[UO_2(TCPA)OAc(H_2O)_2]$ and [Cu(TCPA)OAc] were prepared by mixing an ethanolic solution (25 ml) of HTCPA(0.26 gm, 1 mmole) to the corresponding metal acetates (1 mmole) in 25 ml ethanol or water. The $[Co(TCPA)_2(H_2O)_2]$ complex was prepared by the same method using ethanolic solution (50 ml) of HTCPA (0.52 gm, 2 mmole). The $[Pd(TCPA)_2]$ was prepared by adding aqueous solution (25 ml) of Na_2PdCl_4 (0.09 gm, 1 mmole) to ethanolic solution (50 ml, 2 mmole) in presence of sodium acetate. The mixtures were heated under reflux for 0.5 h.

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

$$\text{(i)}\ \ MCl_2 + HTCPA \xrightarrow[\text{Reflux, 1 h}]{\text{EtOH}} [M(HTCPA)Cl_2(H_2O)_n]$$

(M = Mn(II); n=2 and Cd(II) or Hg(II); n=0)

$$\text{(ii)}\ \ MCl_2 + HTCPA \xrightarrow[\text{Reflux, 1 h}]{\text{EtOH}} [M(TCPA)Cl(H_2O)_3]+HCl$$

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

$$\text{(iv)}\ Co(OAc)_2 + 2HTCPA \xrightarrow[\text{Reflux, 0.5 h}]{\text{Aqueous EtOH}} [Co(TCPA)_2(H_2O)_2]+2AcOH$$

$$\text{(v)}\ Cu(OAc)_2 + HTCPA \xrightarrow[\text{Reflux, 0.5 h}]{\text{Aqueous EtOH}} [Cu(TCPA)OAc]+AcOH$$

$$\text{(vii)}\ Na_2PdCl_4 +2HTCPA \xrightarrow[\text{Reflux, 0.5 h}]{\text{Aqueous EtOH}} [Pd(TCPA)_2]+2NaCl+2HCl$$

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 (Λ_m) in DMSO at 25 ÚC (TABLE 1) for all complexes are in the range (1 - 12) $ohm^{-1}\ cm^2\ mol^{-1}$, indicating their nonelectrolytic nature[6].

IR and H^{1}NMR spectral studies

The principal IR bands of (HTCPA) and its metal

TABLE 1 : Analytical and physical data of HTCPA and its metal complexes

Compound	Empirical Formula	Yelid %	Color	M.P. °C	% calc (found)				Λ^a_m in DMSO
					C	H	M	Cl^-	
HTCPA	$C_{13}H_{12}\ N_2O_2S$	90	Yellwish White	164	60.0(59.7)	4.6(4.8)	-	-	-
$[Mn(HTCPA)Cl_2(H_2O)_2]$	$MnC_{13}H_{16}N_2O_4SCl_2$	80	White	>300	37.0(37.2)	3.8(3.6)	13.0(13.2)	16.8(16.9)	2
$[Cd(HTCPA)Cl_2]$	$CdC_{13}H_{12}N_2O_2SCl_2$	84	White	>300	35.2(35.0)	2.7(2.7)	25.3(25.4)	16.0(16.4)	4
$[Hg(HTCPA)Cl_2]$	$HgC_{13}H_{12}N_2O_2SCl_2$	80	White	Charge at 245	29.4(29.2)	23(2.3)	37.7(37.5	13.3(13.1)	6
[Cu(TCPA)OAc]	$CuC_{15}H_{14}O_4N_2S$	85	Pale brown	>300	47.2(47.0)	3.7(4.0)	16.6(16.4)	-	12
$[Ni(TCPA)Cl(H_2O)_3]$	$NiC_{13}H_{17}N_2O_5SCl$	90	Green	230	38.3(38.1)	3.4(4.4)	14.4(14.2)	8.7(8.5)	10
$[Co(TCPA)Cl(H_2O)_3]$	$CoC_{13}H_{17}N_2O_5SCl$	89	Brown	>300	38.3(38.1)	3.4(4.1)	14.4(14.4)	8.7(8.5)	9
$[Co(TCPA)_2(H_2O)_2]$	$CoC_{26}H_{26}N_4O_6S_2$	88	Green	225	50.9(50.7)	4.3(4.4)	9.6(9.4)	-	8
$[Cu(TCPA)_2]$	$CuC_{26}H_{22}N_4O_4S_2$	85	Brown	Charge at 210	53.6(53.4)	3.8(4.0)	10.9(10.7)	-	8
$[Pd(TCPA)_2]$	$PdC_{26}H_{22}N_4O_4S_2$	90	Yellow	240	50.0(49.7)	3.5(3.9)	17.0(17.2)	-	1
$[UO_2(TCPA)OAc(H_2O)_2]$	$UC_{15}H_{18}N_2O_8S$	90	Yellow	>300	28.8(28.4)	2.9(3.0)	38.1(38.4)	-	2

