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

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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-carboxaldehyde 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.

INTRODUCTION
A large number of Schiff bases derived from 2-thiophene aldehydes or ketones[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 undertaken 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 (100 ml) 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, recrystallized from absolute ethanol and finally dried in a desiccator over fused CaCl$_2$, yield H$^+$ 23.6 gm, m.p 164° C.
Synthesis of metal chelates

The complexes, \( \text{[M(HTCPA)Cl}_2(\text{H}_2\text{O})_n] \) (\( \text{M} = \text{Mn}(\text{II}), n=2; \text{Cd}(\text{II}) \text{ or } \text{Hg}(\text{II}), n=0 \)) and \( \text{[M(TCPA)Cl}_2(\text{H}_2\text{O})_n] \) (\( \text{M} = \text{Ni}(\text{II}) \text{ or } \text{Co}(\text{II}) \)) 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 \([\text{Cu(TCPA)}_2] \) 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, \([\text{UO}_2(\text{TCPA})\text{OAc}(\text{H}_2\text{O})_2] \) and \([\text{Cu(TCPA)}\text{OAc}] \) 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 \([\text{Co(TCPA)}(\text{H}_2\text{O})_2] \) complex was prepared by the same method using ethanolic solution (50 ml) of HTCPA (0.52 gm, 2 mmole). The \([\text{Pd(TCPA)}_2] \) was prepared by adding aqueous solution (25 ml) of \( \text{Na}_2\text{PdCl}_4 \) (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

\[
\text{(i) } \text{MC}_2 + \text{HTCPA} \rightarrow \text{[M(HTCPA)Cl}_2(\text{H}_2\text{O})_n] \text{ EtOH, Reflux, 1 h (M = Mn(II); n=2 and Cd(II) or Hg(II); n=0)}
\]

\[
\text{(ii) } \text{MC}_2 + \text{HTCPA} \rightarrow \text{[M(TCPA)Cl}_2(\text{H}_2\text{O})_n]+\text{HCl} \text{ EtOH, Reflux, 1 h (M = Ni(II) or Co(II))}
\]

\[
\text{(iii) } \text{Co(OAc)}_2 + 2\text{HTCPA} \rightarrow \text{[Co(TCPA)(H}_2\text{O})_2]+2\text{AcOH} \text{ Aqueous EtOH, Reflux, 0.5 h}
\]

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

\[
\text{(vii) } \text{Na}_2\text{PdCl}_4 + 2\text{HTCPA} \rightarrow \text{[Pd(TCPA)}_2]+2\text{NaCl+2HCl} \text{ Aqueous EtOH, Reflux, 0.5 h}
\]

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 dimethylsulfoxide (DMSO). The molar conductivities \( (\Lambda_m) \) in DMSO at 25°C (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 complexes...
complexes are listed in TABLE 2.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(C=O)</th>
<th>$\nu$((C-S)Ring)</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(C=N)$^*$</th>
<th>$\nu$(N-N)</th>
<th>$\nu$(C-O)</th>
<th>$\nu$(M-O)</th>
<th>$\nu$(M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTCPA</td>
<td>1681</td>
<td>1345</td>
<td>1635</td>
<td>-</td>
<td>1223</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Mn(HTCPA)Cl$_2$(H$_2$O)$_2$]</td>
<td>1670</td>
<td>1345</td>
<td>1609</td>
<td>-</td>
<td>1303</td>
<td>-</td>
<td>506</td>
<td>420</td>
</tr>
<tr>
<td>[Cd(HTCPA)Cl$_2$]</td>
<td>1657</td>
<td>1342</td>
<td>1610</td>
<td>-</td>
<td>1302</td>
<td>-</td>
<td>510</td>
<td>420</td>
</tr>
<tr>
<td>[Hg(HTCPA)Cl$_2$]</td>
<td>1655</td>
<td>1347</td>
<td>1609</td>
<td>-</td>
<td>1293</td>
<td>-</td>
<td>512</td>
<td>430</td>
</tr>
<tr>
<td>[Cu(TCPA)OAc]</td>
<td>-</td>
<td>1355</td>
<td>1605</td>
<td>1630</td>
<td>1280</td>
<td>1115</td>
<td>507</td>
<td>435</td>
</tr>
<tr>
<td>[Ni(TCPA)Cl(H$_2$O)$_3$]</td>
<td>-</td>
<td>1355</td>
<td>1610</td>
<td>1633</td>
<td>1309</td>
<td>1126</td>
<td>510</td>
<td>422</td>
</tr>
<tr>
<td>[Co(TCPA)Cl(H$_2$O)$_3$]</td>
<td>-</td>
<td>1345</td>
<td>1603</td>
<td>1630</td>
<td>1224</td>
<td>1143</td>
<td>520</td>
<td>420</td>
</tr>
<tr>
<td>[Co(TCPA)$_2$(H$_2$O)$_2$]</td>
<td>-</td>
<td>1369</td>
<td>1603</td>
<td>1640</td>
<td>1293</td>
<td>1083</td>
<td>515</td>
<td>430</td>
</tr>
<tr>
<td>[Cu(TCPA)$_2$]</td>
<td>-</td>
<td>1357</td>
<td>1600</td>
<td>1630</td>
<td>1245</td>
<td>1117</td>
<td>515</td>
<td>420</td>
</tr>
<tr>
<td>[Pd(TCPA)$_2$]</td>
<td>-</td>
<td>1354</td>
<td>1610</td>
<td>1636</td>
<td>1305</td>
<td>1126</td>
<td>520</td>
<td>434</td>
</tr>
<tr>
<td>[UO$_2$(TCPA)OAc(H$_2$O)$_2$]</td>
<td>-</td>
<td>1387</td>
<td>1610</td>
<td>1645</td>
<td>1249</td>
<td>1096</td>
<td>514</td>
<td>428</td>
</tr>
</tbody>
</table>

