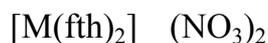
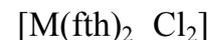


fth



INTRODUCTION

There has been continuing interest in coordination chemistry of the hydrazones that derived from heterocyclic acid hydrazides and aldehydes or ketones (Dianu *et al.*, 2010 ; Nair and Thankamani, 2011). The remarkable biological activity of acid hydrazides and their corresponding aroylhydrazones and the dependence of their activity on the mode of coordination with transition metal ions present in the living system have been also of significant interest by many workers. (Rollas *et al.*, 2007 ; Vicini *et al.*, 2006).

The coordination compounds of aroylhydrazones have been reported to be useful due to their pharmacological and analytical applications (Singh *et al.*, 1982 ; Kumar *et al.*, 2004 Aguelles *et al.*, 2004; Vallinath *et al.*, 2010).

An important feature in the chemistry of aroylhydrazones and their complexes is the acid character of the hydrogen of the NH group of the hydrazide moiety; this allows for either neutral or anionic ligands. When coordinating as anionic ligands the conjugation is extended to include the carbonyl group (Fig.1). It has been proposed that such conjugation system enhanced the biological activity of such compounds (Latheef *et al.*, 2009 ; Martinez *et al.*, 1996). Therefore, the reaction of aroylhydrazones with transition metal ions can proceed according to two pathways attaining the ketonic (Fig.1) or enolic structure for the hydrazide part of the molecule (Seleem *et al.*, 2006) .

The mode of bonding depends on the nature of both the ligand and metal ions, the anion of the metal salt, the pH of the reaction medium and the solvent used (Iskander *et al.*, 2003).

As little work has appeared on the isolation and characterization of metal chelates with hydrazones derived from thiophene-2-carboxylic acid hydrazide and mainly concerned with the synthesis and structural studies of organotin adducts with 2,6-diacetylpyridine bis(2-thenoyl hydrazone (Carini *et al.*, 1989 ; de Sausa *et al.*, 1999) and di-2-pyridylketone-2-thenoyl hydrazone (Carcelli *et al.*, 1995). The present investigation reports the synthesis and characterization of some divalent transition metal complexes of the hydrazone derived from thiophene-2-carboxylic acid hydrazide and 2-furaldehyde (fth):

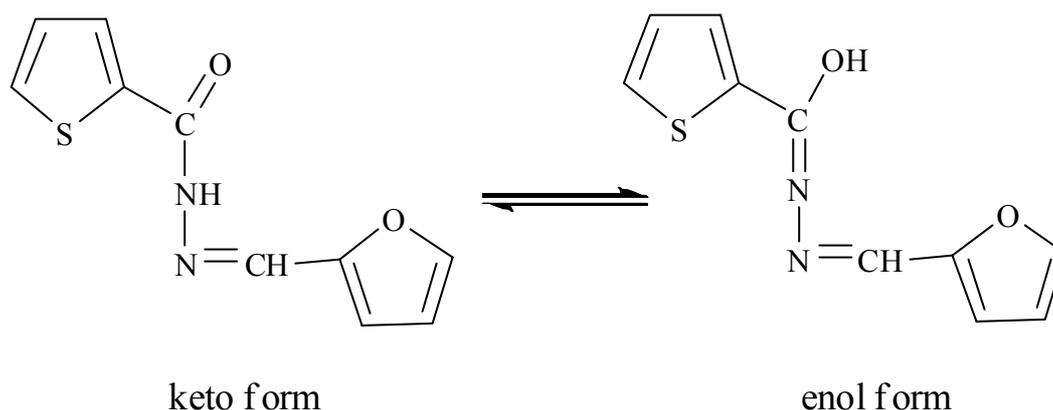


Fig 1 : Structure of 2-furaldehyde-2-thenoylhydrazone

EXPERIMENTAL

Materials and Methods:

All chemical used were reagent grade from B.D.H or Fluka chemical companies, used as supplied, except for 2-furaldehyde which was purified by vacuum distillation according to literature (Perrin *et al.*, 1980).

