

## Synthesis, Characterization, Antifeeding and Insect Growth-Regulating Activities of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) Complexes with N-Acetylacetonyl-3-Aminocoumarin

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### Abstract

Metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) have been synthesized using N-acetylacetonyl-3-aminocoumarin as chelating agent. The ligand behaves as a monobasic tridentate ONO donor towards Ni(II) and as monobasic bidentate ON donor towards other cations. All the complexes have been proposed to have octahedral geometry on the basis of analytical, thermal conductivity, spectral and magnetic data. The complexes have been screened against *Spodoptera litura*; *F (Lepidoptera: noctuidae)* for antifeeding and insect growth-regulating activities. The results show appreciable antifeeding and insect growth-regulating activities associated with metal complexation at higher and lower doses respectively.

**Keywords:** Metal complexes; N-Acetylacetonyl-3-aminocoumarin; Antifeeding activity; Insect growth-regulating activity.

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## 1. Introduction

Several vital functions of living organisms are thought to be due to the chemistry of metal-bound biomolecules. Investigations involving synthesis, stability, structure and reactivity of metal-containing compounds are well advanced. When a metal ion is bound to a biologically active organic molecule, it may result in apparent modification of the activity, generally depending on the specificity of the binding site and the stereochemistry of the metal complex.

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Coumarin and its derivatives represent one of the most active class of compounds possessing a wide spectrum of biological activity [1-11]. Many of these compounds have proved to possess antitumor [1-4], antibacterial [5,6], antifungal [7-9], anticoagulant [10] and anti-inflammatory activities [11]. In addition, these compounds are used as additives in food and cosmetics [12]. The coumarins have been much less studied although they too have been cited as insect antifeedants and insect-growth-regulators [13-16].

Although coumarin is a plant product known to possess insecticidal effect, no significant attempt has been made so far to study the antifeeding (AF) and insect-growth-regulating (IGR) activities with azomethine derivatives of 3-aminocoumarin and their metal complexes. The present paper reports AF and IGR activities of newly synthesized transition metal complexes of N-acetylacetylonyl -3-amino coumarin (H-acacAc) against *Spodoptera litura* with the aim of providing knowledge that may be of use in the development of new agrochemical products.

## 2. Experimental

### 2.1. *Materials*

The reagents and chemicals used were of BDH(AR) or E. Merck (AR) grade. All solvents were distilled under anhydrous conditions before use.

### 2.2. *Analytical and physical measurements.*

The mass spectrum of the ligand was recorded on a VG-Micromass 7070-H spectrometer. Elemental analyses were carried out by micro analytical methods. Metal contents were determined using a Varian Spectra 30/40 atomic absorption spectrometer, employing the necessary standards. DTA studies were carried out on a Leeds and Northrup, U.S.A. instrument. Thermal decompositions were effected at normal atmosphere in Robert-Grimshaw ceramic sample holders at a heating rate of 10°C/min using  $\alpha$ -alumina as reference. Conductance measurements were carried out on a Digisun D1-909 digital conductometer. IR spectra were recorded on a Perkin-Elmer-783 spectrophotometer using KBr pellets. Reflectance electronic spectra were recorded in Nujol mulls on a Cary 2390 UV spectrometer. Magnetic susceptibilities were measured on a vibrating sample magnetometer of EG & G Princeton, research model.

### 2.3. *Synthesis of N-acetylacetylonyl-3-aminocoumarin (H-acacAC).*

To a 0.05 mole (8 g) of 3-amino-coumarin dissolved in hot methanol, 0.05 mole (5 ml) of acetyl acetone was added and refluxed for four h. Lemon yellow crystals (10 g) that separated out were filtered and washed with methanol, petroleum ether and dried under vacuum. Yield: 75%; m.p.184°C.

#### 2.4. *Synthesis of metal complexes.*

A general method was adopted for the preparation of all the complexes. A hot methanolic solution of the ligand was added to a methanolic solution of the metal chloride (ligand/metal ratio 1:1). A distinct reduction of the pH was observed. The pH of the solution was then increased to 7 using a methanolic ammonia solution and the contents were refluxed on a hot water bath for 6-8 h. The separated solid complex was filtered, washed with methanol, petroleum ether and dried in vacuum desiccator over P<sub>2</sub>O<sub>5</sub>.

