

## Synthesis and Characterization of Mn(II), Co(II), Ni(II),Cu(II) and Zn(II) Complexes with Acetylhydrazones

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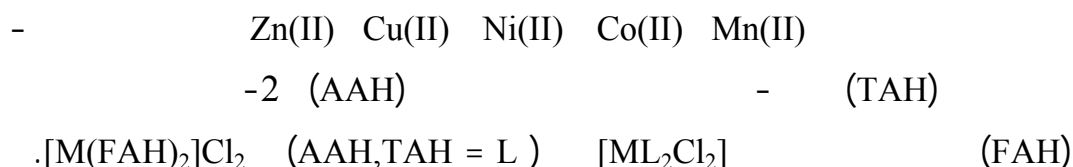
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### ABSTRACT

Complexes of Mn(II), Co(II), Ni(II),Cu(II) and Zn(II) with p-tolualdehyde acetyl hydrazone (TAH), p- anisaldehyde acetyl hydrazone (AAH) and 2- furylaldehyde acetyl hydrazone (FAH) of the types  $[ML_2Cl_2]$  where L=TAH and AAH and  $[M(FAH)_2]Cl_2$  were synthesized. The complexes were characterized on the basis of analytical molar conductance, molecular weight, magnetic moment, infrared and electronic spectra. From the elemental analysis and molecular weight data 1:2 (metal : ligand) was proposed. The molar conductance measurements showed that TAH and AAH complexes were non-electrolytes and FAH complexes were 1:2 electrolytes in DMF and DMSO. The magnetic moment coupled with the electronic spectra suggested an octahedral geometry for all the complexes .

IR spectral studies indicated that TAH and AAH functions as neutral bidentate ligands via carbonyl oxygen and azomethine nitrogen atoms while FAH act as neutral tridentate ligand coordinated through furan ring oxygen atom in addition to carbonyl oxygen and azomethine nitrogen atoms.

### Zn(II) Cu(II) Ni(II) Co(II) Mn(II)



DMSO	DMF		2:1		:
.1:2		FAH		AAH	TAH

AAH TAH

FAH

## INTRODUCTION

Hydrazone ligands and their complexes have been studied for their antifungal and antibacterial activity, as iron chelators in the treatment of anemias and as antiviral drugs . (Agüelles *et al.*, 2004 ; Rollas and Küçükgeznel, 2007). In addition they have been studied also as a group of useful spectrophotometric reagents (Singh *et al.*,1982 ; Kumar *et al.*, 2004 ; Vallinath *et al.*, 2010).

Hydrazone compounds derived from aromatic and heterocyclic hydrazides with aldehydes and ketones have extensively been investigated and revealed a versatile behavior in metal coordination depending on the nature of both the ligands and the metal ions, the anions of the metal salt, the pH of the reaction medium and the solvent used (Hueso -Urena *et al.*, 2000 ; Maurya *et al.*, 2002 ; Iskander *et al.*, 2003 ; Prasad and Agarwal, 2008 ; Despaigne *et al.*, 2009) ; El-Halabi *et al.*, 2009 ; Yaul *et al.*, 2009 .

Hydrazones derived from acetylhydrazide ( $\text{CH}_3\text{CONHNH}_2$ ) which have biological properties (Dimmock *et al.*, 2000) were very little reported (Abd El- Wahed *et al.*, 2003; Rajaei *et al.*, 2010). Therefore, it was of interest to investigate the coordination behavior of a number of acetylhydrazones derived from p-tolualdehyde (TAH), p-anisaldehyde (AAH) and 2-furylaldehyde (Fig. 1) with some divalent transition metal chlorides.