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

complexes are listed in TABLE 2.

TABLE 2 : IR spectral data of HTCPA and its metal complexes

Compound	υ(C=O)	υ((C-S)$_{Ring}$	υ(C=N)	υ(C=N)*	υ(N-N)	υ(C-O)	υ(M-O)	υ(M-N)
HTCPA	1681	1345	1635	-	1223	-	-	-
[Mn(HTCPA)$Cl_2(H_2O)_2$]	1670	1345	1609	-	1303	-	506	420
[Cd(HTCPA)Cl_2]	1657	1342	1610	-	1302	-	510	420
[Hg(HTCPA)Cl_2]	1655	1347	1609	-	1293	-	512	430
[Cu(TCPA)OAc]	-	1355	1605	1630	1280	1115	507	435
[Ni(TCPA)Cl$(H_2O)_3$]	-	1355	1610	1633	1309	1126	510	422
[Co(TCPA)Cl$(H_2O)_3$]	-	1345	1603	1630	1224	1143	520	420
[Co$(TCPA)_2(H_2O)_2$]	-	1369	1603	1640	1293	1083	515	430
[Cu$(TCPA)_2$]	-	1357	1600	1630	1245	1117	515	420
[Pd$(TCPA)_2$]	-	1354	1610	1636	1305	1126	520	434
[UO_2 (TCPA)OAc $(H_2O)_2$]	-	1387	1610	1645	1249	1096	514	428

The IR spectrum (Figure 1) of (HTCPA) shows three strong bands at 1681,1635 and 1223 cm^{-1} assigned to υ(C=O)[7], υ(C=N)[8] and υ(N-N)[9], respectively. The υ(C-S-C)[10] stretching band of thiophene moiety appears as astrong band at 1345 cm^{-1}. The medium intensity band at 3410 cm^{-1} is probably due to υ(NH)[11] vibration.

