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# Structural elucidation of novel mixed ligand complexes of 2-thiophene carboxylic acid $[M(TCA)_2(H_2O)_x(im)_2]$ [x=2 M: Mn(II), Co(II) or Cd(II), x=0 Cu(II)]

**Abstract:** Novel mixed ligand complexes containing thiophene-2-carboxylic acid (HTCA) and imidazole (im) ligands, $[M(TCA)_2(H_2O)_2(im)_2]$ (M: Mn, Co, Cd) and $[Cu(TCA)_2(im)_2]$ were obtained. The complexes were characterized by X-ray single crystal diffraction. Also, spectroscopic (IR and UV-Vis), magnetic and thermal properties were investigated. The thiophene-2-carboxylate acted in a monoanionic monodentate manner and bonded to the metals via its carboxylate oxygen. The im ligands bonded to the metals via hydrogen free nitrogen atoms. The geometry around the metal centers was octahedral $[MO_4N_2]$ for Mn(II), Co(II) and Cd(II) complexes and square-planar $[CuO_2N_2]$ for the Cu(II) complex. Due to intermolecular interactions in the solid state, the Co(II), Mn(II) and Cd(II) complexes showed three-dimensional networks, while the copper complex was a one-dimensional network. In consideration of the anhydrous form of the complexes, the thermal stability of the complexes was of the following order: Co (273°C)>Cu (229°C)>Cd (175°C)>Mn (167°C).

**Keywords:** imidazole; intermolecular interactions; thiophene carboxylato; thiophene carboxylic.

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## Introduction

The five-membered sulfur-containing heterocycle thiophene, is a chemically stable compound and easy to process, and its derivatives have attracted attention due to their applications in drug design, biodiagnostics, electronic and optoelectronic devices, conductive polymer technology and construction of supramolecular frameworks (Drozdzewski et al., 2004a; Panagoulis et al., 2007; Cagnin et al., 2010; Mishra et al., 2011; Zhang et al., 2011).

The carboxylic acid derivatives of thiophene can be widely used in pharmacological and medical aspects and some of these derivatives have been widely studied on semi-synthetic cephalosporins (first-generation antibiotics), antiallergic, antimigraine and intestinal antibacterial agents, as well as for influenza treatment (Drozdzewski et al., 2004a). Thiophene carboxylic acid (HTPC) also has potential in the preparation of DNA hybridization indicators, single-molecule magnets, photoluminescence materials and treatment of osteoporosis as inhibitors of bone resorption in the tissue culture (Drozdzewski et al., 2004a,b; Yuan et al., 2004; Feng et al., 2005; Panagoulis et al., 2007; Boulsourani et al., 2011a,b; Zhou et al., 2011; Karastogianni et al., 2013; Kuchtanin et al., 2013).

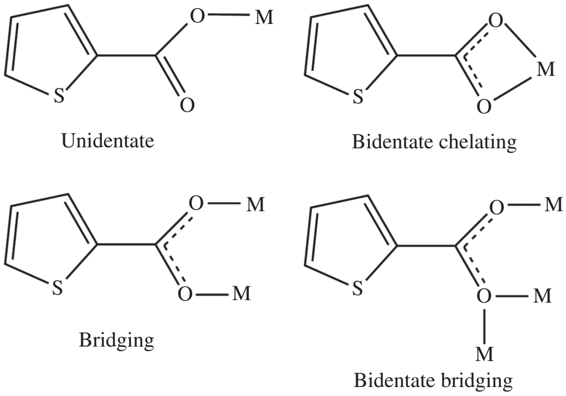
HTPC not only shows biological activity, but can also coordinate to metal ions. It has been found that the biological activities of HTPC are considerably increased when they are bonded to the metals (Zheng et al., 2007).

The Co(II), Ni(II), Cu(II) and Zn(II) complexes of HTPC have received increasing attention as potential antifungal and antitumor agents (Drozdzewski et al., 2004a,b).

Metal complexes of carboxylic acids have been studied extensively, but there are few works on complexes of HTPC.

The carboxylato groups in TPC generally coordinate to metals, while the sulfur atoms do not and the versatility of this group as a ligand is illustrated by four coordination modes (Scheme 1) to form mono, di, three or polynuclear or polymeric structures. Not only can HTPC coordinate to metal ions in unidentate, bidentate chelating, and bridging, but also bidentate bridging form (Scheme 1) (Yuan et al., 2004; Zheng et al., 2007).

Imidazole (im), which is nitrogen containing a five-membered heterocyclic ring, can be seen in a number of natural products such as amino acids, histidine and purines, which comprise many of the most important bases in nucleic acids; also, its derivatives have gained in



**Scheme 1** The coordination modes of thiophen-2-carboxylate.

importance due to their biological and pharmacological activities (Vijesh et al., 2013).

Interestingly there was only one compound containing both TPC and im ligands, in the literature (Zheng et al., 2007).