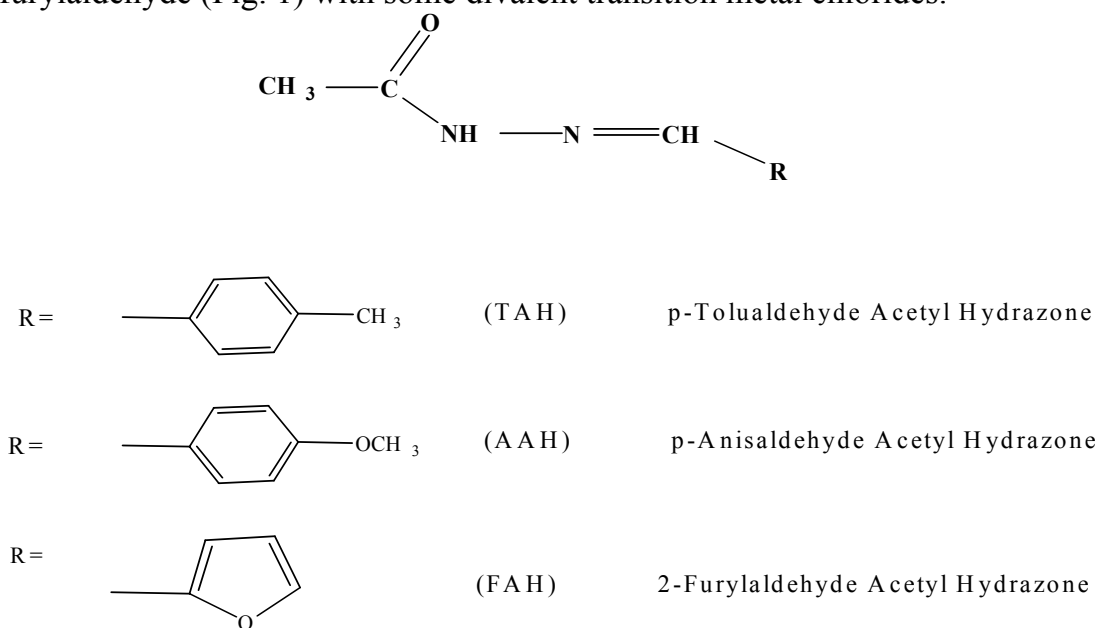


Fig. 1 :Acetylhydrazones (ligands)

## EXPERIMENTAL

### Materials and Methods

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

The metal contents of the complexes were determined spectrophotometrically using Shimadzu AA670 atomic absorption spectrophotometer, after decomposition with concentrated nitric acid. Elemental analysis of carbon, hydrogen and nitrogen for two of the prepared complexes were performed on Perkin Elmer 2400 analyzer at Al al-Bayt University laboratories, Jordan.

IR spectra of the ligands and their complexes were recorded as KBr pellets in the region 4000-400  $\text{cm}^{-1}$  on Tensor 27 Bruker FT-IR spectrophotometer. Conductivity measurements were measured on  $10^{-3}$  M solutions of the complexes in DMSO and DMF at 25°C, using PMC3 Jeneway and Terminal 740 wtw conductivity meters. Electronic spectra were recorded on Shimadzu UV-1650 PC- spectrophotometer for  $10^{-3}$  M solutions of the ligands and their complexes in ethanol solvent at 25°C . Relative molecular weights of the ligands and their complexes were estimated cryscopically (Danials *et al.*, 1962) using Beckmann thermometer. Magnetic susceptibility measurements of the complexes were performed using Bruker BM6 instrument at room temperature. Melting points were determined using Electrothermal 9300 apparatus.

### Preparation of Ligands

#### Preparation of Acetylhydrazide :

This was prepared by the reaction of ethylacetate and hydrazine hydrate as described previously (Al-Saady and Al-Daher, 2000), and purified by dissolving in minimum quantity of hot chloroform followed by precipitation with dry ether. The white crystals are highly hygroscopic stored in dry conditions m.p. 62°C (Ahmed and Chaudhuri , 1971).

#### Preparation of p-Tolualdehyde acetylhydrazone (TAH) :

This was prepared following a general procedure (Sacconi, 1953) by reacting an ethanolic solution (20 ml) of acetylhydrazide (1.48g , 0.02 mole) with p-tolualdehyde (2.40 , 0.02 mole) in ethanol (10 ml) under reflux with constant stirring for 2h . On cooling the white crystalline hydrazone formed was filtered off, washed with cold absolute ethanol (5 ml) then with dry ether (5 ml) and recrystallized from absolute ethanol.

#### Preparation of p-Anisaldehyde acetylhydrazone (AAH) :

This was prepared in same way as mentioned above, using (2.72g , 0.02 mole) of anisaldehyde .