Yields: Complexes for Cr(III) : 55%, Mn(II) : 45%, Fe(III) : 60%, Co(II) : 55%, Ni(II) : 65%, and Cu(II) : 60%.

#### 2.5. *Pharmacology*

To trace antifeedant and IGR activities, the compounds were primarily screened on *Spodoptera litura* ;F (*Lepidoptera: noctuidae*). The insects were reared on a natural diet of mulberry leaves in the larval stages and sugar syrup was supplied for the adults. The total rearing period comprised 12 h of photoperiod and 12 h of dark period. The experiment was carried out at a temperature of 27°C +/-1°C. The insects were in various stages of life cycle viz egg, larval, pupal and adult. The long duration period being the larval stage is also of voracious feeding habit. Proper feeding of the larvae was taken care by the regular supply of mulberry leaves.

1% and 5% acetone solutions of the ligands, metal salts and their corresponding metal complexes and related compounds were prepared. These solutions used as media for transporting the chemical to the insect body or on to the leaf surface on which the insects/larvae reared.

Antifeeding test: The fifth instar larvae was selected for testing the antifeedant activity. Leaf discs of uniform area of 78 cm<sup>2</sup> were punched out from mulberry leaves with their petioles intact. The leaf discs to be treated were dipped in the prepared acetone solutions of the various test compounds for 2 min. The leaf discs were air dried and placed in a conical flask containing small amount of water to facilitate water translocation and thus enable to keep the leaf disc fresh throughout the duration of the experiment. Five fifth instar larvae of the test insects which have been pre-starved for 6 h were introduced on the leaf discs and allowed to feed on them for 2 h. One set of the control leaf discs was dipped in pure acetone and another set was kept without any chemical. The results were recorded after 2, 12 and 24 h. The area of the leaf disc consumed was measured by Dethiers method [17].

The fifth instar larvae were topically treated leaves with the ligand and their corresponding metal complex solutions at different dosages. A continuous observation on the larvae was maintained from the time of the treatment with the ligand and complex solutions through the formation of the adult until its death. In each experiment, 10 insects

were employed and the experiments were repeated thrice for IGR juvenile hormone activity test [18].

### 3. Results and Discussions

#### 3.1. Characterization of the ligand

Elemental analysis indicated that the ligand has the molecular formula given in Table 1. The mass spectrum shows parent peak at  $m/e$  243 which is consistent with the molecular formula (Fig. 1).

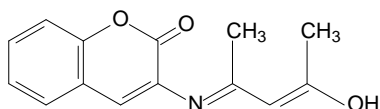


Fig. 1. Proposed structure of ligand (H-acacAc).

The IR spectrum of the free H-acacAC ligand shows a broad band in the range  $3300\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  centered at  $3400\text{ cm}^{-1}$ . This band has been assigned to the presence of enolic hydroxyl group [19]. The band located at  $1700\text{ cm}^{-1}$  with shoulders at  $1720\text{ cm}^{-1}$  and at  $1740\text{ cm}^{-1}$  attributed to  $\nu(\text{C}=\text{O})$  moiety of the coumarin [20]. This band structure is indicating the involvement of the lactone carbonyl in multiple inter and intra molecular hydrogen bonding. These observations suggest that the free H-acacAC is predominantly in the form of the enolic tautomer. The band observed at  $1630\text{ cm}^{-1}$  has been attributed to the  $\nu(\text{C}=\text{C})$  stretch [21]. The high intensity band at  $1600\text{ cm}^{-1}$  [22] is assigned to the azomethine stretching. The enolic stretching,  $\nu(\text{C}-\text{O})$  is observed at  $1130\text{ cm}^{-1}$ . The ethereal C-O-C stretch is identified at  $1020\text{ cm}^{-1}$ . The band at  $1380\text{ cm}^{-1}$  is assigned to the  $\nu(\text{C}-\text{N})$ .