In this work, we combined the two important compounds, HTPC and im, in the mixed ligand Mn(II), Co(II), Cu(II) and Cd(II) complexes, and extensively characterized the products.

## Results and discussion

### Synthesis

To synthesize the Mn(II) and Cd(II) complexes, mixtures of metal salts and im were added to a solution of Na-TPC, which was prepared by addition of NaOH to HTPC solution. To prepare the Co(II) complex, a solution of the metal salt, HTPC and im, along with $NH_3$ were added. Suitable crystals were obtained by slow evaporation for X-ray single crystal analyses.

Interestingly, when we tried to obtain a copper compound by using our above-mentioned method or the method of Zheng et al., we continually isolated the known square pyramidal $[Cu(H_2O)(Imd)_2(TCA)_2]$ (Zheng et al., 2007). We therefore prepared the copper complex by microwave-assisted hydrothermal synthesis.

### Crystal structure

The structures of the complexes were confirmed by single crystal X-ray studies. All hydrogen atoms were placed in calculated positions. In Table 1, the experimental details for data collection and structure refinement of the complexes are summarized. Selected bond lengths and angles are provided in Table 2 and the intermolecular and intramolecular interactions are given in Table 3.

All complexes crystallized in the monoclinic space group $P2_1/n$ and showed similar orientations. In all complexes, the TPC bonded to the metals in a monodentate fashion via one of its carboxylato-O atoms. The monodentate im ligand coordinated to the metal via its nitrogen atom (Figure 1).

While the geometry around metals for the Mn(II), Co(II) and Cd(II) complexes were distorted trans-octahedral, $[MN_2O_4]$, the Cu(II) complex had a trans-square planar, $[MN_2O_2]$, environment around the metal center.

The distorted octahedral environments around the Mn(II), Co(II) and Cd(II) metal centers, contain two TPC, two Im and two aqua ligands. The Cu(II) complex contains two TPC and two Im ligands to form the square planar environment around the metal center (Figure 1).

The M-O bond lengths in the complexes (except the Cu complex), reflected the van der Waals radius order of the metals and the Co-O distances were significantly shorter than the others. As expected, the Cu-O bond lengths were shorter than the other M-O distances in the square planar complex.

In the Mn(II), Co(II) and Cd(II) complexes, the aqua ligands, by using one of the hydrogen atoms, created intramolecular hydrogen bonds with the non-coordinated oxygen atoms (O2) of TPC ligands, and by using other hydrogen atoms formed intermolecular hydrogen bonds with the coordinated oxygen atoms (O1) of TPC ligands to connect the molecules along the a axis. Through this direction, the C–H···π interaction was seen between the C3 atom of the thiophene ring and the im ring (Figures 2 and 3; Table 3).

In addition to these interactions, in the Mn(II) and Cd(II) complexes, the C7 atom of the im ring formed intermolecular hydrogen bonds with the non-coordinated oxygen atom of a symmetry related TPC ligand (Table 3), and there were also detected π···π interactions between the im and thiophene rings, so the molecules that located along the b and c axes, are linked to each other (Figure 2, Table 3).

In the Co(II) complex, N-H···O interactions were found between the N2 atom of the im ring and the O2 atom of the TPC ligand to extend molecules in the same manner (Figure 3) instead of C-H···O interactions which were detected for Mn(II) and Cd(II) complexes.

Therefore, overall, the Co(II), Mn(II) and Cd(II) complexes showed H bonded three-dimensional networks.

In the square-planar Cu(II) complex, the N-H of the im formed a hydrogen bond with the un-coordinated oxygen