#### Preparation of 2-Furylaldehyde acetylhydrazone (FAH) :

The same procedure described above for TAH was adopted, using (1.92g , 0.02 mole) of purified 2-furylaldehyde .

#### Preparation of Metal Complexes:

An ethanolic solution (20 ml) of the appropriate metal (II) chlorides (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 ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  ; 0.136g ,  $\text{ZnCl}_2$ ] was added to a magnetically stirred hot ethanolic solution (10 ml) of the respective acetyl hydrazone (0.002 mole) [0.352g, TAH ; 0.384g, AAH ; 0.304g, FAH]. The mixture was refluxed for 2-3h , upon which solid complexes were separated (in case of

the complexes 6-9 and 12-15 (Table 1) which filtered, washed with ethanol (3 ml) then ether (3 ml) and finally dried in an oven at 80°C.

For complexes (1-5 , 10, 11), after completion of the reaction, the mixture was reduced to nearly half its volume. The concentrated solution was then left to stand overnight at room temperature which resulted in the formation of solid products. The products, thus obtained was filtered, washed and dried as mentioned above.

## RESULTS AND DISCUSSION

The acetylhydrazones (Fig. 1) were prepared by reacting equimolar amounts of acetylhydrazide ( $\text{CH}_3\text{CONHNH}_2$ ) with the respective aldehyde [p-tolualdehyde (TAH), p-anisaldehyde (AAH) or 2-furylaldehyde (FAH)] in absolute ethanol. The complexes were prepared by direct reaction of the hydrazones with the metal (II) chlorides in absolute ethanol. Based on elemental analyses and molecular weight determination, the complexes were found to have the compositions shown in (Tables 1 and 2). They were soluble in common organic solvents such as DMSO and DMF and to less extent in ethanol. Their solubility, melting temperatures and crystalline nature of most of them suggesting that they are non-polymeric (Chohan *et al.*, 2000). The molar conductance measurements of the complexes in DMSO and DMF (Table 1) correspond to non-electrolytic nature for TAH and AAH complexes and 1:2 electrolytes for FAH complexes (Geary, 1971), these complexes may be formulated as  $[\text{M}(\text{L})_2\text{Cl}_2]$  and  $[\text{M}(\text{FAH})_2]\text{Cl}_2$  where  $\text{M}=\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$  or  $\text{Zn}(\text{II})$  and  $\text{L}=\text{TAH}$  or  $\text{AAH}$ . The structures of the complexes were characterized by FT-IR, magnetic measurements and electronic spectra.

Table 1 : Analytical and some physical data of the ligands and their complexes

Complex No.	Compd.	Color	% Yield	m.p. (°C)	M%		Molecular weight		$\Lambda_m \text{ ohm}^{-1} \text{ cm}^2 \cdot \text{mol}^{-1}$	
					Found	Calculated	found	calculated	DMF	DMSO
	TAH	White	88	120-121	---	---	166	176	---	---
1.	$[\text{Mn}(\text{TAH})_2\text{Cl}_2]$	Pale yellow	54	182-183	11.71	11.49	481	477.9	24.4	16.8
2.	$[\text{Co}(\text{TAH})_2\text{Cl}_2]$	Pink	78	241-242	11.68	12.22	467	481.9	32.1	19.3
3.	$[\text{Ni}(\text{TAH})_2\text{Cl}_2]$	Greenish blue	82	312*	11.61	12.18	474	481.7	31.6	15.0
4.	$[\text{Cu}(\text{TAH})_2\text{Cl}_2]$	Dark green	71	159*	12.70	13.06	460	486.5	12.0	23.8
5.	$[\text{Zn}(\text{TAH})_2\text{Cl}_2]$	White	69	234-235	14.16	13.38	474	488.4	23.5	21.4
	AAH	White	76	131-132	---	---	207	192	---	---
6.	$[\text{Mn}(\text{AAH})_2\text{Cl}_2]$	Pale yellow	61	144*	10.35	10.77	488	509.9	9.7	5.1
7.	$[\text{Co}(\text{AAH})_2\text{Cl}_2]$	Pink	75	237-238	11.28	11.46	544	513.9	34.2	19.7
8.	$[\text{Ni}(\text{AAH})_2\text{Cl}_2]$	Green	88	281-282	10.83	11.42	530	513.7	13.5	8.9
9.	$[\text{Cu}(\text{AAH})_2\text{Cl}_2]$	Dark yellow	80	184-185	11.56	12.26	502	518.5	29.2	22.6
10.	$[\text{Zn}(\text{AAH})_2\text{Cl}_2]$	White	65	249*	12.34	12.56	509	520.4	9.4	11.7
	FAH	White	82	139	---	---	123	152	---	---
11.	$[\text{Mn}(\text{FAH})_2]\text{Cl}_2$	Pale yellow	57	163-164	12.14	12.77	383	429.9	126.8	71.8
12.	$[\text{Co}(\text{FAH})_2]\text{Cl}_2$	Pink	61	116-117	14.28	13.58	446	433.9	166.3	62.7
13.	$[\text{Ni}(\text{FAH})_2]\text{Cl}_2$	Pale green	72	240*	14.15	13.53	418	433.7	143.6	75.6
14.	$[\text{Cu}(\text{FAH})_2]\text{Cl}_2$	Green	53	198*	15.17	14.48	411	438.5	187.3	68.2
15.	$[\text{Zn}(\text{FAH})_2]\text{Cl}_2$	White	79	196-197	14.61	14.84	425	440.4	121.5	71.8