IR spectra of the ligand and its complexes were recorded as KBr pellets in the region 4000-400 cm^{-1} on Tensor 27 Bruker FT-IR spectrophotometer. Electronic spectra were recorded on Shimadzu UV-1650 PC-spectrophotometer for 10^{-2} M solution of the complexes in DMF at room temperature using 1cm cells. The metal contents of the complexes were determined spectrophotometrically using Shimadzu AA670 atomic absorption spectrophotometer, after decomposition with concentrated nitric acid. Conductivity measurements were performed on 10^{-3} M solutions of the complexes in DMF at room temperature, using PMC3 Jeneway and Terminal 740 wtw conductivity meters. Magnetic susceptibility measurements of the complexes were carried out using Bruker BM6 instrument at ambient temperature. Melting points were determined using Electrothermal 9300 apparatus.

Preparation of the Ligand

Preparation of thiophene-2-carboxylic acid hydrazide:

This was prepared by the reaction of ethylthiophene-2-carboxylate with hydrazine hydrate in absolute ethanol by the procedure reported earlier(Al-Saady and Al-Daher, 2000), m.p. 136 $^{\circ}\text{C}$.

Preparation of 2-Furaldehyde-2-thenoylhydrazone (fth):

This was prepared following a general procedure (Sacconi, 1953). as follows:

Thiophene-2-carboxylic acid hydrazide (2.84g, 0.02 moles) was dissolved in 20 ml of absolute ethanol. To this solution, 2-furaldehyde (1.92g, 0.02 mole) in 20 ml ethanol was added. The reaction mixture was refluxed on a water bath for ca. 4h. The partial removal of solvent followed by cooling on ice produced a yellow crystalline product, which was filtered, washed with cold alcohol and dried under vacuum. m.p. 161 $^{\circ}\text{C}$.

Preparation of Metal Complexes:**Preparation of M(II) complexes of the type $[M(\text{fth-H})_2]$ M=Co(II),Ni(II),Cu(II), Zn(II).**

2-Furaldehyde-2-thenoylhydrazone (fth) (0.44g, 0.02 mole) in hot absolute ethanol (20 ml) was magnetically stirred and (0.112g, 0.02 mole) of KOH was added followed by an ethanolic solution (20 ml) of M(II) acetate hydrate (0.001 mole) [0.247g $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$; 0.247g $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$; 0.198g $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 0.217g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$]. The reaction mixture was then refluxed for 2h and allowed to cool, where solid complexes were separated. The complexes formed were filtered, washed with ethanol (5 ml) and ether (5 ml) and dried in an oven at $80\text{ }^\circ\text{C}$.

Preparation of M(II) complexes of the type $[M(\text{fth})_2\text{Cl}_2]$ **M=Co(II),Ni(II),Cu(II), and Zn(II)**

An ethanolic solution (20 ml) of the appropriate metal(II) chloride hydrate (0.001 mole) [0.197g, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; 0.237g, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; 0.237g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; 0.170g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; and 0.136g of anhydrous ZnCl_2] was added to magnetically stirred hot ethanolic solution (20 ml) of (0.002 mole, 0.440g) of the ligand (fth). The mixture was refluxed for 2h, upon which solid complexes were separated (in case of complex 5) which filtered, washed with absolute ethanol (5 ml) then ether (5 ml) and finally dried in an oven at $80\text{ }^\circ\text{C}$.

For complexes (2, 8, 10) after completion of the reaction, the reaction mixture was concentrated and left to stand overnight at room temperature which resulted in the formation of solid products. The products, thus obtained were filtered, washed and dried as mentioned above.

Preparation of M(II) complexes of the type $[M(\text{fth})_2](\text{NO}_3)_2$ **M=Co(II),Ni(II),Cu(II), and Zn(II)**

To solution of M(II) nitrate hydrate (0.001 mole) [0.291g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 0.291g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 0.242g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; 0.297g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in hot acetone (20 ml) a solution of (0.440g, 0.002 mole) of 2-furaldehyde-2-theonylhydrazone (fth) in hot acetone (20 ml) was added. The reaction mixture was then refluxed on a water bath with constant stirring for 2h. Complexes crystallized out on concentration and cooling, were filtered and washed with hot acetone (5 ml) then with diethyl ether (5 ml) and finally dried in an oven at $80\text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

The reaction of appropriate metal (II) acetate with the hydrazone, derived from thiophene-2-carboxylic acid hydrazide and 2-furaldehyde (fth), in the presence of KOH in a molar ratio of 1:2:2 using absolute ethanol as solvent gave a monomeric complexes of the type $[M(\text{fth-H})_2]$ [M=Co(II), Ni(II), Cu(II) and Zn(II)]. The formulation were in accordance with the data of elemental analysis and physicochemical measurements (Tables 1-3). The molar conductances, determined at concentration of ca. $1 \times 10^{-3}\text{ M}$, in DMF of the complexes (1,4,7 and 10) show small values in the range $6.2\text{-}16.5\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$, indicating that the complexes are non-electrolytes (Geary, 1971) and that the ligand is deprotonated acting as monobasic ligand due to enolisation (Fig.1).

