

Synthesis and Characterization of Mn(II), Co(II), Ni(II),Cu(II), Zn(II) and Cd(II) Complexes with Thiophene -2- carboxylic Acid Hydrazide

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ABSTRACT

Metal (II) complex of thiophene -2- carboxylic acid Hydrazide (TCH) ligand of the type $[M(TCH)_2X_2]$ where M= Mn(II), Co(II), Ni(II),Cu(II), Zn(II) and Cd(II) , X=Cl⁻, NO₃⁻ have been prepared and characterized by metal analysis, molar conductance, magnetic moment measurements and electronic and IR spectral data. Based on physico- chemical studies, an octahedral geometry was assigned for all the complexes and the ligand (TCH) acted as neutral bidentate ligand, coordinating via the carbonyl oxygen and the amino nitrogen atoms.

Keywords: Thiophene -2- carboxylic acid hydrazide, Transition metal complexes.

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M=Mn⁺², Co⁺², Ni⁺²,

$[M(TCH)_2X_2]$

(TCH)

.NO₃⁻, Cl⁻=X

, Cu⁺², Zn⁺², Cd⁺²

.IR

(TCH)

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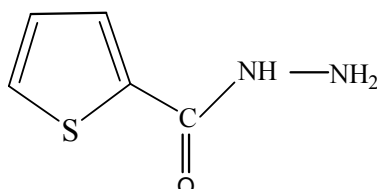
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INTRODUCTION

The discovery that isonicotinic acid hydrazide (INH) and other hydrazides have tuberculostatic properties (Fox, 1960), and these properties increases (in vitro) in the presence of copper (II) ions (Sorkin *et al.*, 1952), rendered great importance to the study of acid hydrazide complexes (Iskander *et al.*, 1974).

Acid hydrazides as complex forming ligands are of considerable interest, for they provide various active potential donor sites. They may function as neutral bidentate ligands forming chelate complexes (Kriza *et al.*, 2010, Sallomi and Al-Daher, 1979; 1980; 1983) Their behavior as neutral monodentat ligand has also been reported (Ahmed and Chaudri, 1971; Al-Saady and Al- Daher , 2000).

Recently (Mahalingam *et al.*, 2009), thiophene -2- carboxylic acid hydrazide (TCH) was found to act as neutral bidentate ligand coordinated through the acyl oxygen and the amine nitrogen atoms in the X-ray crystal structural study of the octahedral complex [RuCl₂ (TCH) (DM S O) ₂]. Therefore it was of interest to study the coordinating behavior of thiophene-2- carboxylic acid hydrazide with various divalent metal ions.



Thiophene-2-Carboxylic acid Hydrazide (TCA)

EXPERIMENTAL

Material and Methods

All chemicals were of reagent grade and used as supplied from Fluka or BDH chemical companies, IR spectra were recoded on a Tensor 27Co. Bruker (FT-IR) spectrophotometer in the rang (4000- 400cm⁻¹) using KBr pellets. The metal content were estimated spectrophoto-metrically using Shimadzu atomic absorption 670. Conductivity measurements were made on 10⁻³M solutions of the complexes in absolute ethanol at ambient temperature using conductivity meter Jenway PMC3. Electronic spectra were recorded on Shimadzu 1650 PC UV – Vis spectrophotometer for 10⁻³M solutions of the complexes in ethanol using (1 cm) quartz cell. The magnetic measurements were carried out at 25C° on the solid by Farady's method using Bruker BM6 apparatus . Melting points were recorded on a Electrothermal 9300 apparatus and are uncorrected.

Preparation of the Ligand :

Ethyl thiophene-2- carboxylate :

was prepared according to litrature (Vogel, 1989) using thiophene -2- carboxylic acid chloride.

preparation of thiophene-2-carboxylic acid hydrazide:

This was prepared by the reaction of ethyl thiophene-2- carboxylate with hydrazine hydrate in absolute ethanol by the procedure reported in previous paper (Al-Saady and Al-Daher , 2000) m.p. 136C°.

Preparation of the Metal Complexes :**Preparation of complexes of the type $[M(TCH)_2Cl_2]$** **M=Mn(II) , Co(II) , Ni(II) , Zn(II) and Cd(II)**

A hot solution of metal (II) chloride (0.001 mole) in absolute ethanol (15ml) was added with constant stirring to a boiling solution of thiophene 2- carboxylic acid hydrazide (TCH) (0.84 g, 0.002 mole) in absolute ethanol (15ml) After complete addition, the reaction mixture was refluxed for one hour. On cooling, the complex separated out, was filtered and washed with absolute ethanol (2×3 ml) then dried at 80C°.