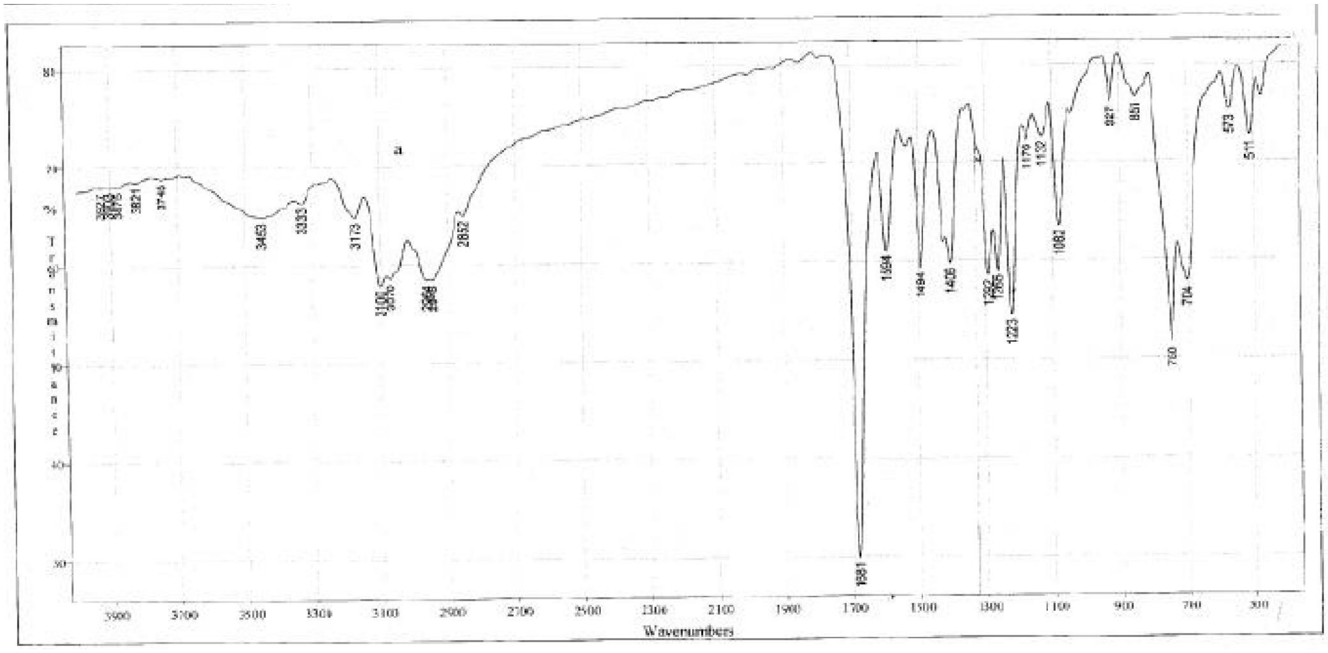


Figure 1 : IR spectra of HTCPA

A comparison of the IR spectra of (HTCPA) and its complexes (TABLE 2) shows that the characteristic absorption bands of the free ligand are shifted on complexation and a new vibration bands characteristic of the complexes appear showing that HTCPA behaves in a neutral bidentate and/ or a mononegative bidentate manner depending upon the metal salts used and the conditions of preparation as well as the pH of the solution[12].

The ^{1}H NMR spectrum of HTCPA (Figure.2) in DMSO-d_6 shows a signal at δ 11.70 ppm, which disappears upon adding D_2O. This signal is assigned to NH proton. The multisignals in the δ 7.8 - 8.6 ppm region are assigned to the aromatic protons of phenyl and thiophene rings.

The IR spectral data of all the reported complexes, except [M(HTCPA)$Cl_2(H_2O)_n$] (M=Cd(II), Mn(II),

