

Evaluation and Rearrangement of Novel Supramolecular 7-(2,3-Dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol Complexes and their Biological Effect

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Abstract

Novel tridentate Schiff base ligand derived from the 2-aminobenzethiol and 8-hydroxy-7-quinolinecarboxaldehyde (oxine) and its metal complexes have been prepared. The reaction of a solution of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H_2L) with di- and tetravalent transition metals have been studied chemically and biologically. The optimized bond lengths, bond angles and calculated the quantum chemical parameters for the ligand (H_2L) [the cyclic form (A) and the Schiff base form (B)] were investigated. The complexes have been characterized by elemental analyses, IR spectra, thermal analyses and ¹H-NMR spectroscopy. The spectral studies of the isolated complexes showed that the rearrangement of the benzothiazoline to the Schiff base had occurred. The data suggest that the Co(II) and Ni(II) complexes are binuclear and octahedral dimmers, while the rest are monomeric with square planar/tetrahedral geometries. The ESR spectrum of the Cu(II) complex show axial type symmetry with $g_{\parallel} > g_{\perp} > 2.002$, indicating $d_{x^2-y^2}$ ground state with significant covalent bond character. Five doses were topically applied against the newly emerged adults of the red palm weevil *Rhynchophorus ferrugineus*. Percent of adult mortality was 98.2%, which occurred after adult treatment with the highest dose (2.2 mg/ml) of Ni(II) complex. The lowest mortality was 5.6% which obtained due to effect of oxine after adult was treated with dose of 0.25 mg/ml. Five doses were topically applied against the newly emerged adults of the stored product weevil, *Sitophilus granaria*. While the lower mortality, 5% caused due to effect of least dose, 0.15 mg/ml of the compound oxine.

Keywords: 2-Aminobenzethiol; Biological effect; Quantum chemical parameters; Schiff base; Supramolecular structure; ESR; Molecular structures

Introduction

Schiff bases continue to occupy an important position as ligands in metal coordination chemistry even after almost a century since their discovery. Sulphur and nitrogen have long been used to increase the biological activity of organic moiety [1,2] and quinoline compounds have also found applications in medicinal chemistry [3]. However, no systematic study has been performed on such complexes.

It has been well established that condensation of 2-aminobenzethiol with carbonyl compound does not normally lead to the isolation of the corresponding Schiff base, but thiazoline or benzothiazoline is obtained [4]. However, metal ions may act as a template and favor the formation of Schiff base.

Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis and as polymer stabilizers [5,6]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, antiinflammatory, antiviral, and antipyretic properties [2,5]. It has been suggested that azomethine linkage (C=N) might be responsible for the biological activities of Schiff bases.

Studies of the complexing ability and analytical applications of heterocyclic azomethines derived from thiazoline compounds are very important [7-9]. It is well known that some drugs have increased activity when administered as metal complexes and a number of metal chelates inhibit tumor growth [10].

The number and diversity of nitrogen and oxygen chelating agents used to prepare new coordination and organometallic compounds has increased rapidly recently [11-13].

The behavior of the C=N bond is strongly dependent on the

structure of the amine moiety, which in turn controls the efficiency of the conjugation and may incorporate structural elements able to modulate the steric crowding around the coordination [14].

The Red palm weevil *Rhynchophorus ferrugineus* Oliv. Coleoptera-Curculionidae is a devastating insect pest of date palm in the Arabian Gulf region [15]. It was reported on date palm, for the first time, from the United Arab Emirates in the mid-1980s then its reported distributed expanded its range westwards till reached the entire Gulf area [16,17].

A survey of literature reveals that no work has been carried out on the synthesis of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H_2L) ligand and its Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Zr(IV) complexes. The present work aims at highlighting the synthesis and characterization of novel supramolecular chemistry of complexes with H_2L and studies their spectral properties. Molecular and electronic structures of the investigated ligand (H_2L) have been discussed. The effect of the ligand and its complexes on the red palm weevil *Rhynchophorus ferrugineus* (Oliv.) and on the stored food weevils *Sitophilus granary* were studied.

Experimental

All chemicals were reagent grade (BDH Chemical Ltd.) and were

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used as supplied. The experimental techniques were as described previously [18-20]. 8-Hydroxy-7-quinoline carboxaldehyde (oxine) was previously prepared by El-Sonbati [21].