**Table 1** Crystal and refinement data of the complexes.

| Complex | Mn | Co | Cu | Cd |
|---|---|---|---|---|
| Formula | $C_{16}H_{18}MnN_4O_6S_2$ | $C_{16}H_{18}CoN_4O_6S_2$ | $C_{16}H_{14}CuN_4O_4S_2$ | $C_{16}H_{18}CdN_4O_6S_2$ |
| $M_A$ | 481.40 | 485.39 | 453.97 | 538.86 |
| Temp (K) | 296.15 | 296.15 | 293(2) | 296.15 |
| Crystal system | Monoclinic | | | |
| Space group | $P2_1/n$ | | | |
| a (Å) | 5.5959(1) | 5.5636(2) | 6.5896(3) | 5.6859(2) |
| b (Å) | 15.1016(3) | 15.0047(4) | 7.4860(5) | 14.8429(6) |
| c (Å) | 11.9488(2) | 11.7425(3) | 19.0819(7) | 12.0897(5) |
| $\gamma$ (°) | 94.141(1) | 93.374(1) | 90.621(3) | 94.781(2) |
| Volume (Å$^3$) | 1007.12(3) | 978.57(5) | 941.25(8) | 1016.76(7) |
| Z | 2 | 2 | 2 | 2 |
| $\rho_{calc}$ (mg/mm$^3$) | 1.587 | 1.647 | 1.602 | 1.760 |
| μ (mm$^{-1}$) | 0.904 | 1.133 | 1.412 | 1.320 |
| F(000) | 494.0 | 498.0 | 462.0 | 540.0 |
| Crystal size (mm) | 0.45×0.2×0.15 | 0.5×0.35×0.15 | 0.32×0.28×0.15 | 0.45×0.3×0.15 |
| 2Θ | 4.36–83.9 | 11.42–88.22 | 6.52–59 | 4.36–82.72 |
| Index ranges | -10≤h≤10 | -6≤ h≤ 10 | -8≤ h≤ 8 | -7≤ h≤ 9 |
| | -27≤k≤27 | -28≤ k≤29 | -4≤ k≤ 10 | 18≤ k≤ 27 |
| | -21≤ l≤ 22 | -21≤ l≤22 | -25≤ l≤13 | -16≤ l≤18 |
| Reflect. collected | 41526 | 33742 | 4314 | 18965 |
| Indep. reflect | 6831 | 6791 | 2287 | 4719 |
| | [R(int)=0.0248] | [R(int)=0.0223] | [R(int)=0.0403] | [R(int)=0.0158] |
| Goodness-of-fit on F$^2$ | 1.102 | 1.073 | 1.044 | 1.067 |
| Final R indexes [I>=2σ (I)] | R1=0.0658 | R1=0.0481 | R1=0.1003 | R1=0.0719 |
| | wR2=0.2053 | wR2=0.1317 | wR2=0.2742 | wR2=0.2213 |
| Final R indexes (all data) | R1=0.0764 | R1=0.0593 | R1=0.1407 | R1=0.0784 |
| | wR2=0.2217 | wR2=0.1423 | wR2=0.3243 | wR2=0.2307 |

**Table 2** Selected distances (Å) and angles (°) of the complexes.

| | Mn | Co | Cd | Cu |
|---|---|---|---|---|
| Bond | Length | Length | Length | Length |
| M-N1 | 2.2268(12) | 2.1094(9) | 2.257(3) | 1.970(6) |
| M-O1 | 2.2175(11) | 2.1708(8) | 2.352(3) | 2.020(5) |
| M-O3 | 2.2241(12) | 2.1241(9) | 2.365(3) | – |
| S1-C2 | 1.6923(16) | 1.6984(12) | 1.678(5) | 1.687(8) |
| S1-C5 | 1.663(3) | 1.675(2) | 1.661(5) | 1.666(8) |
| Bond | Angles | Angles | Angles | Angles |
| O1$^1$-M-O3$^1$ | 90.56(4) | 88.00(3) | 90.21(11) | – |
| O1$^1$-M-O3 | 89.44(4) | 92.00(3) | 89.79(11) | – |
| O1-M-O3 | 90.56(4) | 88.00(3) | 90.21(11) | – |
| O1-M-O3$^1$ | 89.44(4) | 92.00(3) | 89.79(11) | – |
| N1-M-O1 | 92.58(5) | 88.17(4) | 93.39(12) | 90.8(2) |
| N1$^1$-M-O1 | 87.42(5) | 91.83(4) | 86.61(12) | 89.2(2) |
| N1$^1$-M-O1$^1$ | 92.58(5) | 88.17(4) | 93.39(12) | 90.8(2) |
| N1-M-O1$^1$ | 87.42(5) | 91.83(4) | 86.61(12) | 89.2(2) |
| N1-M-N1$^1$ | 180.0 | 180.0 | 179.999(1) | 180.0 |
| N1-M-O3$^1$ | 90.52(5) | 91.19(4) | 90.06(13) | – |
| N1$^1$-M-O3 | 90.52(5) | 91.20(4) | 90.06(13) | – |
| N1$^1$-M-O3$^1$ | 89.48(5) | 88.81(4) | 89.94(13) | – |
| N1-M-O3 | 89.48(5) | 88.80(4) | 89.94(13) | – |
| Symmetry | $^1$-x, -y, -z | $^1$2-x, -y, 2-z | $^1$1-x, -y, 2-z | $^1$1-x, -y, -z |

atom of TPC of the complex unit at x, 1+y, z, and additionally, there were found π···π interactions between the im rings at 1-x, 1-y, -z. So, by contrast, the copper complex showed only a one-dimensional network (Figure 4, Table 3).

## IR spectra

The IR spectrum of HTPC showed peaks at 2548 cm$^{-1}$, 1689 cm$^{-1}$ and 1353 cm$^{-1}$ attributed to OH, C=O+ $COO^-_{asym.}$ and $COO^-_{sym.}$ vibrations, respectively. The N-H and C=N peaks of im were seen at 3124 cm$^{-1}$ and 1669 cm$^{-1}$, respectively.