On the other hand, metal (II) chlorides and metal (II) nitrates reacted with the same ligand (fth) in a 1:2 molar ratio and absence of KOH in absolute ethanol and acetone, respectively, producing complexes (2,5,8 and 11) of the type $[M(\text{fth})_2\text{Cl}_2]$ and (3,6,9 and 12)

of the type $[M(\text{fth})_2](\text{NO}_3)_2$. Metal analysis and molar conductance data (Table 1) confirmed these formulas (complexes 2,5,8 and 11 were non-electrolytes and 3,6,9 and 12 were 1:2 electrolytes).

All the prepared complexes are air and moisture stable solids. They are soluble in DMF and DMSO, sparingly soluble in methanol, ethanol and acetone and insoluble in ether and chloroform. Their melting temperatures, solubility and crystalline nature suggest that they are non-polymeric (Chohan *et al.*, 2000) .

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

Complex No.	Complex	Color	m.p (°C)	% Yield	Λ_m^* ohm ⁻¹ cm ² . mol ⁻¹ .	Metal analysis %	
						DMF	Calculated
	fth(C ₁₀ H ₈ N ₂ O ₂ S)	Pale yellow	161	85			
1	[Co(fth-H) ₂]	Brown	168-170	76	9.3	11.86	11.54
2	[Co(fth) ₂ Cl ₂]	Pink	240	64	15.5	10.34	10.07
3	[Co(fth) ₂](NO ₃) ₂	Pink	144	71	122	9.46	9.64
4	[Ni(fth-H) ₂]	Pale green	192 d	68	165	11.82	12.24
5	[Ni (fth) ₂ Cl ₂]	Yellowish green	250 d	84	21.5	10.31	10.63
6	[Ni (fth) ₂](NO ₃) ₂	Green	164-166	79	123.7	9.43	9.24
7	[Cu(fth-H) ₂]	Dark green	284-286	58	16.4	12.67	13.42
8	[Cu (fth) ₂ Cl ₂]	Green	240	62	14.2	11.06	11.17
9	[Cu(fth) ₂](NO ₃) ₂	Greenish brown	282	74	119.8	10.13	9.82
10	[Zn(fth-H) ₂]	Pale yellow	296-298	73	6.2	12.99	13.60
11	[Zn(fth) ₂ Cl ₂]	Pale yellow	280d	68	4.6	11.34	11.08
12	[Zn (fth) ₂](NO ₃) ₂	Pale yellow	120-122	76	113.9	10.39	10.57

- 10⁻³ M solution .

Infrared spectra and mode of chelation :

The bonding mode of the ligand was elucidated by comparison of IR spectra of fth and its complexes. The main vibrational bands of the ligand and its complexes are shown in (Table 2) .

The IR spectrum of the ligand exhibit two bands at 3222 cm⁻¹ and 1638 cm⁻¹ due to $\nu_{(\text{NH})}$ and $\nu_{(\text{C}=\text{O})}$ stretches. The absence of these bands in the spectra of the complexes (1,4,7 and 10), is consistent with enolisation of the amide functionality and subsequent coordination of the enolic oxygen to the metal ion. A new band appearing in the 1028-1038 cm⁻¹ range assigned to the $\nu_{(\text{C}-\text{O})}$ (enolic) mode (Lee and Koo, 2005). This is further supported by the formation of new strong intensity band $\nu_{(\text{NCO}^-)}$ at 1525-1537 cm⁻¹ (Affan *et al.*, 2009) .

On the other hand, the spectra of the complexes (2,3,5,6,8,9,10,11 and 12) in this region are different, showing that the $\nu_{(C=O)}$ band shifts to lower frequencies in these complexes, which is indicative of bonding of the carbonyl oxygen to the metal ion. The position of the $\nu_{(NH)}$ absorption are almost unchanged or shifted slightly to smaller frequencies in these complexes probably due to the hydrogen bond in which the N-H group is involved being weaker than in free ligand (de Sousa *et al.*, 1999).