Preparation of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H_2L)

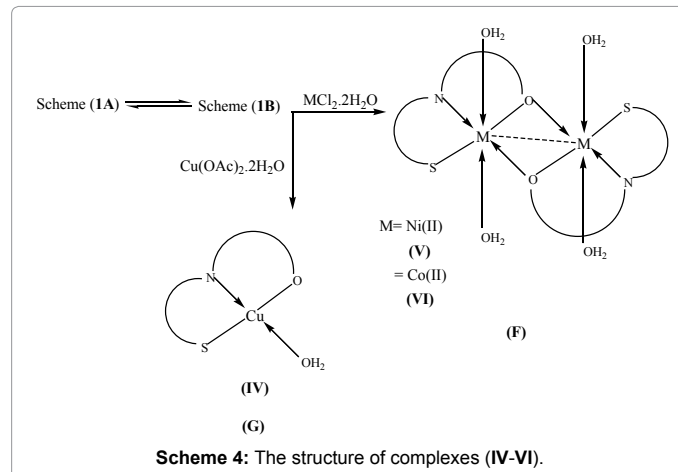
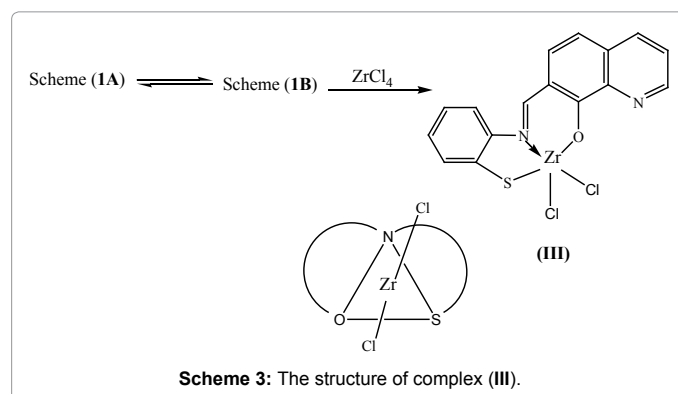
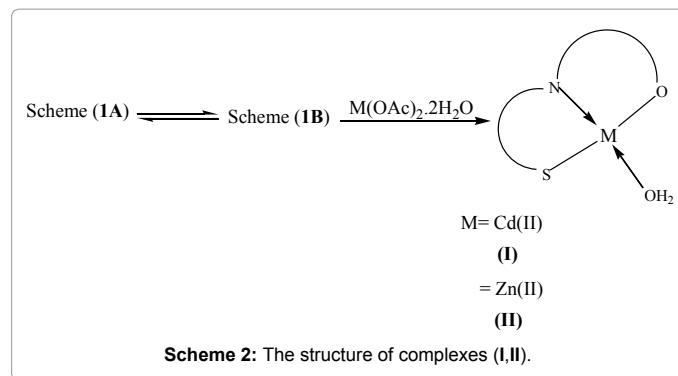
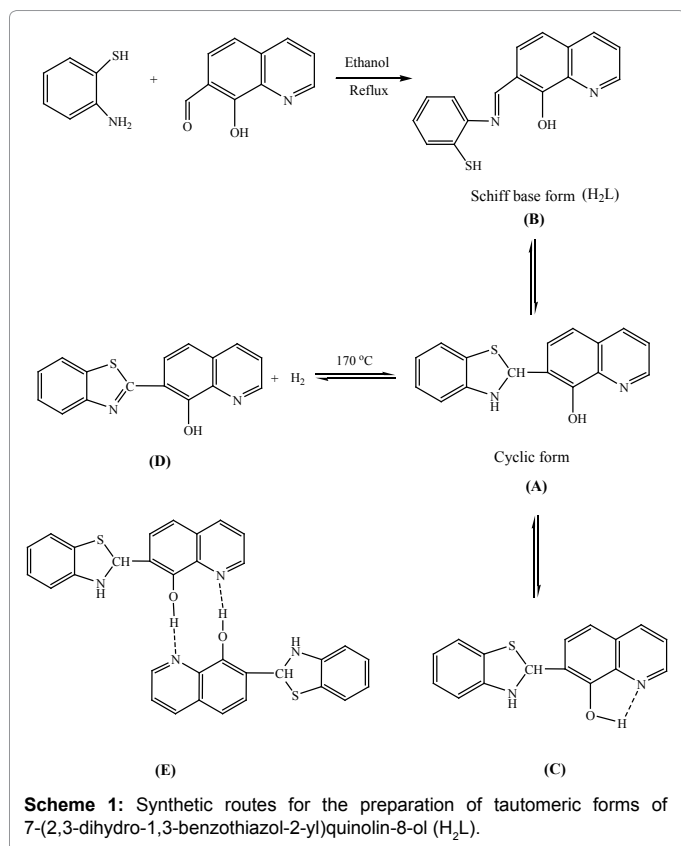
A solution of 8-hydroxy-7-quinolinecarboxaldehyde (oxine) (0.06 mol) in DMF:Ethanol (15 ml) was treated with 2-aminobenzenethiol (0.06 mol) in ethanol (15 ml) (Scheme 1). The reaction was refluxed for 3.5 hrs. The pale brown precipitate formed was purified by recrystallization from hot ethanol. Yield 55%, (Found: C 68.4, H 4.1, N 9.6, S 11.1% Calculated for $C_{16}H_{12}N_2SO$: C 68.6, H 4.3, N 10.0, S 11.4%). The purity was checked by elemental analyses, IR and 1H NMR spectroscopies.