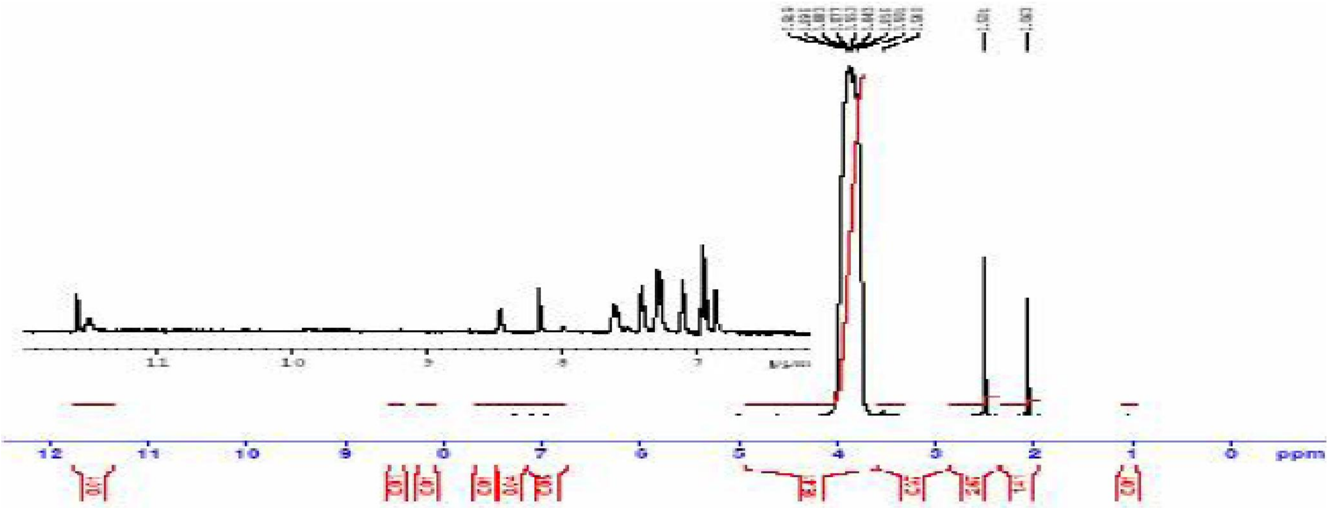
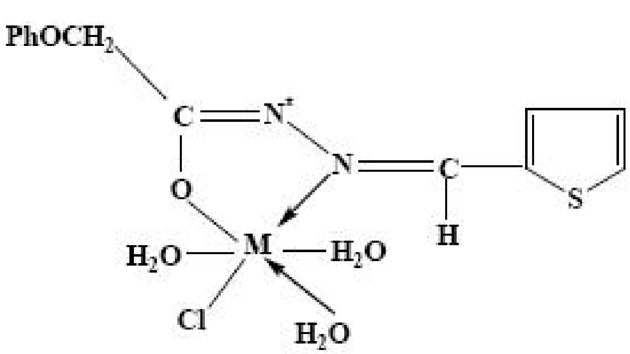
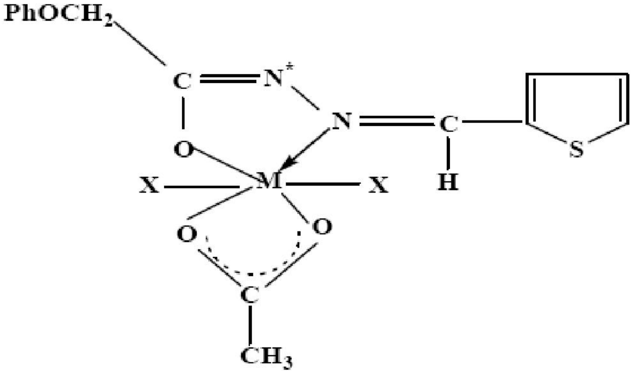


Figure 2 : ^{1}H NMR spectrum of HTCPA

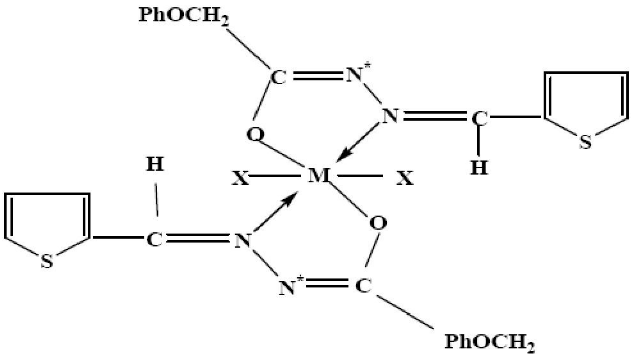
Hg(II); n=0 or 2), show that HTCPA coordinates in a mononegative bidentate manner via the azomethine nitrogen (C=N) and the enolized carbonyl oxygen (=C-OH)[12] with the displacement of hydrogen atom from the latter group, forming five member ring including the metal ions. This mode of complexation (Structure 2 - 4) are supported by the following observations: (i) the disappearance of υ(C=O)[7]and υ(NH)[11] with simultaneous appearance of new bands in the 1630- 1645 and 1083-1126 cm^{-1} regions, assignable to υ $(C=N^*)$[13] and υ(C-O)[14], respectively, (ii) υ(C=N)shifts to lower wavenumber,while υ(N-N) shifts to higher wavenumber (iii)υ(C-S-C)[15] remains more or less in the same position, indicating the non involvement of the sulphur atom in coordination and (iv) the appearance of new bands in the 507-520 and 410-435 cm^{-1} regions assigned to υ(M-O)[16] and υ(M-N)[17], respectively.