Table 2 : C,H,N Analysis of two of the prepared complexes.

Comp. No.	Complex	Formula	% C		%H		%N	
			Found	Calc.	Found	Calc.	Found	Calc.
10	[Zn(AAH) <sub>2</sub> Cl <sub>2</sub> ]	ZnC <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	45.81	46.15	4.39	4.61	10.52	10.76
13	[Ni(FAH) <sub>2</sub> Cl <sub>2</sub> ]	NiC <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	39.47	38.73	3.51	3.68	11.98	12.91

### Infrared Spectra and Mode of Coordination :

In order to study the bonding mode of ligands to metals in the complexes, IR spectra of the free ligands were compared with those of the metal complexes. The structurally significant IR bands of the free hydrazone ligands and their complexes have been reported in Table 3. The free ligands showed a medium intensity bands in the region 3185-3220 cm<sup>-1</sup> assigned to  $\nu(\text{NH})$  stretching vibrations, which have been observed in the 3189-3241 cm<sup>-1</sup> region in the spectra of the complexes. It can be observed that there is either no considerable shift or slight positive shift in the  $\nu(\text{NH})$  vibrations indicating non-involvement of amide NH function in the coordination (Agarwal *et al.*, 2006). The slight positive shift in the  $\nu(\text{NH})$  vibrations in case of the complexes may be attributed to the decrease in hydrogen bonding in complex formation .

A strong intensity bands were observed at the region 1666-1665 cm<sup>-1</sup> of the spectra of the uncomplexed ligand assigned for amide I  $\nu(\text{C}=\text{O})$  vibrations. In the IR spectra of the complexes a considerable negative shift in  $\nu(\text{C}=\text{O})$  (11-30 cm<sup>-1</sup>) was observed indicating a decrease in the stretching force constant as a consequence of coordination through the carbonyl-oxygen atom of the free ligand (Despaigne *et al.*, 2009 ; Abd El-Wahed *et al.*, 2003).

Another important bands which occur at 1608-1638 cm<sup>-1</sup> region in the free ligand spectra were attributed to  $\nu(\text{C}=\text{N})$  (azomethine) mode. In the spectra of all the complexes , these bands were shifted to lower frequencies by 10-40 cm<sup>-1</sup> , indicating the involvement of the nitrogen atom of the azomethine group in coordination (Prasad and Agarwal, 2008 ; Agarwal *et al.*, 2006) . The band due to  $\nu(\text{N}-\text{N})$  mode appears at the region 950-1022 cm<sup>-1</sup> in the spectra of uncomplexed ligands. This band which on coordination shifts up by 6-28 cm<sup>-1</sup> to higher wave numbers with respect to free ligand , falls within the range commonly observed for coordinated  $>\text{N}-\text{N} <$  residue (Maurya *et al.*, 2002 , Hueso-Urena *et al.*, 2000) and again confirms coordination via the azomethine group nitrogen atom . The high frequency shift is expected because of the diminished repulsion between the lone pairs of adjacent nitrogen atoms .