The bands of the free HTPC at 2548 cm$^{-1}$, disappeared in IR spectra of the complexes and indicated that the carboxylic acid proton is removed to form thiophen-2-carboxylato anion on complexation. In all complexes, due to the coordination of the metal environment, the C=N bands of im shifted to lower frequencies and were seen at 1613 cm$^{-1}$, 1600 cm$^{-1}$, 1602 cm$^{-1}$ and 1600 cm$^{-1}$ for Mn(II), Co(II), Cd(II) and Cu(II) complexes, respectively, and N-H peaks were shifted to the higher frequencies [for Mn(II) and Co(II)=3175 cm$^{-1}$,

**Table 3** Geometries of intermolecular and intramolecular interactions.

| D–H–A | D–H (Å) | H–A (Å) | D–A (Å) | D-H-A(°) |
|---|---|---|---|---|
| Mn | | | | |
| O3–H3A–O2 | 0.86 | 1.93 | 2.6732(19) | 142.9 |
| O3–H3B–O1$^{1}$ | 0.86 | 2.06 | 2.8052(17) | 143.6 |
| C7–H7–O2$^{2}$ | 0.93 | 1.86 | 2.769(2) | 164.7 |
| C3-H3$\cdots\pi^{3}$ | 0.93 | 2.76 | 3.666(2) | 164 |
| $\pi\cdots\pi^{4,5}$ | | | 3.8984(16) | 4.14(13) |
| $^{1}$-1+x, +y, +z, $^{2}$1/2+x, 1/2-y, -1/2+z; $^{3..}$1-x, -y, -z $^{4,5}$ ±1/2+x,1/2-y,±1/2+z | | | | |
| Co | | | | |
| O3–H3A–O2$^{1}$ | 0.85 | 1.88 | 2.6549(15) | 151.1 |
| O3–H3B–O1$^{2}$ | 0.85 | 2.06 | 2.8121(12) | 147.4 |
| N2–H2–O2$^{3}$ | 0.86 | 1.94 | 2.7734(15) | 164.0 |
| C3-H3$\cdots\pi^{4}$ | 0.93 | 2.74 | 3.6442(19) | 165 |
| $\pi\cdots\pi^{5.6}$ | | | 3.8726(11) | 4.09(10) |
| $^{1}$2-x, -y, 2-z $^{2}$1-x, -y, 2-z; $^{3}$5/2-x, 1/2+y, 3/2-z; $^{4..}$-1+x, y, z $^{5,6}$ 1/2-x, ±1/2+Y,1/2-z | | | | |
| Cd | | | | |
| O3–H3A–O2 | 0.85 | 1.93 | 2.678(5) | 146.3 |
| O3–H3B–O1$^{1}$ | 0.85 | 1.98 | 2.784(4) | 156.7 |
| C7–H7–O2$^{2}$ | 0.93 | 1.85 | 2.760(5) | 165.3 |
| C3-H3$\cdots\pi^{3}$ | 0.93 | 2.72 | 3.632(5) | 168 |
| $\pi\cdots\pi^{4,5}$ | | | 3.838(3) | 3.0(3) |
| $^{1}$1+x, +y, +z; $^{2}$-1/2+x, 1/2-y, 1/2+z; $^{3}$1-x, 1-y, 1-z $^{4,5}$±1/2+x,1/2-y,±1/2+z | | | | |
| Cu | | | | |
| N2–H2–O2$^{1}$ | 0.86 | 1.93 | 2.753(9) | 160.2 |
| $\pi_{imd}\cdots\pi_{imd}{}^{2}$ | | | 4.083(5) | 0 |
| $^{1}$+x, 1+y, +z; $^{2..}$1-x, 1-y, -z | | | | |

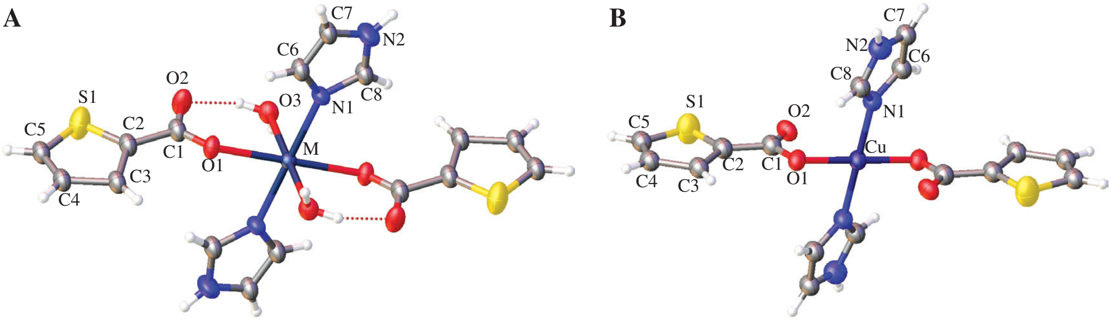


**Figure 1** The structures of the complexes. (M=Mn, Co or Cd).

for Cd(II)=3167 cm$^{-1}$ and for Cu(II)=3139 cm$^{-1}$]. The band between 3370 cm$^{-1}$ and 3290 cm$^{-1}$ was attributed to the aqua ligands for Mn(II), Co(II) and Cd(II) complexes.