Structure 2 : (M = Ni(II) or Co(II))

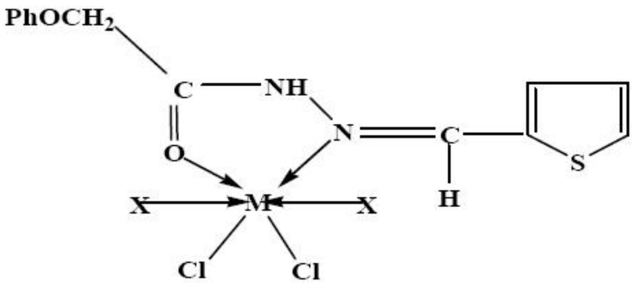


Structure 3 : (M = Cu(II), X=nil; M = $U(VI)O_2$, $X=H_2O$)



Structure 4 : (M = Cu(II) or Pd(II), X = nil; M = Co(II), X = H_2O)

On the other hand, the IR spectral data of $[M(HTCPA)Cl_2(H_2O)_n]$, (M=Cd(II), Mn(II), Hg(II); n=0 or 2) shows that HTCPA behaves as a neutral bidentate[12] ligand coordinating via the carbonyl oxygen atom (C=O) in the keto form and the nitrogen atom of the azomethine group (C=N) forming a five member ring including the metal atom. This mode of complexation (Structure 5) is suggested by the following observations: (i) both υ(C=N) and υ(C=O) shift to lower wavenumber, (ii) υ(N-N) shifts to higher wavenumber, (iii) υ(C-S-C)[15] remains more or less in the same position indicating the non involvement of the sulphur atom in coordination and (iv) the appearance of new bands in the 506-512 and 420 -430 cm^{-1} regions assigned to υ(M-O)[16] and υ(M-N)[17], respectively.



Structure 5 : (M= Cd(II)or Hg(II),X=nil and Mn(II),X=H_2O)

In the ^1H NMR spectrum of $[Cd(HTCPA)Cl_2]$ complex (Figure.3), the signal due to the hydrazide NH undergoes a weak field shifting to δ 11.3 ppm, suggesting coordination of the adjacent hydrazide (C=O) and(C=N) to the metal ion.[18]

The uranyl complex exhibits two bands at 929 and 873 cm^{-1} assigned to υ_3 and υ_1 vibrations, respectively, of the dioxouranium ions[19]. 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[20] :

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

The calculated force constant is found to be 7.125 mdyne $Å^{-1}$. The value of the force constant for the uranyl complex was then substituted into the relation given by Jones[21] to calculate the bond distance (R_{U-O}):

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

The value of the bond distance (R_{U-O}) =1.73 as well as the calculated value of the bond force, F_{UO}, fall in the usual range for the uranyl complex[22].