The medium intensity band at 1276 cm<sup>-1</sup> in the IR spectrum of the free FAH ligand assigned to furan ring  $\nu(\text{C}-\text{O}-\text{C})$  stretching vibration was shifted to lower values with 13-24 cm<sup>-1</sup> suggesting the involvement of the oxygen atom of furan ring moiety in coordination (Sallomi , 2000 ; Taher , 2010). The low frequency skeletal vibrations due to M-O and M-N stretching provide also direct evidence for the complexation . In the present investigation, bands in the 508-587 cm<sup>-1</sup> region of the complexes spectra have been assigned to  $\nu(\text{M}-\text{O})$  and the bands observed in the 431-490 cm<sup>-1</sup> region to  $\nu(\text{M}-\text{N})$  vibration respectively (Agarwal *et al.*, 2006 , Chohan *et al.*, 2000). The overall infrared spectral evidence suggests that the ligands TAH and AAH act as neutral bidentate ligands, coordinated through carbonyl oxygen and azomethine nitrogen atoms, while the ligand FAH acts as neutral

tridentate ligand coordinates via hetero (oxygen) atom in addition to carbonyl oxygen and azomethine nitrogen atoms .

Table 3 : Some selected infrared frequencies ( $\text{cm}^{-1}$ ) of the ligands and their complexes.

Compd. No.	$\nu$ (NH)	amide I $\nu$ (C=O)	azomethine $\nu$ (C=N)	$\nu$ (N-N)	$\nu$ (C-O-C) Furan ring	$\nu$ (M-O)	$\nu$ (M-N)
TAH	3210 (m)	1665 (s)	1638 (s)	983 (w)	---	---	---
1	3219 (m)	1654 (s)	1626 (s)	995 (w)	---	515 (w)	488 (w)
2	3228 (m)	1650 (s)	1616 (s)	997 (w)	---	508 (w)	485 (w)
3	3214 (m)	1648 (m)	1620 (s)	999 (w)	---	517 (w)	490 (w)
4	3236 (m)	1639 (m)	1628 (s)	1011 (w)	---	525 (w)	431 (w)
5	3214 (m)	1641 (s)	1611 (s)	1606 (w)	---	510 (w)	437 (w)
AAH	3185 (m)	1665 (s)	1608 (s)	950 (m)	---	---	---
6	3189 (m)	1633 (s)	1596 (s)	975 (m)	---	527 (w)	442 (w)
7	3192 (m)	1628 (s)	1597 (s)	972 (w)	---	538 (w)	445 (w)
8	3204 (m)	1631 (s)	1587 (s)	962 (m)	---	527 (w)	448 (w)
9	3185 (m)	1649 (s)	1591 (m)	958 (w)	---	530 (w)	460 (w)
10	3188 (m)	1628 (s)	1583 (s)	973 (m)	---	519 (w)	466 (w)
FAH	3220 (m)	1664 (s)	1634 (s)	1022 (m)	1276 (m)	---	---
11	3227 (m)	1637 (s)	1616 (s)	1042 (m)	1258 (m)	571 (m) , 525 (w)	459 (w)
12	3241 (m)	1632 (s)	1605 (m)	1037 (w)	1263 (m)	571 (w) , 532 (w)	467 (w)
13	3229 (m)	1624 (s)	1613 (s)	1033 (w)	1260 (m)	587 (w) , 547 (w)	460 (w)
14	3238 (m)	1648 (s)	1622 (m)	1028 (w)	1261 (m)	538 (w) , 508 (m)	476 (w)
15	3225 (m)	1633 (s)	1594 (s)	1038 (w)	1252 (m)	583 (m) , 556 (m)	477 (w)

(s) strong , (m) medium , (w) weak

### Magnetic properties and Electronic Spectra

The magnetic moments values and electronic absorption bands of the complexes are recorded in (Table 4) two absorptions were observed in the UV spectra of the ligands at the ranges  $40650\text{-}35211\text{ cm}^{-1}$  and  $31055\text{-}32051\text{ cm}^{-1}$  (Table 5) were assigned to the allowed,  $\pi \longrightarrow \pi^*$  and  $n \longrightarrow \pi^*$  transitions, respectively .