Preparation of complexes of the type $[M(TCH)_2(NO_3)_2]$: M=Mn(II) , Co(II) , Ni(II) , Zn(II) and Cd(II)

The same procedure mentioned above was adopted by using (1:2) metal to ligand molar ratio, and the appropriate, metal (II) nitrate, except that after one hour reflux, the reaction mixture was evaporated to half its volume then left to cool overnight upon which crystalline complex was obtained, separated by decantation washed with absolute ethanol (3ml) then dried at 80C°.

Preparation of copper (II) complexes $[Cu(TCH)_2X_2]$ **X=NO₃ or Cl :**

These were prepared in the same way as mentioned above using 1:2 metal to ligand molar ratio and the appropriate copper (II) salt except that the reactions were carried out in ice cold absolute ethanol by stirring the reaction mixture for three hours.

The crystalline complexes were separated on standing for three days, which were filtered, washed with cold absolute ethanol (3ml) and then dried in a vacuum desiccator. (to prevent reduction of Cu (II) to Cu(I)).

RESULTS AND DISCUSSION

The direct reaction of metal (II) salts with thiophene-2-carboxylic acid hydrazide (TCH) as ligand in 1:2 (M:L) molar ratio in absolute ethanol yielded complexes (1-12) Table 1 , of the general formula $[M(TCH)_2X_2]$ where M=Mn(II) , Co(II) , Ni(II) , Cu(II) , Zn(II) and Cd(II) and X=Cl⁻ or NO₃⁻ . All the synthesized complexes are air and moisture stable solids. They are soluble in ethanol, DMF and DMSO and insoluble in non- polar organic solvents. Their melting temperatures, solubility and crystalline nature suggest that they are non-polymeric (Chohan *et al.*, 2000 ; Chohan and Sherazi , 1997). The molar conductance measurements of the complexes in absolute ethanol are within the range (3.6-27.8) ohm⁻¹.mol⁻¹.cm² correspond to non-electrolytes (Geary, 1971) indicating the neutral nature (i.e. non-electrolyte) of the complexes.

The reaction of TCH with copper (II) salts were carried out in ice cold ethanol to prevent reduction of Cu(II) to Cu(I). In boiling ethanol the reaction of TCH with copper (II) chloride proceeded with evolution of nitrogen and a pale green solid formed which could not be identified. The clear almost colourless filtrate was left to stand for three days when white crystalline solid (m.p. 258) crystallizes out in good yield, IR spectrum of which indicating that it may be the corresponding dihydrazide. The oxidation reduction reaction of aroylhydrazides with cupric ions were reported earlier (Iskander *et al.*, 1974).

Table 1: Physical properties and analytical data of the ligand and it metal complexes

Complex No.	Complex	Color	m.p (°C)	% Yield	$\Lambda_m^* \text{M. ohm}^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$.
ligand	TCH (C ₅ H ₆ N ₂ O)	Pale Yellow	136	%82	-----
1	[Mn(TCH) ₂ Cl ₂]	Pale Yellow	140-141	73	21.4
2	[Mn(TCH) ₂ (NO ₃) ₂]	Pale Yellow	164	60	24.1
3	[Co (TCH) ₂ Cl ₂]	Pink	201	59	16.6
4	[Co (TCH) ₂ (NO ₃) ₂]	Red	210	63	18.6
5	[Ni(TCH) ₂ Cl ₂]	Pale green	240	68	11.7
6	[Ni(TCH) ₂ (NO ₃) ₂]	Blue	242	64	27.8
7	[Cu(TCH) ₂ Cl ₂]	Green	238	63	25.4
8	[Cu(TCH) ₂ (NO ₃) ₂]	Brown	124	54	4.2
9	[Zn(TCH) ₂ Cl ₂]	White	204	72	27.2
10	[Zn(TCH) ₂ (NO ₃) ₂]	White	212	64	3.6
11	[Cd(TCH) ₂ Cl ₂]	White	242	67	20.2
12	[Cd(TCH) ₂ (NO ₃) ₂]	White	184	64	4.1

* 10⁻³ M solution in absolute ethanol

** calculated in parentheses

Infrared spectra and mode of chelation

The modes of coordination of thiophene-2-carboxylic acid hydrazide (TCH) to metal ions were investigated by comparing the IR spectra of the complexes with that of TCH.