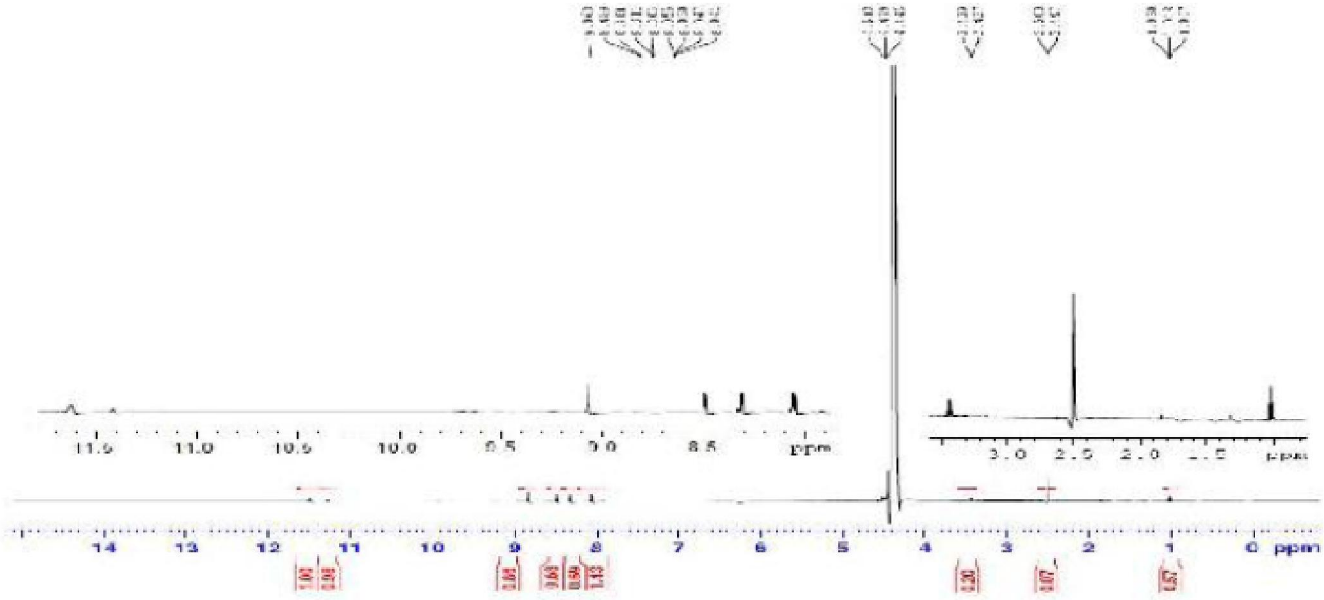


Figure 3 : ^1H NMR spectrum of $[Cd(HTCPA)Cl_2]$

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 [Cu(TCPA)OAc] and $[Cu(TCPA)_2]$ complexes show a broad band with a maximum in the range 14310-14880 due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in a square planar geometry (Figure 4,5). The bands in the range 34090 - 38229 cm^{-1} may be assigned to charge transfer. Also, the values of μ_{eff} (1.85-2.3 BM) lie within the range of Cu(II) ion[23,24]

The electronic spectra of $[Co(TCPA)Cl(H_2O)_3]$ and $[Co(TCPA)_2(H_2O)_2]$ complexes exhibit two absorption bands in the 13889 -16950 and 18369 - 20400 cm^{-1} regions, assignable to $^4T_{1g}\rightarrow{}^4A_{2g}$ and $^4T_{1g}\rightarrow{}^4T_{1g}$ (P) transitions, respectively. The calculated D_q, B and β values (TABLE 17) lie in the range reported for octahedral structure[25]. Also, the magnetic moment values (4.8-5.2 BM) are additional evidence for an octahedral structure.

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

Compound	Band Position	Assignment	B	β	D_q	M_{eff} (B.M)
[Cu(TCPA)OAc]	14.310 34.090	$^2B_{1g} \longrightarrow {}^2A_1g$ CT	-	-	-	1.85
$[Cu(TCPA)_2]$	14.880 38.229	$^2B_{1g} \longrightarrow {}^2A_1g$ CT	-	-	-	2.3
$[Co(TCPA)Cl(H_2O)_3]$	13.889 18.369	$^4T_{1g} \longrightarrow {}^4A_{2g}(f)$ $^4T_{1g} \longrightarrow {}^4T_{1g}(p)$	852	0.88	740	4.8
$[Co(TCPA)_2(H_2O)_2]$	16.950 20.400	$^4T_{1g} \longrightarrow {}^4A_{2g}(f)$ $^4T_{1g} \longrightarrow {}^4T_{1g}(p)$	909	0.94	905	5.2
$[Ni(TCPA)Cl(H_2O)_3]$	15.385 26.385	$^3A_{2g} \longrightarrow {}^3T_{1g}(f)$ $^3A_{2g} \longrightarrow {}^3T_{1g}(p)$	912	0.88	936	3.1
$[Pd(TCPA)_2]$	25.974 39.454	$^1A_{1g} \longrightarrow {}^1B_{1g}$ CT	-	-	-	Diamagnetic
$[UO_2\ (TCPA)OAc\ (H_2O)_2]$	17.241 25.542	$^1?^+_g \longrightarrow {}^2\pi_u$ $n \longrightarrow \pi^*$	-	-	-	Diamagnetic
$[Mn(HTCPA)Cl_2(H_2O)_2]$	18.518 30.590	$^6A_{1g} \longrightarrow {}^4T_{1g}(G)$ $^6A_{1g} \longrightarrow {}^4T_{2g}(G)$	-	-	-	5.3