The electronic spectrum of H-acacAC reveals a multiple band in the region of  $40000\text{ cm}^{-1}$  to  $35710\text{ cm}^{-1}$ . This has been attributed to the  $\pi-\pi^*$  and  $n-\pi^*$  transitions which are possible mainly due to the lactone oxygen of the coumarin moiety [23]. The broad band identified in the region of  $25000\text{ cm}^{-1}$  to  $22220\text{ cm}^{-1}$  is attributed to the  $n-\pi^*$  transition of the azomethine group.

The NMR spectrum of H-acacAC reveals the presence of two  $-\text{CH}$  protons at 5.38 ppm. The methyl protons are indicated in the range of 2.19 ppm to 2.31 ppm. The ring protons are identified in the range of 7.38 ppm to 7.41 ppm [24]. The signal expected for enolic hydroxyl proton is recorded at 12.1 ppm, substantiated by  $\text{D}_2\text{O}$  exchange studies. The absence of the signals due to methylene protons and the presence of two  $-\text{CH}$  protons confirmed enolization.

### 3.2. Characterisation of metal complexes

The complexes are soluble in acetone, chloroform, 1,4-dioxane, THF, DMF and DMSO. They melt in the temperature range of 120°C to 264°C. Some of them melt at temperatures lower than the melting point of the free ligand.

The melting points of these complexes are – Cr(III) 125°C, Mn(II) 173°C, Fe(III) 120°C, Co(II) 135°C, Ni(II) 264°C, Cu(II) 120°C.

### 3.3. Elemental analysis

It appears from the analytical data (Table 1) that the ligand undergoes deprotonation of its enolic proton during the complex formation with metal chloride. The analytical data reveals M:L ratio of 1:2 in Cr(III) and Co(II) and 3:4 in Cu(II) and Mn(II) complexes. In Fe(III) and Ni(II) complexes, the M: L ratios are 2:5 and 2:3 respectively. In Cr(III) and Co(II) complexes, the data are indicative of the presence of coordinated ammonia molecules (which are confirmed by spectral data). The absence of chloride in the cobalt complex and the presence of chloride in other complexes are noted.

### 3.4. Molar conductance studies

The conductance measurements, recorded for  $10^{-3}$  M solutions of the metal complexes in DMSO are listed in Table 1. The data reveals that the Cr(III) and Fe(III) complexes are conductors and the Mn(II), Co(II), Ni(II) and Cu(II) complexes are non conductors. The Cr(III) complex exhibits a molar conductance of 130 mhos and the Fe(III) complex, a value of 65 mhos. These values reveal that the former is a 1:2 electrolyte and the later is a 1:1 electrolyte [20].

Table 1. Elemental analyses and molar conductance data of metal complexes of HacacAc

Comp No	Empirical formula	M%		C%		H%		N%		Cl%		$\Lambda_M$ (mho cm <sup>2</sup> mole <sup>-1</sup> )
		Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	
1	[Cr <sub>2</sub> (acacAC) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	8.68	8.84	56.39	57.09	4.53	4.59	7.02	7.14	6.00	6.03	130
2	Mn [Mn <sub>2</sub> (acacAC) <sub>4</sub> Cl <sub>2</sub> ]	13.52	13.69	55.08	55.82	3.90	3.99	4.60	4.65	5.83	5.90	
3	[Fe <sub>2</sub> (acacAC) <sub>3</sub> ]Cl	8.10	8.23	61.09	61.89	4.35	4.42	5.10	5.16	2.58	2.62	65
4	[Co <sub>2</sub> (acacAC) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	10.38	10.52	59.25	60.00	4.76	4.82	7.40	7.50			
5	[Ni <sub>2</sub> (acacAC) <sub>3</sub> ]Cl	13.18	13.36	56.58	57.34	4.04	4.10	4.71	4.78	3.98	4.04	
6	Cu[Cu <sub>2</sub> (acacAC) <sub>3</sub> Cl <sub>2</sub> ]	15.31	15.50	53.91	54.65	3.86	3.90	4.49	4.55	5.65	5.77	

### 3.5. Infrared spectral studies.

The characteristic infrared frequencies of metal complexes are given in Table 2. Non-ligand bands have been identified at 3350 cm<sup>-1</sup> and 3450 cm<sup>-1</sup> in the Cr(III) and at 3000

$\text{cm}^{-1}$  and  $3400 \text{ cm}^{-1}$  in the Co(II) complexes. These bands are characteristics of N-H stretching vibrations and thus have been assigned to the  $\nu$  (N-H) (stretch) arising as a result of coordinated ammonia molecules [25].