The strong intensity absorption at 1614 cm^{-1} in the spectrum of the uncomplexed hydrazone is ascribed to the $\nu_{(C=N)}$ vibration, which is specific for the azomethine group. This was satiated at lower wave numbers, $1580\text{-}1608\text{ cm}^{-1}$, in all the complexes (1-12), consequently confirming the coordination of azomethine nitrogen atom to the metal ions (Agarwal *et al.*, 2006 ; Chandra *et al.*, 2009 ; Dianu *et al.*, 2010). The band due to $\nu_{(N-N)}$ mode appears at 933 cm^{-1} in the spectrum of the free ligand was shifted to higher frequency by $12\text{-}39\text{ cm}^{-1}$ which further supports the coordination of the azomethine nitrogen atom. The high frequency shift is expected because of diminished repulsion between the lone pairs of adjacent nitrogen atoms (Maurya *et al.*, 2002)

The band at 1290 cm^{-1} in the IR spectrum of the free fth assigned to furan ring $\nu_{(C-O-C)}$ stretching vibration was shifted to lower values in the spectra of the complexes (1,3,4,6,7,9,10 and 12) suggesting the involvement of the oxygen atom of the furan ring moiety in coordination in these complexes (Sallomi, 2000; Taher, 2000). While this band remains almost unchanged in the spectra of the complexes (2,5,8 and 11) indicating the non-participation of the furan ring oxygen atom in coordination of the chloro-complexes. Conclusive evidence of the bonding is also shown by observation that new bands appear in the spectra of all the complexes at $468\text{-}553\text{ cm}^{-1}$ and $430\text{-}472\text{ cm}^{-1}$ which are assigned to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ stretching vibration, respectively (Agarwal *et al.*, 2006 ; Chohan *et al.*, 2000; Chandra *et al.*, 2009).

The Bands observed in the IR spectrum of the free ligand at $841,712$ and 652 cm^{-1} were assigned to $\nu_{(C-S-C)}$ thiophene ring stretching vibration, ν_{CS} asymmetric and, ν_{CS} symmetric vibration, respectively (Spinu and Kriza, 2000). These bands were found almost unchanged in the spectra of all complexes indicating that the sulfur atom of the thenoyl moiety is not taking part in the coordination of the ligand fth to the metal ions. This behavior was also reported in the X-ray structural studies of organotin complexes with 2,6-diacetylpyridine bis (2-thenoylhydrazone) and di-2-pyridylketone-2-thenoylhydrazone (Carini *et al.*, 1989; Carcelli *et al.*, 1995).

The nitrate complexes (3,6,9 and 12) exhibits a very strong bands at the region $1371\text{-}1385\text{ cm}^{-1}$ and medium intensity band at the region $825\text{-}833$, which are attributed to the ν_3 and ν_2 vibrations, respectively of uncoordinated nitrate ion of D_{3h} symmetry (Chandra *et al.*, 2009).

Table 2 : Some selected infrared frequencies (cm^{-1}) of the ligand and its complexes .

Complex No.	ν (NH)	Amide I	ν (C=N) azomethine	ν (NCO ⁻)	ν (C-O)	ν (N-N)	ν (O-C-O) furan ring	ν (M-O)	ν (M-N)
fth	3222(m)	1638 (s)	1614(s)	----	----	933(m)	1290(s)	----	----
1	----	----	1599(s)	1535(s)	1028(s)	946(m)	1227(m)	519(m),468(w)	455(w)
2	3185(m)	1614(s)	1586(s)	----	----	960(m)	1287(m)	496(m)	438(m)
3	3221(m)	1618(s)	1589(s)	----	----	958(m)	1242(m)	548(m),503(w)	442(w)
4	----	----	1606(s)	1537(s)	1030(s)	945(m)	1230(m)	507(m), 472(w)	453(w)
5	3192(m)	1614(s)	1591(s)	----	----	960(m)	1289(m)	498(m)	444(w)
6	----	1615(s)	1593(s)	----	----	947(m)	1442(m)	553(w), 511(w)	472(w)
7	----	----	1604(s)	1537(s)	1030(s)	951(m)	1227(m)	525(m), 490(w)	472(w)
8	3220	1618(s)	1585(s)	----	----	955(m)	1296(m)	486(m)	445(m)
9	----	1618(s)	1580(s)	----	----	972(m)	1248(m)	550(m), 484(w)	430(w)
10	----	----	1608(s)	1525(s)	1038(s)	949(m)	1217(m)	515(m), 488(m)	442(w)
11	3217(m)	1620(s)	1587(s)	----	----	952(m)	1292(m)	496(m)	459(w)
12	3215(m)	1618(s)	1593(s)	----	1022(m)	----	1244(m)	552(w), 503(w)	445(w)