The magnetic moments of the pale yellow Mn(II) complexes are in the range 5.66-5.86 B.M. corresponding to five unpaired electrons . However, their electronic spectra show high intensity absorption at  $31645\text{-}29345\text{ cm}^{-1}$  due to coordinated ligand absorption and charge transfer transitions only indicating high spin octahedral geometry due to spin and lapport forbidden (Cotton *et al.*, 1999) .

The cobalt(II) complexes show a magnetic moments values of 4.74-5.15 B.M. at room temperature. These high values of magnetic moments are due to orbital contribution. The stoichiometries suggest a coordination number of six for the central cobalt(II) ion and attaining an octahedral geometry (Agarwal *et al.*, 2006). The electronic spectra of these pink color complexes are also consistent with their octahedral environment around the cobalt(II) ions . The spectra display bands at  $9259 - 9845\text{ cm}^{-1}$  ,  $14850 - 16417\text{ cm}^{-1}$  and  $18867 - 19171\text{ cm}^{-1}$  attributed to

${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)(\nu_1)$  ,  ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)(\nu_2)$  and  ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)(\nu_3)$

Transitions, respectively in a high - spin octahedral geometry (Cotton *et al.*, 1999 ; Agarwal *et al.*, 2006). The electronic spectra of the three nickel(II) complexes are very

similar to each other and exhibited three typical absorption bands at 9100-9266  $\text{cm}^{-1}$  corresponding to the transition

${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}(\nu_1)$ , 14450-15408  $\text{cm}^{-1}$  due to  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$  and 23924-24875  $\text{cm}^{-1}$  for  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$  which clearly indicates the octahedral stereochemistry of the complexes (Prasad and Agarwal, 2008 ; Cotton *et al.*, 1999). Also, the values of the magnetic moments 3.08-3.16 B.M. may be taken as additional evidence for octahedral nickel (II) geometry (Cotton *et al.*, 1999) .

The magnetic moments of copper(II) complexes were recorded at room temperature. The complexes show a magnetic moments in the range 1.82-2.06 B.M. corresponding to one unpaired electron. The electronic spectra of these complexes exhibited broad bands in the range 10526-12820  $\text{cm}^{-1}$  due to two or three transitions  ${}^2\text{B}_{1g} \longrightarrow {}^2\text{E}_g$ ,  ${}^2\text{B}_{1g} \longrightarrow {}^2\text{B}_{2g}$  and  ${}^2\text{B}_{1g} \longrightarrow {}^2\text{A}_{2g}$ . This band is characteristic in position and width with those reported for octahedral copper (II) complexes (Dianu *et al.*, 2010 ; Lever , 1984).

The electronic absorption spectra of Zn(II) complexes show intense broad bands in the region 31645-28498  $\text{cm}^{-1}$  may be attributed to charge transfer transitions. Except this, these diamagnetic complexes show no appreciable absorptions in the region below 26000  $\text{cm}^{-1}$  in absolute ethanol solutions. In accordance with the  $d^{10}$  electronic configuration of Zn(II) .

Table 4 : Magnetic susceptibility and electronic spectra of the ligands and their complexes.

Complex No.	$\mu_{\text{eff}}$ BM	Electronic spectra $\text{cm}^{-1}$
TAH	---	40650 , 32051
1	5.86	29345
2	4.79	28728,19047,16417,9673
3	3.15	31557,24875,14925,9175
4	1.82	27472,12820
5	dia	28498
AAH	---	39525,31055
6	5.66	29761
7	4.74	30674,19171,14880,9845
8	3.08	29411,24390 , 14450 , 9266
9	1.83	25975,10526
10	dia	29585
FAH	---	35211,31847
11	5.84	31645
12	5.15	32051,18867,14850,9259
13	3.16	30864,23923,15408 , 9100
14	2.06	23809 ,10822
15	dia	31645

## CONCLUSION

Acetylhydrazones prepared by condensation of acetylhydrazide and p-tolualdehyde (TAH), p- anisaldehyde (AAH) or 2- Furylaldehyde (FAH) (Fig. 1) act as ligands coordinated to M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions forming octahedral chelates

of the type  $[M(L)_2Cl_2]$  where  $L=TAH$  and  $AAH$  acting as neutral bidentate ligands coordinated through carbonyl oxygen and azomethine nitrogen atoms (Fig. 2a). While the ligand  $FAH$  formed complexes of the type  $[M(FAH)_2]Cl_2$  in which the two  $FAH$  ligands act as neutral tridentates. These possibly accommodate themselves around the central metal ion in such a way that stable chelate rings are formed (Fig. 2b) giving in turn, stability to the formed metal complexes.