Table 2. The IR absorption frequencies (in  $\text{cm}^{-1}$ ) of metal complexes.

Compound	$\nu(\text{OH})$ enolic	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O})$	New Bands
HacacAc	3300- 3500	1700 1720	1630	1600	1380	1130	
$[\text{Cr}_2(\text{acacAC})_4(\text{NH}_3)_2]\text{Cl}_2$	-	1700	1630	1570	1360	1170 1200	3450, 3350, 970, 800, 730, 650, 580, 560.
$\text{Mn}[\text{Mn}_2(\text{acacAC})_4\text{Cl}_2]$	-	1720	1630	1570	1360	1160 1180	640, 570, 260..
$[\text{Fe}_2(\text{acacAC})_3]\text{Cl}$	-	1720	1630	1570	1360	1140 1150	820, 640, 560.
$[\text{Co}_2(\text{acacAC})_4(\text{NH}_3)_2]$	-	1720	1630	1570	1340	1160 1180	3400, 3300, 970, 850, 670, 560, 460.
$[\text{Ni}_2(\text{acacAC})_3\text{Cl}]$	-	1650	1610	1560	1360	1150 1160	930, 640, 560, 320.
$\text{Cu}[\text{Cu}_2(\text{acacAC})_4\text{Cl}_2]$	-	1720	1660	1580	1360	1160 1170	860, 800, 680, 560, 340, 240.

The broad trough of medium intensity observed in the free ligand spectrum in the range of  $3300 \text{ cm}^{-1}$  to  $3500 \text{ cm}^{-1}$  was absent in all the complexes [26]. This clearly indicates that the deprotonation of the enolic hydroxyl group has taken place.

In the IR spectra of all the complexes except that of Ni(II), a sharp peak has been identified in the range of  $1700 \text{ cm}^{-1}$  to  $1720 \text{ cm}^{-1}$ . This has been assigned to the ring carbonyl stretching frequency. As compared with the corresponding band in the free ligand, this band has not undergone any apparent shift. It is therefore, concluded that the ring carbonyl did not participate in coordination in all these complexes [27]. In the case of Ni(II), this band has undergone a downward shift by  $70 \text{ cm}^{-1}$  [28] and has been identified at  $1650 \text{ cm}^{-1}$ . This is indicative of ion of the ring carbonyl in coordination.

$\nu$  (C=C) has been identified in Cr(III), Mn(II), Fe(III) and Co(II) complexes at  $1630 \text{ cm}^{-1}$ , in the Cu(II) complex at  $1660 \text{ cm}^{-1}$  and in Ni(II) complex at  $1610 \text{ cm}^{-1}$ . The corresponding free ligand band was observed at  $1630 \text{ cm}^{-1}$ .

The sharp peak at  $1600 \text{ cm}^{-1}$  in the free ligand is observed at  $1560 \text{ cm}^{-1}$  in the Ni(II) complex and at  $1570 \text{ cm}^{-1}$  in the rest of the complexes. This band has been assigned to the azomethine stretching frequency. In comparison with the free ligand, this band has experienced a downward shift by  $30 \text{ cm}^{-1}$  to  $40 \text{ cm}^{-1}$  which indicates the participation of the azomethine nitrogen in coordination [29]. In place of  $\nu$  (C-O) (enolic) at  $1130 \text{ cm}^{-1}$  in the ligand, the spectrum of each complex shows two bands in the range of  $1140$  to  $1200 \text{ cm}^{-1}$ . These bands indicate a positive shift of  $\nu$  (C-O) suggesting coordination through enolic oxygen. One of these bands shows a large shift in the range of  $30 \text{ cm}^{-1}$  to  $70 \text{ cm}^{-1}$

which can be attributed to bridging phenomenon [30]. It is interesting to note that each complex shows the presence of two types of enolic oxygens, one non-bridging and the other bridging. The ligand H-acacAC may be mentioned as a unique example indicating the flexibility of chelating agent in metal binding interactions. There is no change in the ring  $\nu$  (O-C-O) frequency suggesting that there is no bonding between the oxygen atom of coumarin ring and the metal atom in each of the complexes [31].