s= strong , m= medium , w= weak

Electronic Spectra and Magnetic properties:

Absorption spectra of the ligand and its complexes were obtained in DMF and the resulting data are given in (Table3). The electronic spectrum of the fth ligand presents an absorption maxima at 31847 cm^{-1} and 27778 cm^{-1} due to $\pi \rightarrow \pi^*$ of the aromatic rings and to $n \rightarrow \pi^*$ transition in the C=O and C=N chromophoric groups, respectively. These transitions were found in the spectra of the complexes but shifted to lower frequencies, indicating coordination of the ligand to the metal ions. Intense absorption at the region

24041-25773 cm^{-1} was observed in the spectra of all complexes were assigned to a ligand to metal charge transfer (LMCT) band (Lee and Koo, 2005).

In the electronic spectra of Co(II) complexes (1-3), the three absorption bands at 9090-9293 cm^{-1} , 10917-11286 cm^{-1} and 18939-19724 cm^{-1} were assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) \rightarrow and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) transitions, respectively. They are characteristic for octahedral stereochemistry of the Co(II) ion. The magnetic moment of 4.69-4.95 BM supports this geometry for high-spin Co(II), (Cotton *et al.*, 1999, Agarwal *et al.*, 2006; Chandra *et al.*, 2009).

For Ni(II) complexes (4-6), three absorption bands at 9105-9542 cm^{-1} , 13927-15504, and 20120-21978 cm^{-1} were registered in their electronic spectra. These bands can be assigned to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (ν_1), ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) transition, respectively and are specific for Ni(II) ion in octahedral coordination, which was also confirmed by the magnetic moment of 2.57-3.08 BM (Cotton *et al.*, 1999; Prasad and Agarwal, 2008).

The electronic spectra of Cu(II) complexes (7-9) contain a wide band satiated at the region 13888-14492 cm^{-1} . This band is characteristic for a Cu(II) ion with tetragonally distorted octahedral stereochemistry and can be assigned to two or three transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{2g}$. The magnetic moment of 1.79-1.98 BM suggests a monomeric octahedral geometry (Lever, 1984 ; Dianu *et al.*, 2010).

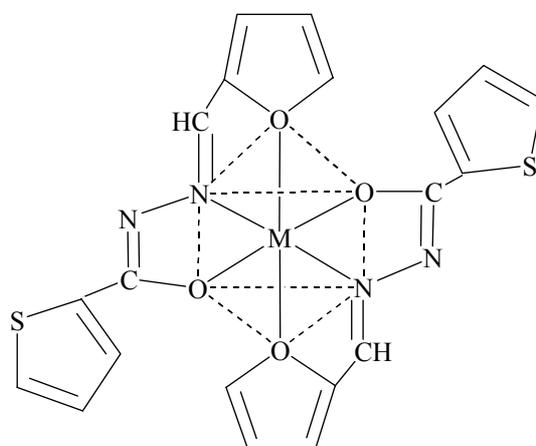
The electronic absorption spectra of Zn(II) complexes (9-12) show no appreciable absorptions in the region below 25000 cm^{-1} in DMF solution. In accordance with the filled d-orbital electronic configuration of Zn(II) (Cotton *et al.*, 1999).

Table 3: Magnetic susceptibility and electronic spectra of the ligand and its complexes .