Oxidation of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H_2L)

Oxidation was carried out by bubbling air for four hrs in benzene solution of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H_2L). The oxidation product was benzothiazol. Found C, 68.87; H, 3.50; N, 9.77; S, 11.51%. Calculated for $C_{16}H_{10}N_2SO$; C, 69.07; H, 3.61; N, 10.07; S, 11.37%. No band was observed in the IR spectrum above 3130 cm^{-1} , indicating the absence of NH.

General method for preparing complexes

Reaction of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol with metal ions: The complexes were prepared by methods similar to the reported in earlier publications [14,22-24] according to the following procedures:



1) Mono(7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol)Cd and Zn [(I) and (II)] (Scheme 2)

$M(OAc)_2 \cdot 2H_2O$ (0.5 mmol) in ethanol (15 ml), was added to ligand (H_2L) (0.5 mmol) in DMF:Ethanol (1:2 v/v) (25 ml) and the resulting mixture was stirred at room temperature for 3 h. The formed precipitate was filtered off, washed with ethanol and ether, respectively, and dried in vacuum over P_2O_5 .

2) Chloro(7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol) zirconium [(III)] (Scheme 3)

Solution of $ZrCl_4$ (1 mmol) and the ligand (H_2L) (1 mmol) in DMF:Methanol (1:2 v/v) (45 ml) was mixed and stirred for 4 h. The obtained precipitate was filtered, washed with MeOH and dried in vacuum over P_2O_5 .

3) Bi(7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol)Cu/Ni/Co [IV-VI] (Scheme 4)

The reaction of the ligand with $MX_2 \cdot nH_2O$ was carried out by stirring a mixture of DMF:Ethanol solutions of the ligand and the $MX_2 \cdot nH_2O$ for four hours at room temperature. The obtained product was filtered off and washed with ethanol, then dried in vacuum over P_2O_5 .

Insect rearing

Colonies of *Rhynchophorus ferrugineus* are serious pest of coconut causing damage and often killing the palm in its prime of life. The hatched grubs burrow into the trunk and feed on tissue of the stem. In the present study, the adult, larvae and pupal stages were collected from large cavities of infested date trees from Nagran region in KSA particularly for those received no chemical insecticides. Laboratory culture of *Rhynchophorus ferrugineus* was established under $26 \pm 2^\circ C$ and $60 \pm 5\%$ R.H. Insect was fed on the freshly shred sugar-cane stem tissues. The colony was checked daily for the deposited eggs between sugar-cane tissues and changed when becoming moldy. The sugar-cane pieces on which the adults laid their eggs were transferred to small plastic cages until hatching. The newly hatched larvae were cultured on a medium consisting of sugar-cane shreds.