To determine the coordination modes of the carboxylato group, the difference between the asymmetric and symmetric carboxylato vibrations ($\Delta=\overline{v}_{asym}-\overline{v}_{sym}$) was calculated. The differences between the frequencies were determined as 162, 154, 160 and 154 for Mn(II), Co(II), Cd(II) and Cu(II) complexes, respectively. These results for Δ values indicated that the carboxylato group participates in a monodentate manner for the complexes (Nakamoto, 1978; Zheng et al., 2007; Cagnin et al., 2010; Palanisami and Murugavel, 2011; Abbas et al., 2013).

## UV-Vis spectra and magnetic susceptibility data

The room temperature magnetic moments which are in accord with the geometry around the metal centers, were found to be 4.87, 4.61, diamagnetic and 1.65 BM for the Mn(II), Co(II), Cd(II) and Cu(II) complexes, respectively.

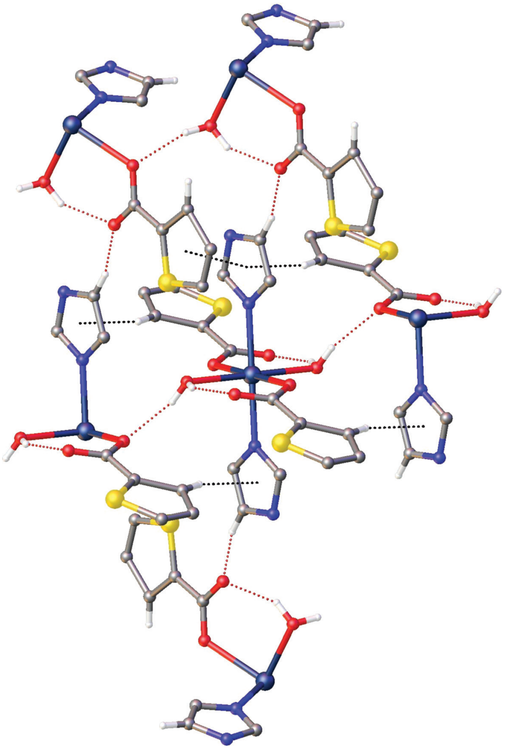


**Figure 2** The O-H···O, C-H···O, C-H···π and π ···π interactions in the Mn and Cd complexes.

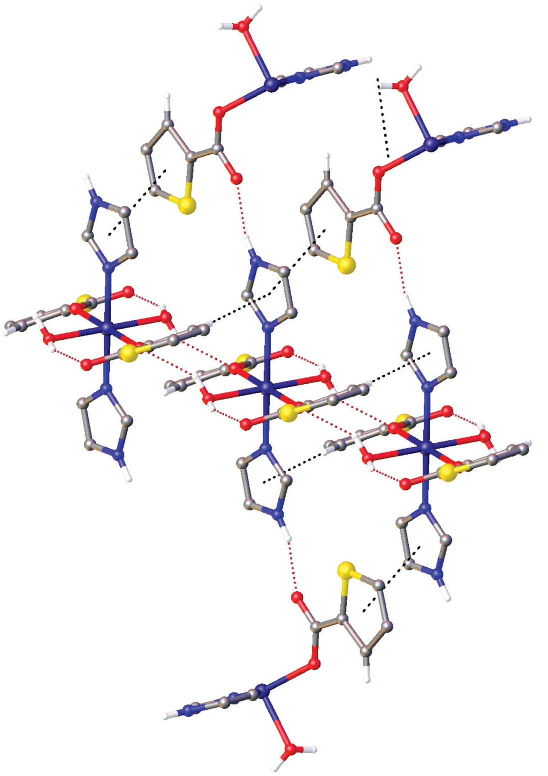


**Figure 3** The O-H···O, N-H···O, C-H···π and π ···π interactions in Co complex.

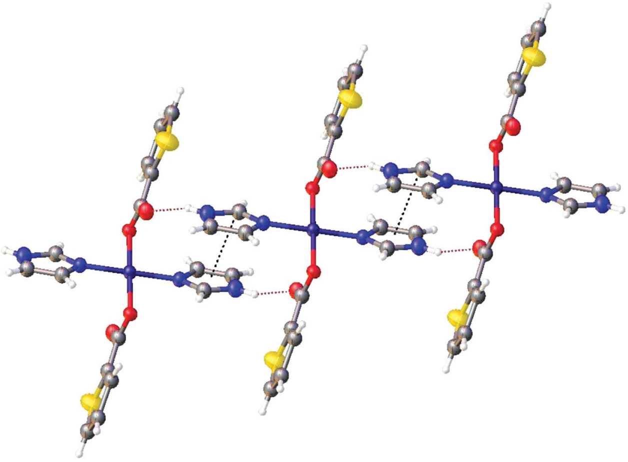


**Figure 4** The N-H···O and π ···π interactions in the copper complex.

The UV-Vis spectra of the complexes in DMF solutions showed one band [except the Cd(II) complex], at 494 nm (ε=9 $lmol^{-1}$ $cm^{-1}$), 566 nm (ε=23 $lmol^{-1}$ $cm^{-1}$) and 668 nm (ε=75 $lmol^{-1}$ $cm^{-1}$) for Mn(II), Co(II) and Cu(II) complexes, respectively.