The new bands identified in complexes at  $340\text{ cm}^{-1}$ ,  $320\text{ cm}^{-1}$ ,  $260\text{ cm}^{-1}$  and  $240\text{ cm}^{-1}$  have been assigned to the metal chloride stretching frequencies. New non-ligand bands have been observed at  $560\text{ cm}^{-1}$ ,  $640\text{-}650\text{ cm}^{-1}$  and at  $800\text{ cm}^{-1}$  in all complexes. In Cr(III) and Co(II) complexes, additional non-ligand bands have been identified at  $450\text{ cm}^{-1}$ ,  $580\text{ cm}^{-1}$ ,  $730\text{ cm}^{-1}$ ,  $850\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  respectively. These new bands can be attributed to M-N, M-O stretching vibrations [32]. The greater number of non-ligand bands in the Cr(III) and Co(II) complexes may be attributed to the presence of coordinated ammonia molecules [33].

From the IR data, it has been concluded that the ligand H-acacAC behaves as a monobasic tridentate ONO donor in the case of Ni(II) complex, coordinating through the ring carbonyl, azomethine nitrogen and the enolic oxygen atoms. In all the other complexes, the ligand is found to coordinate through the azomethine nitrogen and enolic oxygen, thereby acting as a monobasic bidentate ON donor. The enolic oxygen acts as a bridge between the two metal centers.

### 3.5. Magnetic studies

The magnetic moments reveal the paramagnetic nature of the complexes. From the magnetic moment data in Bohr Magneton (BM) units; Cr(III): 4.78, Mn(II): 5.82, Fe(III): 1.30; Co(II): 2.52; Ni(II): 3.13 and Cu(II): 1.86; it is concluded that Fe(III) has a spin paired configuration [27].

### 3.6. Electronic spectral studies.

The multiple band observed in the region of  $40000\text{ cm}^{-1}$  to  $35710\text{ cm}^{-1}$  of the free ligand electronic spectrum has undergone considerable change. The multiplicity of the band is absent in all the complexes. The broad band assigned to the azomethine group in the free ligand spectrum in the range of  $25000\text{ cm}^{-1}$  to  $22220\text{ cm}^{-1}$  has also undergone considerable modification. This supports the possible involvement of azomethine group in coordination.

The electronic spectra of Cr(III) complex has three distinct bands at  $35710\text{ cm}^{-1}$ ,  $25000\text{ cm}^{-1}$  and  $16670\text{ cm}^{-1}$  respectively. These bands are assigned to  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (P),  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (F),  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transitions respectively. These transitions are indicative of an octahedral geometry [33]. The electronic spectrum of the Mn(II) complex exhibits weak absorption bands at  $26320\text{ cm}^{-1}$  and  $33330\text{ cm}^{-1}$ . It is known [34] that  $d-d$  bands of hexa coordinated high-spin Mn(II) complexes have extremely low intensity and in the presence of organic ligands they could rarely be detected. Therefore, an octahedral geometry is proposed. In

the Fe(III) complex, a number of transitions are observed at 28570 cm<sup>-1</sup>, 21740 cm<sup>-1</sup>, 20000 cm<sup>-1</sup>, 16670 cm<sup>-1</sup>, 12200 cm<sup>-1</sup>, 8550 cm<sup>-1</sup> and 7259 cm<sup>-1</sup> respectively. These are attributed to several spin forbidden and charge transfer bands. The transitions may involve <sup>4</sup>π<sub>g</sub>, <sup>4</sup>T<sub>2g</sub>, <sup>4</sup>A<sub>1g</sub>, <sup>4</sup>E<sub>g</sub>, <sup>4</sup>T<sub>g</sub> (D), <sup>4</sup>E<sub>g</sub> (D), <sup>4</sup>T<sub>1g</sub> (P), <sup>4</sup>A<sub>2g</sub> (F), <sup>4</sup>T<sub>1g</sub> (F) etc. in octahedral stereochemistry. Due to the doubly forbidden nature, no specific assignments are made [35]. Thus, for the Fe(III) complex, an octahedral geometry has been proposed.