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

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 $\delta$ 11.70 ppm, which disappears upon adding D$_2$O. This signal is assigned to NH proton. The multisignals in the $\delta$ 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$_2$O)$_n$] (M=Cd(II), Mn(II),
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 \(\nu(C=O)\) \(^{7}\) and \(\nu(NH)\) \(^{11}\) with simultaneous appearance of new bands in the 1630- 1645 and 1083-1126 cm\(^{-1}\) regions, assignable to \(\nu(C=N^*)\) \(^{13}\) and \(\nu(C-O)\) \(^{14}\), respectively, (ii) \(\nu(C=N)\) shifts to lower wavenumber, while \(\nu(N-N)\) shifts to higher wavenumber, (iii) \(\nu(C-S-C)\) \(^{15}\) 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 \(\nu(M-O)\) \(^{16}\) and \(\nu(M-N)\) \(^{17}\), respectively.

On the other hand, the IR spectral data of [M(HTCPA)Cl\(_2\)(H\(_2\)O)] \(_n\), (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 \(\nu(C=N)\) and \(\nu(C=O)\) shift to lower wavenumber, (ii) \(\nu(N-N)\) shifts to higher wavenumber, (iii) \(\nu(C-S-C)\) \(^{15}\) 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

\[ \text{PhOCH}_2 \]

Structure 5 : (M= Cd(II) or Hg(II), X=nil and Mn(II), X=H$_2$O)

\( \nu(M-O) \)\(^{[16]} \) and \( \nu(M-N) \)\(^{[17]} \), respectively.

In the \(^1\)H NMR spectrum of [Cd(HTCPA)Cl$_2$] complex (Figure.3), the signal due to the hydrazide NH undergoes a weak field shifting to \( \delta \) 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 \( \nu_1 \) and \( \nu_2 \) vibrations, respectively, of the dioxouranium ions.\(^{[19]} \). The \( \nu_2 \) value is used for the calculation of the force constant (\( F \)) of the \((O=U=O) \) bond by the method of McGlynn and Smith\(^{[20]} \):

\[ (\nu_2)^2 = (1307)^2(F_{U-O})/14.103 \]

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 (\( R_{U-O} \)):

\[ R_{U-O} = 1.08(F_{U-O})^{\frac{1}{3}} + 1.17 \]

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

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 $^2$A$_{1g}$ 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 $\mu_{eff}$ (1.85-2.3 BM) lie within the range of Cu(II) ion.\(^{[23,24]} \)

The electronic spectra of [Co(TCPA)Cl(H$_2$O)$_3$] and [Co(TCPA)$_2$(H$_2$O)$_2$] 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 $\beta$ 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.
The spectrum of \([\text{Ni(TCPA)Cl(H}_2\text{O)}_3]\) complex exhibit two absorption bands at 15385 and 26385 cm\(^{-1}\) assignable to the \(3A_{2g} \rightarrow 3T_{1g}(F)\) and \(3A_{2g} \rightarrow 3T_{1g}(P)(\nu_3)\) 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 \([\text{Pd(TCPA)}_2]\) complex is diamagnetic and its electronic spectrum shows two bands at 25974 and 39454 cm\(^{-1}\) assignable to \(^1A_{1g} \rightarrow ^1B_{1g}\) and charge transfer, respectively in square planar geometry\(^{[27,28]}\).