## Thermogravimetric analysis

In the thermal analyses works for $[M(TCA)_2(H_2O)_2(im)_2]$ [M=Mn(II), Co(II) and Cd(II)] the complexes underwent complete decomposition in three stages and gave similar thermal analyses curves. The first stages are related to the removal of aqua ligands (Figures 5–7, Table 4). The Cu(II) complex decomposed in two stages (Figure 8, Table 4).

It is not easy to explain reasonably, without mass spectra, the evolution of fragments during thermal decomposition for second and third decomposition stages for all complexes. However, it can be suggested, at the second and third stages, that the im and TCA ligands decomposed to form metals ($Cu_2O$ for copper complex) and after 485°C, 565°C, 566°C and 539°C, increasing the temperature produced metal oxides for Mn, Co, Cd and Cu compounds, respectively.

In consideration of the $DTA_{max}$ values of the anhydrous form of the complexes, the thermal stability of the complexes are suggested as Co (273°C)>Cu (229°C)>Cd (175°C)>Mn (167°C).

# Conclusions

The novel mixed ligand complexes $[M(TCA)_2(H_2O)_2(im)_2]$ (M: Mn, Co, Cd) and $[Cu(TCA)_2(im)_2]$ were synthesized and

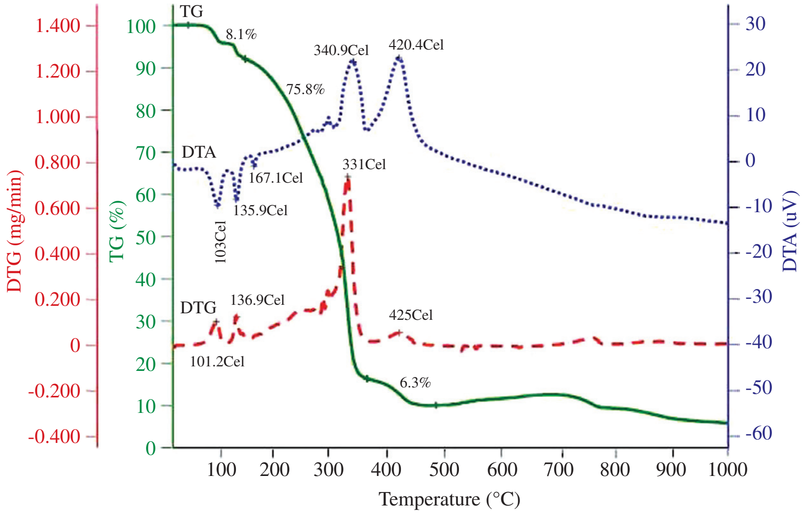


**Figure 5** Thermal analyses curves of the Mn complex.

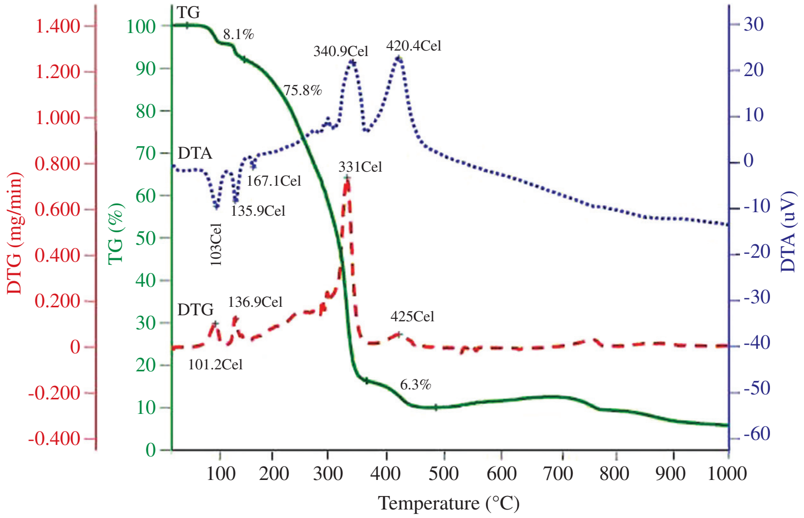