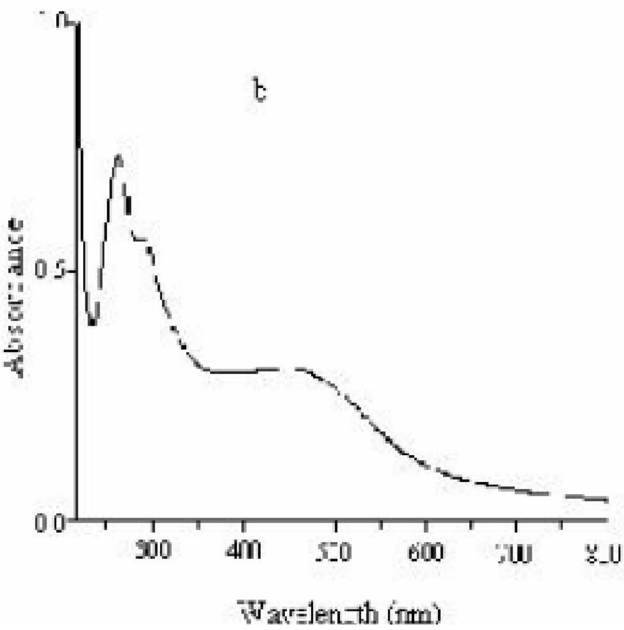


Figure 4 : Electronic spectra of [Cu(TCPA)OAc]

The spectrum of $[Ni(TCPA)Cl(H_2O)_3]$ complex exhibit two absorption bands at 15385 and 26385 cm^{-1} assignable to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\upsilon_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\upsilon_3)$ transitions, respectively in octahedral environments around nickel (II) ion[23]. The calculated values of the ligand filed parameters (TABLE 3) lie in the range reported for octahedral structure. Also, the magnetic moment value (3.1 BM) is consistent with those reported for octahedral geometry[26].

The $[Pd(TCPA)_2]$ complex is diamagnetic and its electronic spectrum shows two bands at 25974 and 39454 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1E_{1g}$ and charge transfer, respectively in square planar geometry[27,28].

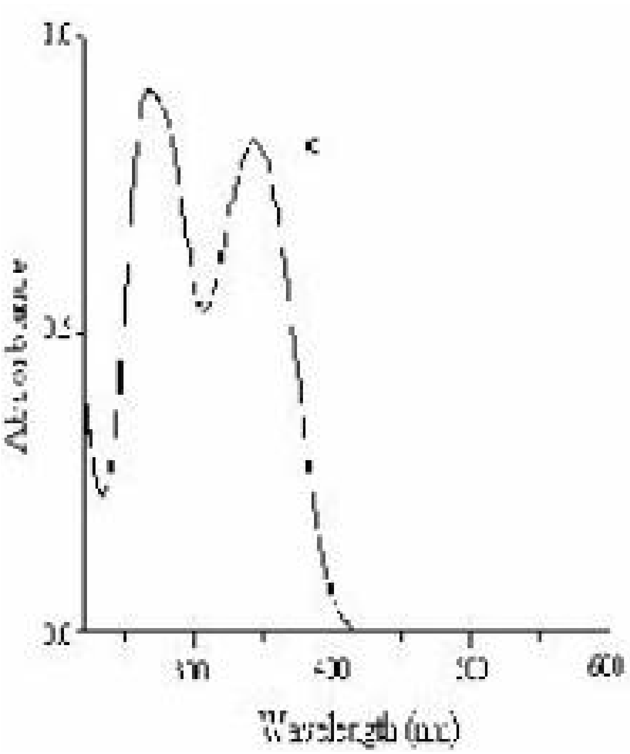


Figure 5 : Electronic spectra of [Cu(TCPA)2]

The UV spectrum of the $[UO_2(TCPA)(H_2O)_2]$ shows two bands at 17241and 25542 cm^{-1} assignable to $^1\Sigma^+_g \rightarrow {}^2\pi_u$ transition of dioxuraium(VI) and charge transfer probably $n \rightarrow \pi^*$ transition, respectively[29].