The IR spectrum of the ligand displayed a highest frequency band at 3442 cm^{-1} which can be assigned to the asymmetric $\nu(\text{N-H})$ vibration of the terminal NH_2 group. The other bands at 3412 cm^{-1} and 3221 cm^{-1} may be due to the symmetric $\nu(\text{N-H})$ vibration of the imino and amino groups. The spectra of the complexes in the NH stretching frequency region are hopelessly complicated as the bands in this region are broad. This is due to many factors of these are the decrease in hydrogen bonding that usually occurs in complex formation which causes a positive shift in the NH stretching, the effect of coordination that causes a negative shift in these frequencies. Thus it is difficult to draw certain conclusion about the coordination from these bands, although a negative shift was observed in these frequencies which may indicate coordination through the amino group (Frontes *et al.*, 2004; Wahed *et al.*, 2004; Mahalingam *et al.*, 2009, Chandra *et al.*, 2009).

The other important IR bands of the ligand and its metal complexes are given in Table (2).

The amide I band $\nu(\text{C=O})$ of the ligand located at 1651 cm^{-1} is shifted to lower frequencies by $12\text{-}26\text{ cm}^{-1}$ in all complexes which may be attributed to coordination via carbonyl oxygen as one of the coordination sites (Kriza *et al.*, 2010). The involvement of carbonyl and amino groups in coordination is also supported by the fact that amide II and NH_2 -bending bands occurring at 1555 cm^{-1} and 1621 cm^{-1} respectively in the TCH spectrum suffer negative shifts of about $12\text{-}31\text{ cm}^{-1}$ and $21\text{-}41\text{ cm}^{-1}$ respectively in the IR spectra of the complexes (Sallomi and Al-Daher, 1983). This conclusion is supported by the movement of the $\nu(\text{N-N})$ frequency at 961 cm^{-1} to higher values in the complexes (Chohan *et al.*, 2000; Reena *et al.*, 2008).

The disappearance of the medium intensity band at 941 cm^{-1} (assigned for NH_2 wagging vibration) in the spectrum of the ligand on complex formation and observation of new bands at the region $1178\text{-}1202\text{ cm}^{-1}$ of the complexes spectra, may be considered as another support for the coordination of NH_2 group (Sallomi and Al-Daher, 1983; Nagano *et al.*, 1964). New bands were also observed at $495\text{-}515\text{ cm}^{-1}$ and $428\text{-}470\text{ cm}^{-1}$ in the spectra of the complexes these may be assigned for $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively (Kriza *et al.*, 2010).

The band at 839 cm^{-1} observed in the spectrum of the free ligand ascribed to ν CSC (thiophene ring) stretching vibration was not affected by coordination which may indicates that the thiophene ring sulphur atom is not taking part in the complex formation (Kriza and Spinu, 2000).

The IR spectra of nitrate complexes (2,4,6,8,10 and 12)Table (3) display three (N-O) stretching bands at $1427\text{-}1475\text{ cm}^{-1}(\nu_5)$, $1296\text{-}1304(\nu_1)$ and $1019\text{-}1072\text{ cm}^{-1}(\nu_2)$. The position of these bands suggested that both nitrate groups are coordinated to the central metal ion as a unidentate fashion. (Nakamoto, 1997 ; Chandra *et al.*, 2009).

Table 2: Selected infrared frequencies (cm^{-1}) of TCH and its complexes

Complex No.	Amide I $\nu(\text{C}=\text{O})$	$\delta(\text{NH}_2)$	Amide II	$\omega(\text{NH}_2)$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{N}-\text{N})$
TCH	1651 _(sh)	1621 _(s)	1555 _(s)	941 _(m)	967 _(w)		
1	1632 _(s)	1595 _(s)	1530 _(s)	1187 _(s)	981 _(w)	453 _(w)	49
2	1635 _(s)	1587 _(s)	1532 _(s)	1180 _(s)	1009 _(w)	459 _(w)	50
3	1637 _(s)	1581 _(s)	1540 _(s)	1198 _(s)	989 _(w)	461 _(w)	50
4	1628 _(s)	1588 _(s)	1528 _(s)	1178 _(s)	970 _(w)	428 _(w)	49
5	1628 _(s)	1583 _(s)	1543 _(s)	1200 _(s)	1005 _(w)	438 _(w)	51
6	1625 _(s)	1580 _(s)	1524 _(s)	1194 _(s)	1001 _(w)	436 _(w)	51
7	1630 _(s)	1600 _(s)	1532 _(s)	1180 _(s)	981 _(w)	450 _(w)	49
8	1628 _(s)	1591 _(s)	1536 _(s)	1202 _(s)	969 _(w)	447 _(w)	50
9	1630 _(s)	1582 _(s)	1530 _(s)	1201 _(s)	1011 _(w)	448 _(w)	50
10	1633 _(s)	1589 _(s)	1536 _(s)	1188 _(s)	1012 _(sh)	463 _(w)	51
11	1629 _(s)	1585 _(s)	1528 _(s)	1201 _(s)	973 _(w)	470 _(w)	49
12	1639 _(s)	1593 _(s)	1537 _(s)	1188 _(s)	990 _(sh)	463 _(w)	49

sh=sholder , s=strong , m=medium , w=weak

Table 3 :Selected infrared frequencies (cm^{-1}) of nitroato complexes.