**Figure 6** Thermal analyses curves of the Co complex.

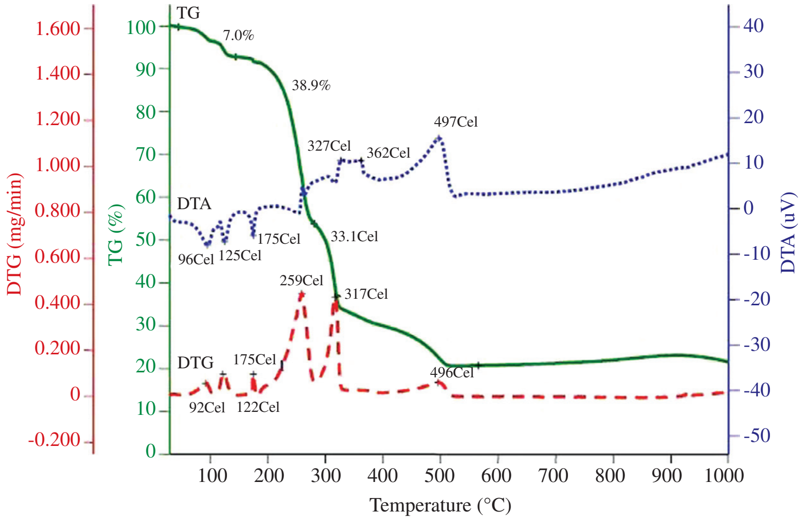


**Figure 7** Thermal analyses curves of the Cd complex.

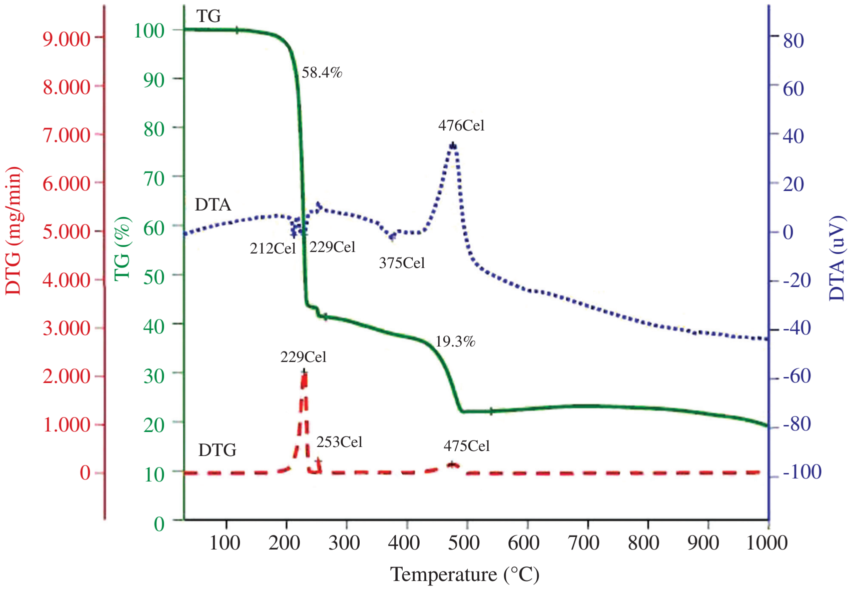


**Figure 8** Thermal analyses curves of the Cu complex.

**Table 4** Thermal analyses data of the complexes.

| Compound | Mn | Co | Cd | Cu |
|---|---|---|---|---|
| Stage 1 | 40–152 | 40–148 | 40-144 | 177–263 |
| DTA$_{max}$ (°C) | 103–136 | 94–127 | 96-125 | 212–229 |
| Mass loss (%) | 8.1 (7.5) | 7.8 (7.4) | 7.0 (6.7) | 58.4 (-) |
| Stage 2 and 3 | 152–485 | 148–565 | 144–566 | 263–539 |
| DTA$_{max}$ (°C) | 167.341.420 | 273.331.482 | 175.259.317.496 | 375.476 |
| Mass loss (%) | 82.1 (81.1) | 76.4 (80.4) | 72.0 (72.4) | 19.3 (-) |
| Total loss (%) | 90.2 (88.6) | 84.2 (87.8) | 79.0 (79.1) | 77.8 (78.9) |
| Residue | MnO | CoO | CdO | CuO |

Calculated values are given in parentheses.

characterized. The thiophene-2-carboxylic acid (HTCA) acted in a monoanionic monodentate manner and bonded to the metals via its carboxylate oxygen. The [$MO_4N_2$] type octahedral geometry was found for Mn(II), Co(II) and Cd(II) complexes and [$CuO_2N_2$] type square-planar geometry for Cu(II) complex. The Co(II), Mn(II) and Cd(II) complexes showed three-dimensional networks, while the copper complex is a one-dimensional network, all linked by intermolecular interactions in the solid state.