The \([\text{UO}_2(\text{TCPA})\text{OAc (H}_2\text{O)}_2]\) shows two bands at 17241 and 25542 cm\(^{-1}\) assignable to \(^1\Sigma^+ \rightarrow 2\pi_u\) transition of dioxyrurium(VI) and charge transfer probably \(n \rightarrow \pi^*\) transition, respectively\(^{[29]}\).

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band Position</th>
<th>Assignment</th>
<th>B</th>
<th>β</th>
<th>Dq</th>
<th>(M_{\text{eff}}) (B.M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu(TTCPA)OAc]})</td>
<td>14.310</td>
<td>(^2B_{1g}) → (^3A_{1g})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>34.090</td>
<td>CT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu(TTCPA)}_2])</td>
<td>14.880</td>
<td>(^2B_{3g}) → (^2A_g)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>38.229</td>
<td>CT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>([\text{Co(TTCPA)Cl(H}_2\text{O)}_3])</td>
<td>13.889</td>
<td>(^4T_{1g}) → (^4A_{2g}(f))</td>
<td>852</td>
<td>0.88</td>
<td>740</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>18.369</td>
<td>(^4T_{1g}) → (^4T_{1g}(p))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Co(TTCPA)}_2(H}_2\text{O)}_2])</td>
<td>16.950</td>
<td>(^4T_{1g}) → (^4A_{2g}(f))</td>
<td>909</td>
<td>0.94</td>
<td>905</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>20.400</td>
<td>(^4T_{1g}) → (^4T_{1g}(p))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ni(TTCPA)Cl(H}_2\text{O)}_3])</td>
<td>15.385</td>
<td>(^3A_{2g} \rightarrow (^3T_{1g}(f))</td>
<td>912</td>
<td>0.88</td>
<td>936</td>
<td>3.1</td>
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<td></td>
<td>26.385</td>
<td>(^3A_{2g} \rightarrow (^3T_{1g}(p))</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>([\text{Pd(TTCPA)}_2])</td>
<td>25.974</td>
<td>(^1A_{1g} \rightarrow (^1B_{1g})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td></td>
<td>39.454</td>
<td>CT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>([\text{UO}_2(\text{TCPA})\text{OAc (H}_2\text{O)}_2])</td>
<td>17.241</td>
<td>(^1\Sigma^+ \rightarrow 2\pi_u)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td></td>
<td>25.542</td>
<td>(n \rightarrow \pi^*)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>([\text{Mn(HTTCPA)Cl}_2(H}_2\text{O)}_2])</td>
<td>18.518</td>
<td>(^6A_{1g} \rightarrow (^4T_{1g}(G))</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>30.590</td>
<td>(^6A_{1g} \rightarrow (^4T_{2g}(G))</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Figure 4 : Electronic spectra of \([\text{Cu(TTCPA)OAc]}\)**

**Figure 5 : Electronic spectra of \([\text{Cu(TTCPA)}_2]\)**
Finally, the $[\text{Mn(HTCPA)}\text{Cl}_2]$ 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 around the metal ion. Also, the value of magnetic moment (5.4 BM) lies in the range measured for high spin d$^5$ system.

Antimicrobial activity

The antimicrobial activities of ligand and complexes against Bacillus thuringiensis and pseudomonas aeurginosa are summarized in Table 5. Growth inhibition zones are proportional to the antimicrobial activity of the tested compound. The data suggest that $[\text{Hg(HTCPA)}\text{Cl}_2]$ complex show higher activity against both gram-positive and gram-negative bacterium. However, cobalt (II) and Manganese (II) complexes have similar antimicrobial activity against gram-positive bacterium.

TABLE 5 : Inhibition zones diameter (I.Z.D.) in mm as a criterion of antibacterial activity of the ligand and its complexes at concentration level of 2 mg ml$^{-1}$

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bacteria</th>
<th>I.Z.D.(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bacillus (G +ve)</td>
<td>Pseudomonas (G -ve)</td>
</tr>
<tr>
<td>HTCPA</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{Hg(HTCPA)}\text{Cl}_2]$</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>$[\text{Mn(HTCPA)}\text{Cl}_2(H_2\text{O})_2]$</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{Cu(TCPA)}\text{OAc}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{Co(TCPA)}\text{Cl(H_2O)_3}]$</td>
<td>23</td>
<td>0</td>
</tr>
</tbody>
</table>

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 this compound retard the corrosion. Also, mercury(II) complex show appreciable antimicrobial activity.

REFERENCES