Complex No.	nitrate frequencies				
	ν_5	ν_1	$\nu\Delta$	ν_2	ν (M–O) NO ₃
2	1427 _(s)	1285 _(sh)	142	1065 _(m)	546 _(m)
4	1435 _(s)	1298 _(s)	137	1030 _(sh)	535 _(m)
6	1442 _(sh)	1306 _(m)	136	1070 _(m)	551 _(m)
8	1447 _(s)	1299 _(sh)	148	1072 _(sh)	557 _(m)
10	1465 _(sh)	1296 _(s)	179	1039 _(m)	553 _(m)
12	1490 _(s)	1302 _(s)	138	1019 _(sh)	538 _(m)

MAGNETIC PROPERTIES

The magnetic moments for manganese(II) complexes (1) and (2) at room temperature of 5.89 and 5.79 B.M. , respectively corresponding to five unpaired electron suggesting an octahedral geometry (Cotton and Wilkinson, 1999; Chandra *et al.*, 2009). For Co(II) complexes (3) and (4) the magnetic moments were 4.75 and 4.92 B.M., respectively, corresponding to three unpaired electrons indicating high spin character. These values are within the rang (4.7-5.2 B.M.) corresponding to an octahedral geometry for the Co(II) ions (Cotton and Wilkinson, 1999). Nickel (II) complexes (5) and (6) show magnetic moments of 2.95 and 2.86 B.M., respectively . These values are within the range (2.8-3.4 B.M.) found for paramagnetic complexes of Ni(II) with octahedral geometry (Cotton and Wilkinson, 1999). The magnetic moments values of Cu(II) complexes (7) and (8) were 2.04 and 2.1 B.M., respectively reasonably correspond to octahedral geometry of Cu(II) complexes (Kriza *et al.*, 2010). The Zn(II) and Cd(II) complexes (9-12) were diamagnetic, as expected for complexes of metal ions with a d^{10} configuration.

Electronic spectra

The data of the electronic spectra of the ligand and these of the complexes (1-12) are given in Table 4.

The spectrum of thiophene-2-carboxylic acid hydrazide (TCH) presented two bands in the UV interval at 40650 cm^{-1} and 30864 cm^{-1} , assigned to

$\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions respectively .

The electronic spectra of the two pale yellow Mn(II) complexes (1) and (2) have only the ligand bands in addition to many very weak absorptions characteristic of d^5 electronic configuration for octahedral high spin complexes, d-d transitions due to spin and laporte – forbidden. The very weak bands arise from promotion of an electron to give various excited states containing only three unpaired electrons which may be assigned to the transitions :

${}^6A_{1g} \longrightarrow {}^4T_1(G)$, ${}^6A_{1g} \longrightarrow {}^4E_g(G)$, ${}^6A_{1g} \longrightarrow {}^4A_{1g}(G)$, ${}^6A_{1g} \longrightarrow {}^4E_g(D)$ and

${}^6A_{1g} \longrightarrow {}^4T_{1g}(P)$. (Chandra *et al.*, 2009; Castineiras *et al.*, 2009).

The electronic spectra of the Co(II) complexes (3) and (4) recorded in ethanol solution, exhibited absorptions in the ranges 9050-9090 cm^{-1} , 16025-16260 cm^{-1} and 19531-20000 cm^{-1} . These bands may be assigned to the transitions : ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \longrightarrow {}^4A_{2g}$ and ${}^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ respectively. The position of these bands suggests an octahedral environment around the Co(II) ion (Lever, 1984; kriza *et al.*, 2010). Both electronic spectra of Ni (II) complexes (5) and (6) exhibit three bands at 9328-9708 cm^{-1} , 15337-15773 cm^{-1} and 25125-26315 cm^{-1} attributed to the transitions

${}^3A_{2g} \longrightarrow {}^3T_{2g}$, ${}^3A_{2g} \longrightarrow {}^3T_{1g}$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ respectively, which are characteristic of an octahedral geometry (Lever, 1984 ; kriza *et al.*, 2010) .