# Experimental

## Materials and measurements

Only commercially available reagent grade chemicals were used. Fourier transform infrared spectroscopy (FT-IR) spectra (4000–450 cm$^{-1}$) were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer, with samples prepared as KBr pellets. Magnetic susceptibility was measured using a Sherwood Scientific MX1 Gouy Magnetic Balance (Cambridge, UK) at room temperature. UV-Vis spectra were recorded with a PG Instruments PG-T80+ UV-Vis spectrometer. An SII-O Extar 6000 thermal analyzer (Japan) was used to record TG, DTG, and DTA curves in static air atmosphere at a heating rate of 10 (°C)min$^{-1}$ from 30 to 700°C using platinum crucibles. Highly sintered $\alpha$–$Al_2O_3$ was used as a reference. Elemental analysis for C, H, and N were performed using a Costech ECS 4010 CHNSO analyzer. A CEM Mars-Xpress microwave digestion system was used in the synthesis of the copper complex with a 50 mL Teflon tube.

## Synthesis of the complexes

### Mn and Cd complexes

Solution A: To the 20 mL water solutions of 2.5 mmol metal salts [0.5 g $MnCl_2{\cdot}4H_2O$ or 0.77 g $Cd(NO_3)_2{\cdot}4H_2O$], 2.4 mmol (0.17 g) im were added.

Solution B: A total of 2.4 mmol (0.32 g) HTCA was dissolved in 40 mL water and stirred for 30 min at 75–80°C. To this solution, 0.2 g NaOH solid was added. To prepare the complexes, Solution A was added to Solution B. The mixtures were additionally stirred and filtered. The crystalline products were obtained by slow evaporation. Yield 65% based on Mn. $C_{16}H_{18}MnN_4O_6S_2$ (481.41 g/mol): calcd. C 39.92, H 3.77, N 11.64 %; found: C 39.71, H 3.47, N 12.13 %. IR(KBr): $\bar{v}$ =3318 bs, 3175 s, 1613 m, 1546 s, 1384 m, $cm^{-1}$. Yield 75% based on Cd. $C_{16}H_{18}CdN_4O_6S_2$ (538.88 g/mol): calcd. C 35.66, H 3.37, N 10.40%; found: C 36.06, H 3.17, N 10.850%. IR(KBr): $\bar{v}$ =3292 bs, 3167 s, 1602 m, 1541 s, 1381 m, $cm^{-1}$.

### Co complex

A total of 2.1 mmol (0.5 g) $CoCl_2{\cdot}6H_2O$ and 1 mmol (0.13 g) HTCA was dissolved in 20 mL water and stirred for 30 min at 75–80°C. To this solution, 1 mmol (0.07 g) im was added and additionally stirred for 20 min. Four drops of concentrated $NH_3$ were added to mixture. The mixture was filtered and the crystalline product was obtained by slow evaporation. Yield 70% based on Co. $C_{16}H_{18}CoN_4O_6S_2$ (485.40 g/mol): calcd. C 39.59, H 3.74, N 11.54%; found: C 39.16, H 4.08, N 11.12%. IR(KBr): $\bar{v}$ =3369 bs, 3175 s, 1600 m, 1537 s, 1383 m, $cm^{-1}$.

### Cu complex

To prepare the copper complex, a hydrothermal synthesis method under microwave radiation was used. To this, 2.34 mmol (0.3 g) HTCA, 7.8 mmol (0.2 g) $CuCl_2{\cdot}2H_2O$ and 1.6 mmol (0.11 g) im and 10 mL water was placed in a 50 mL Teflon tube and by using 800 W energy, step by step heating and cooling was done.
Step 1: The mixture was heated to 80°C in 60 min and held at this temperature for 30 min.
Step 2: The mixture was heated to 100°C in 30 min and held at this temperature for 60 min.
Step 3: The mixture was heated to 130°C in 30 min and held at this temperature for 30 min.
Step 4: The mixture was cooled to 120°C in 60 min and held at this temperature for 60 min.
Step 5: The mixture was cooled to 50°C in 60 min, held at this temperature for 30 min, filtered while hot and set aside for crystals to appear. Yield 80% based on Cu. $C_{16}H_{14}CuN_4O_4S_2$ (453.98 g/mol): calcd. C 42.33, H 3.11, N 12.34%; found: C 41.86, H 2.87, N 12.01%. IR(KBr): $\bar{v}$ =3139 s, 1600 m, 1542 s, 1388 m, $cm^{-1}$.

## X-ray crystallography

By using Mo-Kα radiation, the crystal data were collected using $\omega$-2θ scan techniques on a Bruker Smart Apex CCD diffractometer for the Mn, Co and Cd complexes and on an Agilent SuperNova diffractometer (with an Eos CCD detector) for the copper complex. Software programs on Bruker were used; Bruker APEX2 and Bruker SAINT for data collection for data reduction, respectively (Bruker 2007a,b). The CrysAlisPro software program was used for data collection, cell refinement and data reduction on an Agilent diffractometer (Agilent, 2011).

Using Olex2 (Dolomanov et al., 2009), the structures were solved by the SIR2011 (Burla et al., 2012) structure solution program by direct methods and refined with the ShelXL refinement package using least-squares minimization (Sheldrick, 2008). All H atoms were refined using a riding model. To prepare material for publication, Olex2 were used (Dolomanov et al., 2009).

## Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 949390, 949391, 949392 and 949393. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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