The electronic spectrum of Co(II) shows bands at 20000 cm<sup>-1</sup> (multiplet), 14290 cm<sup>-1</sup> and at 6800 cm<sup>-1</sup> assignable to <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>1g</sub>(P), <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>A<sub>2g</sub>, <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>2g</sub>(F) transitions respectively [36]. Additional bands observed at 27030 cm<sup>-1</sup> and at 29410 cm<sup>-1</sup> have been assigned to charge transfer transitions. The ν<sub>2</sub>/ν<sub>1</sub> ratio is equal to 2.1. The transition patterns and the ν<sub>2</sub>/ν<sub>1</sub> ratio are both supportive of octahedral geometry. In the spectrum of Ni(II), electronic transitions have been observed at 11760 cm<sup>-1</sup>, 20830 cm<sup>-1</sup> and 25000 cm<sup>-1</sup> which are assigned to <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>2g</sub>, <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>A<sub>1g</sub>(F), <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub>(P) respectively [17]. The Charge transfer bands are identified at 35710 cm<sup>-1</sup> and the spin forbidden bands in the range of 16670 to 15380 cm<sup>-1</sup>. Thus, Ni(II) complex is assigned an octahedral geometry. In Cu(II), a multiple band is identified in the range of 18180 cm<sup>-1</sup> to 22220 cm<sup>-1</sup> and charge transfer bands at 26320 cm<sup>-1</sup>, 28570 cm<sup>-1</sup> and at 35710 cm<sup>-1</sup> respectively. The multiple bands have been assigned to <sup>2</sup>E<sub>g</sub>→<sup>2</sup>T<sub>2g</sub> transition. The nature of the band (broadness and multiplicity) suggests tetragonal distortion from the regular octahedral geometry [37].

### 3.7. *The ESR studies*

The ESR spectrum of the Cu(II) complex was recorded at liquid N<sub>2</sub> temperature in the polycrystalline form using DPPH as a reference standard. The g<sub>||</sub> and g<sub>⊥</sub> values have been found to be 2.12 and 2.16. The complex shows axial symmetry. The difference in g<sub>||</sub> and g<sub>⊥</sub> values indicates the octahedral distortion in the complex [38]. Absence of hyperfine interaction reveals that the M-L interaction is far higher and more prominent in comparison with the possible hyperfine interaction in free Cu(II) ion.

On the basis of above spectral analyses the structures of Cr(II), Mn(II), Cu(II), Fe(III), Co(II) and Ni (II) complexes can be predicted as illustrated in Figs. 2a-e.

### 3.8. *Antifeeding and IGR activities*

#### 3.8.1. *Antifeeding activity*

It was observed that during the total experimental period, the insects did not show any repellent behaviour towards the treated leaf surfaces. It was observed that the ligand H-acacAC and its metal complexes did not exhibit any antifeeding activity at lower dosage of 1% (Table 3). The insects were feeding on the leaves normally. At higher dosage of 5%, a gradational drop in the feeding was observed. The metal salts, acac and AC did not exhibit any antifeeding activity either at a lower or at a higher dosage.