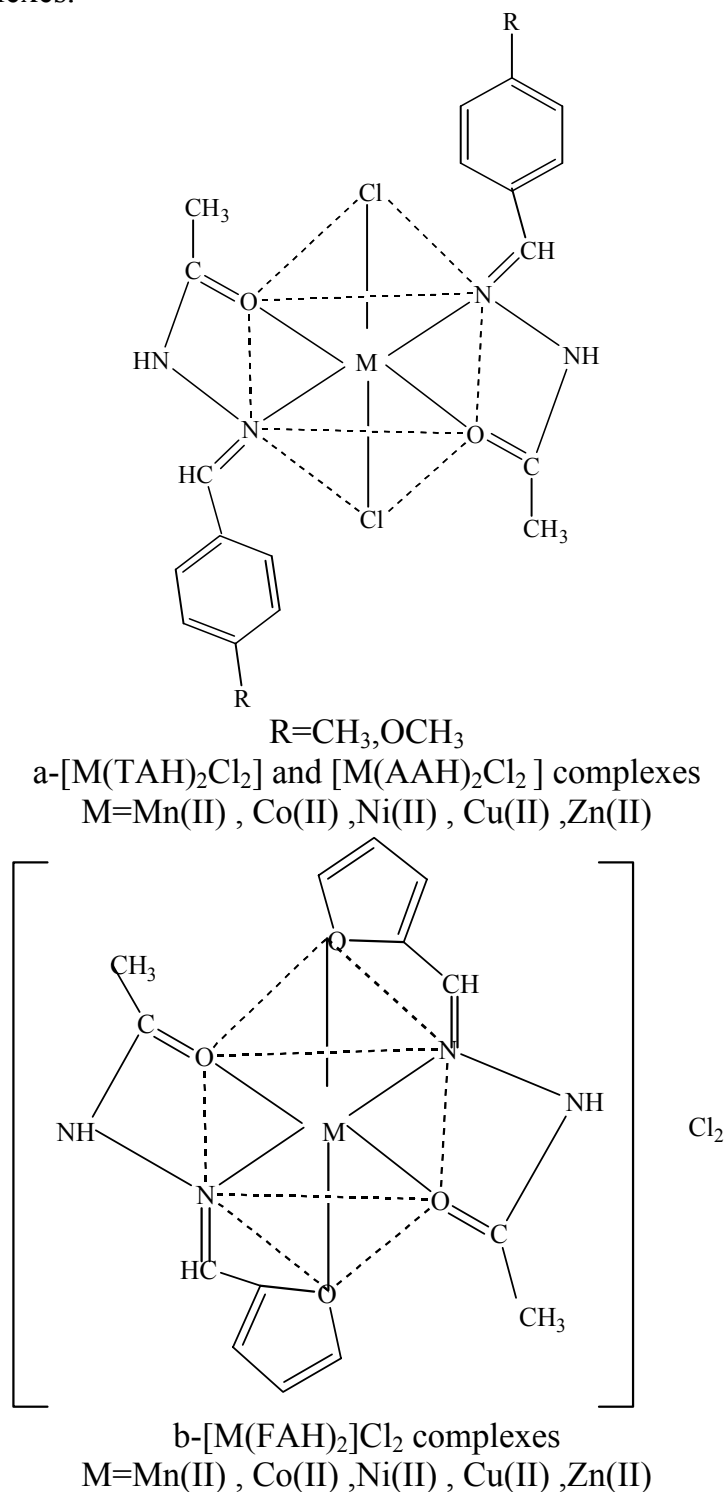


Fig. 2 : The proposed structures for TAH,AAH and FAH complexes with metal (II)chlorides.



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