Finally, the [Mn(HTCPA)Cl_2] complex (figure.6) shows two bands at 18518 and 30590 cm^{-1} which may be due to $^6A_{1g}\rightarrow{}^4T_{1g}$(G) and $^6A_{1g}\rightarrow{}^4T_{2g}$(G) transition, respectively in an octahedral configuration[30] around the metal ion. Also, the value of magnetic moment (5.4 BM) lies in the range measured for high spin d^5 system.

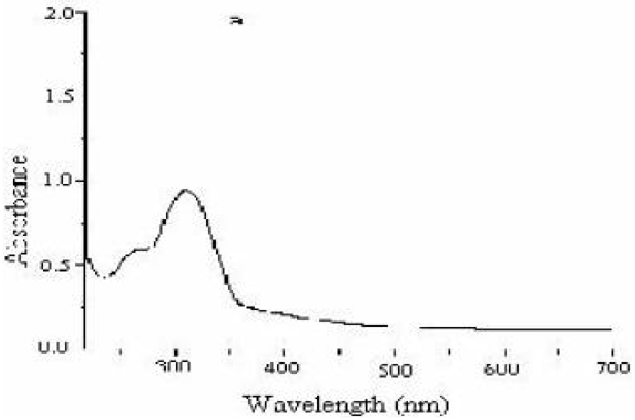


Figure 6 : Electronic spectra of: [Mn(HTCPA)$Cl_2(H_2O)_2$]

Studying the corrosion behavior

The inhibition action of HTCPA on the dissolution of aluminum in 0.5 M HCl was investigated. Aluminum was selected for this study due to its numerous industrial applications and consequently its corrosion inhibition in pickling baths is of great importance. The inhibition efficiency depends on the additive compounds depends on many factors which include the number of adsorption active centers and their charge density, molecular size and the mode of inter action with metal surface[31] Weight loss determinations[32] of aluminum in 0.5 M HCl after 30 min yielded convincing evidence for the application of HTCPA as active corrosion inhibitor (TABLE 4) the maximum efficiency is 40.2% for the concentration of $5x10^{-3}$ mol L^{-1} which indicates excellent corrosion inhibition for aluminum[33]. Also, tests for corrosion current gave result in the same way as weight loss does.

TABLE 4 : (% Inhibition efficiency (%IE) at different concentrations of the investigated compounds for the corrosion of aluminum in 0.5 M HCL at 30ÚC)

Concentration M	HAPPA (%IE)
$5x10^{-5}$	25.0
$1x10^{-4}$	35.0
$5x10^{-4}$	63.3
$1x10^{-3}$	80.0
$5x10^{-3}$	84.2

Antimicrobial activity

The antimicrobial activities of ligand and complexes against Bacillus thuringiensis and pseudomonas aureginosa are summarized in TABLE 5. Growth inhibition zones are proportional to the antimicrobial activity of the tested compound. The data suggest that [Hg(HTCPA)Cl_2] complex show higher activity against both gram-positive and gram-negative bacterium. However, cobalt (II) and Manganese (II) complexes have similar antimicrobial activity[34] against gram-positive bacterium.

TABLE 5 : Inhibition zones diameter (I.Z.D.) in mm as a criterion of antibacterial activity of the ligande and its 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)
HTCPA	10	0
[Hg(HTCPA)Cl_2]	30	16
[Mn(HTCPA)$Cl_2(H_2O)_2$]	15	0
[Cu(TCPA)OAc]	0	0
[Co(TCPA)Cl$(H_2O)_3$]	23	0

CONCLUSION

Our work report the preparation and characterization of some new five memberd ring chelates of HTCPA, the behavior of HTCPA and their ability to coordinate through the various potential sites, however, it was found that the this compound retard the corrosion. Also, mercury(II) complex show appreciable antimicrobial activity.

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