At 5% dosage: Ni >> Co = Cr > Fe > Cu = Mn > H-acacAC



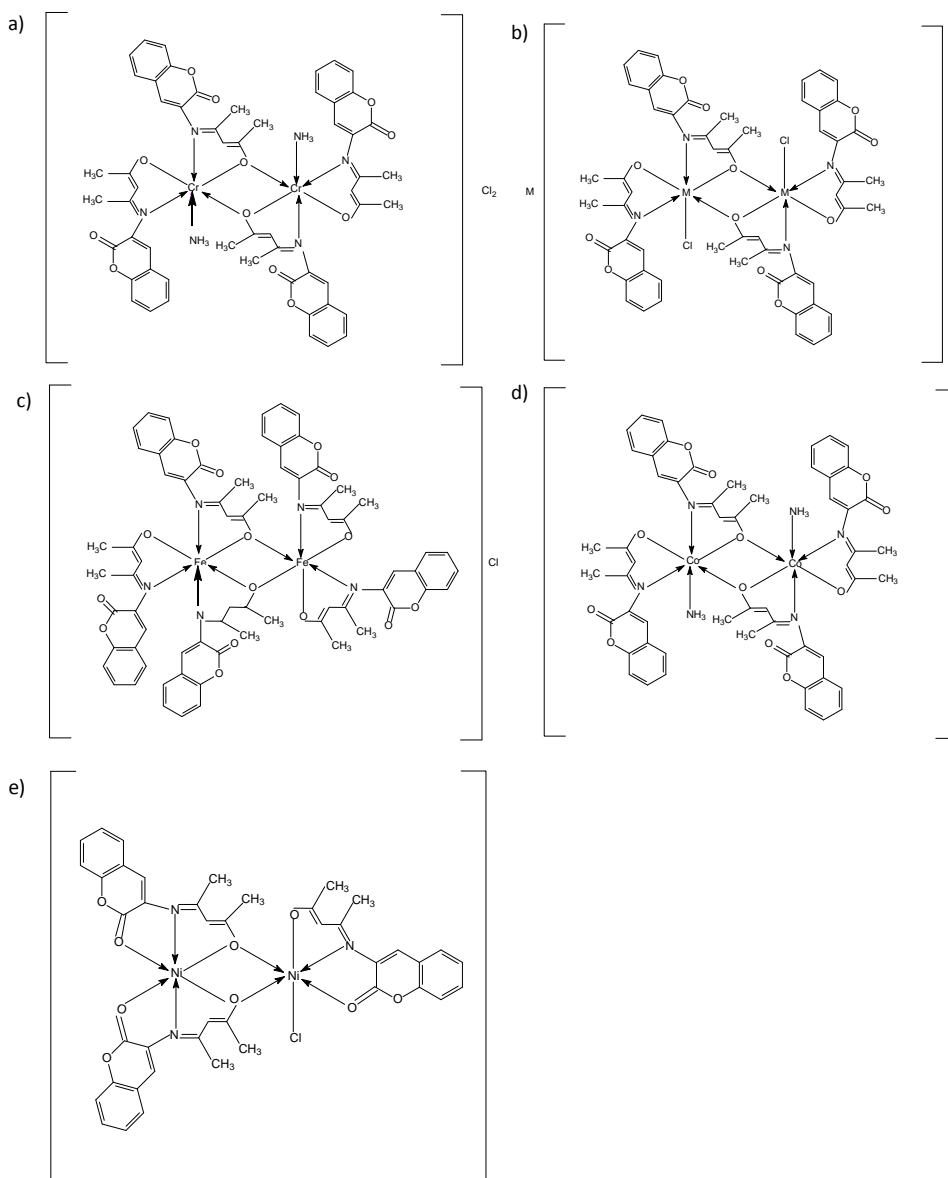


Fig. 2a-e. Predicted structures of a) Cr(III), b) Mn(II) and Cu(II), c) Fe(III), d) Co (II), and e) Ni (II) complexes.

### 3.8.2. IGR activity

IGR activity was not recorded with metal salts, AC, acac. The metal complexes of H-acacAC were found to exhibit IGR activity at lower dosages of 1% alone (Table 3) The activity order of the metal complexes of H-acacAC is as follows:

At 1% dosage: Ni > Co = Cr > Fe > Cu = Mn > H-acacAC

Table 3. Antifeedant and IGR activity.