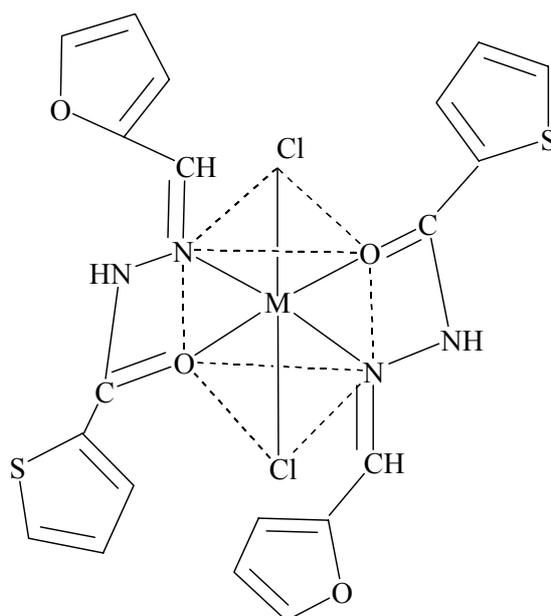
Complex No.	μ_{eff} BM	Electronic spectra cm^{-1}
fth	----	31847, 27778
1	4.73	30250, 27169, 23041, 18939, 10917, 9293
2	4.95	29586, 26955, 25050, 19724, 11236, 9090
3	4.69	29585, 27027, 25000, 19305, 11286, 9090
4	2.73	29762, 27169, 25610, 21231, 15504, 9542
5	3.03	29411, 26178, 25641, 20120, 13927, 9174
6	2.57	29761, 27624, 25641, 21978, 14285, 9105
7	1.98	29412, 25641, 22831, 14285
8	1.85	28901, 24390, 22026, 13888
9	1.79	29155, 27397, 24752, 22222, 14492
10	Dia	30303, 27473, 25510
11	Dia	29498, 27624, 25773
12	Dia	29155, 27100, 25126

CONCLUSION

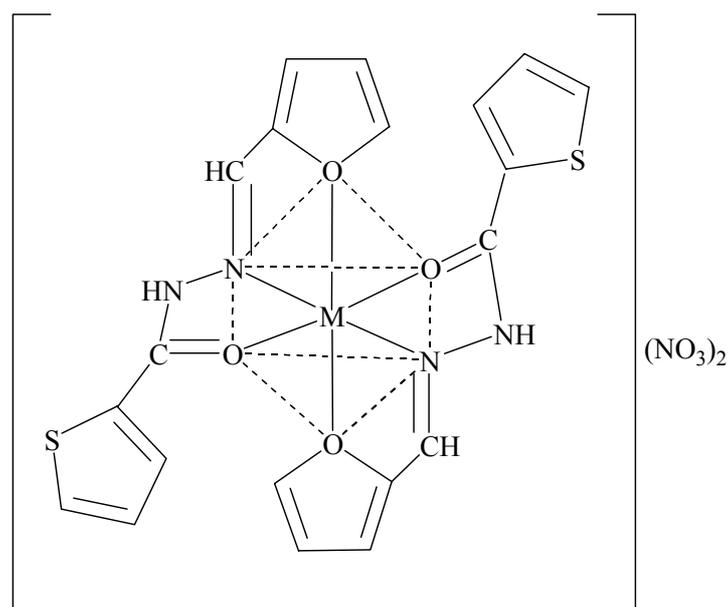
2-Furaldehyde-2-thenoylhydrazone (fth) reacts with M(II) acetate in basic medium to form octahedral complexes of the type $[M(fth-H)_2]$, M= Co (II), Ni (II), Cu(II) and Zn(II). The ligand fth deprotonated and acts as monobasic ONO tridentate, bonding to the metal (II) ions through the enolic oxygen, azomethine nitrogen and furan ring oxygen atoms (Fig. 2a) . The same ligand reacts with metal (II) chlorides and metal (II) nitrates in neutral medium forming also octahedral complexes of the types $[M(fth)_2Cl_2]$ and $[M(fth)_2](NO_3)_2$, respectively. The ligand act as neutral bidentate ON in the chloro-complexes coordinated through carbonyl oxygen and azomethine nitrogen atoms (Fig. 2b). In case of nitrate complexes fth act as neutral tridentate ONO coordinated through carbonyl oxygen, azomethine nitrogen and furan ring oxygen atoms and the nitrate groups were uncoordinated (Fig. 2c) .



a. $[M(fth-H)_2]$



b. $[M(fth)_2Cl_2]$

c. $[M(fth)_2](NO_3)_2$

M= Co(II), Ni(II), Cu(II), Zn(II)

Fig. 2: Proposed structures for the complexes .

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