The electronic spectra of Cu (II) complexes (7) and (8) have broad bands at 14705 cm^{-1} and 13123 cm^{-1} respectively , which can be attributed to the transitions ${}^2B_{1g} \longrightarrow {}^2A_{1g}$, ${}^2B_{1g} \longrightarrow {}^2B_{2g}$ and ${}^2B_{1g} \longrightarrow {}^2E_g$ characteristic for Cu(II) ions in an octahedral environment (Lever, 1984; Dawood and Mahmood, 2006).

In the spectra of zinc(II) and cadmium(II) complexes (9-12), there were only the bands characterizing the ligand, but displaced to lower values compared with the corresponding bands in the spectrum of the free ligand, which proves the coordination of the ligand to the metal ion.

Table 4 : Electronic spectral data and geometries of ligand and complexes.

Complex No.	Electronic spectra cm^{-1}	Geometry
1	40650 , 29585	Octahedral
2	40650 , 29695	Octahedral
3	40759 , 29240 , 19531 , 16025 , 9050	Octahedral
4	40650 , 29585 , 20000 , 16260 , 9090	Octahedral
5	40650 , 28571 , 25125 , 15337 , 9328	Octahedral
6	40650 , 29585 , 26315 , 15773 , 9708	Octahedral
7	40322 , 28901 , 14705	Octahedral
8	40322 , 29411 , 13123	Octahedral
9	40650 , 30051	Octahedral
10	40983 , 29585	Octahedral
11	40759 , 29240	Octahedral
12	40650 , 29950	Octahedral

CONCLUSION

Twelve new complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with thiophene-2-carboxylic acid hydrazide (TCH) ligand were synthesized and characterized. Based on all results obtained by metal analysis, molar conductance, IR, electronic spectroscopy and magnetic measurements, the octahedral geometry structural formula presented in Fig. 1 proposed for the complexes. TCH act as neutral bidentate ligand coordinated through carbonyl oxygen and amino nitrogen atoms. The thiophene ring sulphur atom is not involved in coordination. Nitrate group act as monodentate ligand.

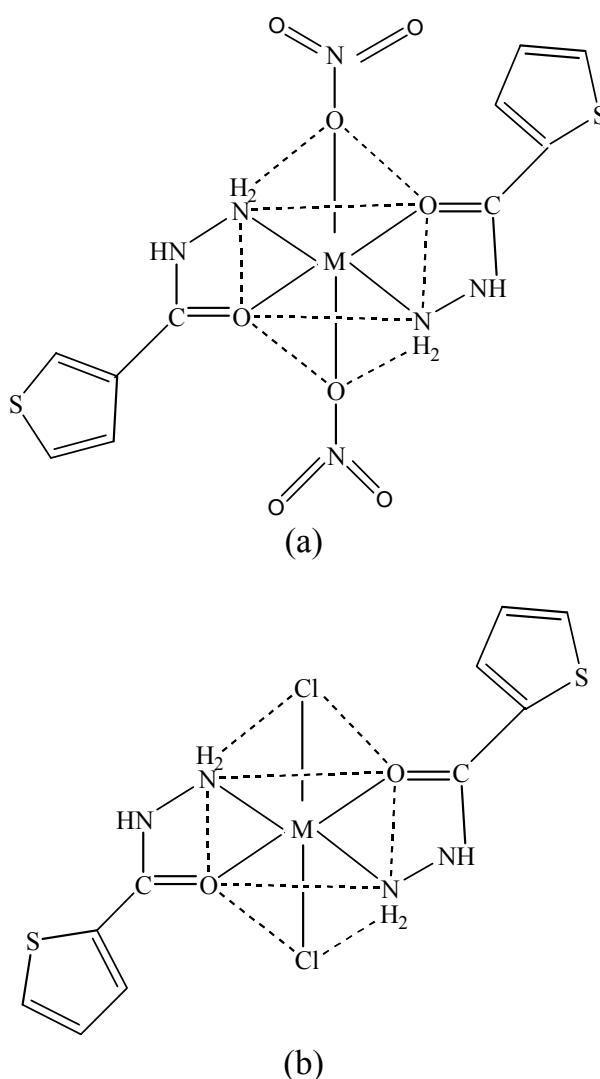


Fig .1: Suggested structures for the complexes $[M(TCH)_2X_2]$
M=Mn(II),Co(II),Ni(II), Cu(II),Zn(II),Cd(II)X=NO₃ (a) , X=Cl (b).

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