Sl.	Compound	Antifeedant activity		IGR activity	
		% concentration		% concentration	
		1	5	1	5
1	Acetone	-	-	-	-
2	AC	-	-	-	-
3	CrCl <sub>3</sub>	-	-	-	-
4	MnCl <sub>2</sub>	-	-	-	-
5	FeCl <sub>3</sub>	-	-	-	-
6	CoCl <sub>2</sub>	-	-	-	-
7	NiCl <sub>2</sub>	-	-	-	-
8	CuCl <sub>2</sub>	-	-	-	-
9	acac	-	-	-	-
10	H-acacAC	-	+	+	-
11	Cr(III)-acacAC	-	+++	+++	-
12	Mn(II)-acacAC	-	+	+	-
13	Fe(II)-acacAC	-	++	++	-
14	Co(II)-acacAC	-	++	+++	-
15	Ni(II)-acacAC	-	+++++	+++++	-
16	Cu(II)-acacAC	-	+	+	-

% activity 30 = ++++++ 25 = +++++ 20 = +++ 15 = ++  
10 = ++ Nil = -

$$\% \text{ Activity} = \frac{\% \text{ protection in treated} - \% \text{ protection in control}}{100 - \% \text{ protection in control}} \times 100$$

Metal ion specificity is observed with Ni(II) complex exhibiting about 30% activity. Activity was calculated adopting the method of Singh and Panth [39]. The activity order is the same for both antifeeding and IGR activities.

Prominent changes were noticed during adult emergence. They are (i) prolongation of larval life; (ii) formation of apparently normal pupae; (iii) mortality during pupal formation; (iv) adult mortality during emergence as a consequence of pupal case attachment; (v) emergence of abnormal adults with crumpled wings and malformed legs; (vi) though some normal adults had emerged, they were dead soon after emergence; (vii) non-emergent pupae; (viii) emergence of few normal adults. All these changes are commonly recorded with exogenous juvenile hormone activity. Similar changes were noticed in different insects when they were tested for IGR with juvenile hormone activity [16]. This was considered as due to interference by the test compounds with the neuro-endocrine system of the test insects or possibly changes brought about in the general metabolism which, in turn, affected the growth of the insect through the neuro-endocrine system [40].

In insects, Juvenile hormones refer to a group of hormones which ensure growth of the larva, while preventing metamorphosis. Because of their rigid exoskeleton, insects can grow only by periodically shedding their exoskeleton (a process known as molting) [41-43]. All these changes are commonly recorded with exogenous juvenile hormone activity. Synthetic analogues of the juvenile hormone are used as an insecticide, preventing the

larvae from developing into adult insects. At high levels of Juvenile hormones, larva can still molt, but the result will only be a bigger larva, not an adult. Thus the reproductive cycle is broken. Similar results were also noticed when the plant originated antifeedant azadirhychtin was tested for juvenile hormone activity [44].

Thus it can be concluded that the metal complexes used in the present study have AF properties at higher dosages and IGR juvenile hormone activity at lower dosages. However, further detailed study is required regarding the activity enhancement of the test compounds with structural modifications, identification of the site of action of the compound, bioassay against various insects and their toxicity evaluation against various insects at laboratory and field levels.

#### 4. Conclusions

The ligand H-acacAC acted as a monobasic tridentate ONO donor in the case of Ni(II) complex, coordinating through the ring carbonyl, azomethine nitrogen and the enolic oxygen atoms. In all the other complexes, the ligand was found to coordinate through the azomethine nitrogen and enolic oxygen, thereby acting as a monobasic bidentate ON donor. The enolic oxygen also acted as a bridge between the two metal centres. On the basis of analytical, conductance, thermal, spectral and magnetic data, octahedral geometry has been proposed and the following formulae have been concluded.

1.  $[\text{Cr}_2(\text{acacAC})_4(\text{NH}_3)_2]\text{Cl}_2$
2.  $\text{Mn}[\text{Mn}_2(\text{acacAC})_4\text{Cl}_2]$
3.  $[\text{Fe}_2(\text{acacAC})_5]\text{Cl}$
4.  $[\text{Co}_2(\text{acacAC})_4(\text{NH}_3)_2]$
5.  $[\text{Ni}_2(\text{acacAC})_3]\text{Cl}$
6.  $\text{Cu}[\text{Cu}_2(\text{acacAC})_4\text{Cl}_2]$

From the pharmacological studies, it is clear that these metal complexes may be used as a new group of pesticides. However, further detailed study is required regarding the activity enhancement of the test compounds with structural modifications, identification of the site of action of the compound.

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