Bioassay of inorganic chemical compounds

Five concentrations of oxine, H_2L (Scheme 1B) and complexes (IV,V) (Scheme 4) were prepared by using Dimethylsulfoxide (DMSO) as solvent: 2.25, 1.12, 0.56, 0.25, and 0.125 mg/ml. Four replicates contained (5 last larval instars each) for each concentration. The adults of *Rhynchophorus ferrugineus* were topically received 3μ for each concentration using Transferpette-micropipette for the treatments. Also the control experiments were conducted by four replicates and the adults were topically treated with Dimethylsulfoxide (DMSO) as solvent only. All treated and control insects were kept at $26 \pm 2^\circ C$ and $60 \pm 5\%$ R.H.

Criteria studied and statistical analysis

The adult mortalities were observed during 24 h. Data obtained were analyzed using t-distribution and refined by Bessel correction [17].

Measurements

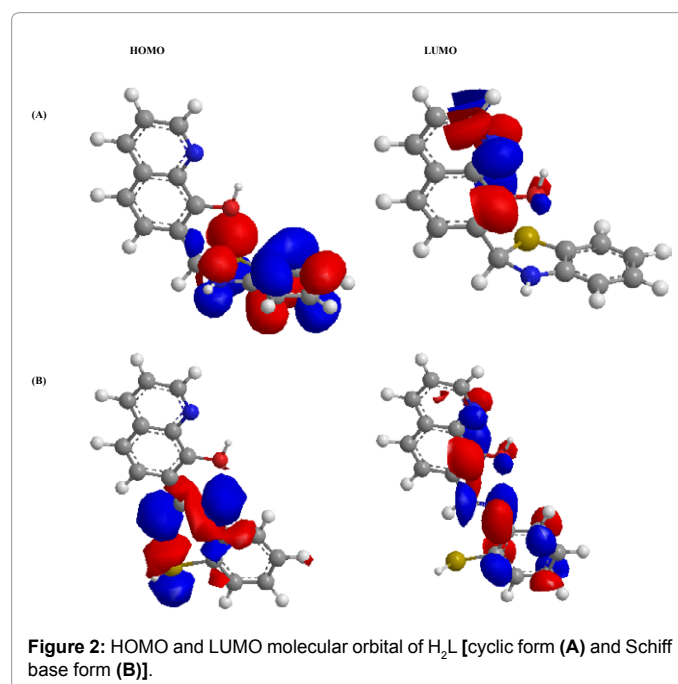
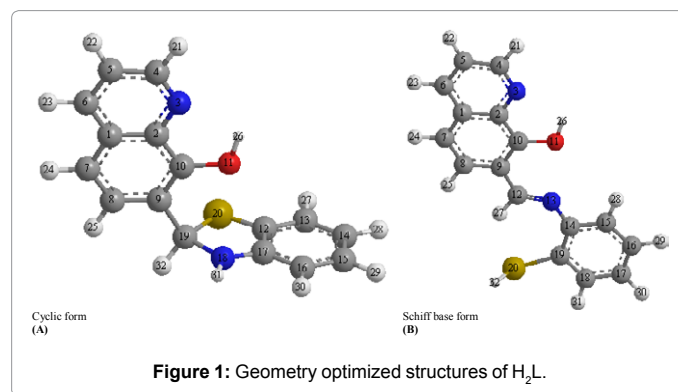
Microanalysis of all samples was carried out at King Khalid University Analytical Center, Saudi Arabia, using a Perkin-Elmer 2400 Series II Analyzer. The metal content in these complexes were estimated by standard methods [25]. IR spectra were recorded on a Perkin-Elmer 1340 spectrophotometer. Ultraviolet-Visible (UV-Vis) spectra of the compounds were recorded in Nuzol solution using a Unicam SP 8800 spectrophotometer. Magnetic measurements were carried out at room temperature using Gouy's method, employing $Hg[Co(SCN)_4]$ for calibration purposes, and were corrected for diamagnetism by using Pascal's constant. Magnetic moments were calculated using the equation: $\mu_{eff} = 2.84 [T\chi_M^{cor.}]^{1/2}$. 1H NMR spectra obtained on JEOL FX900 Q Fourier transform spectrometer with d_6 -DMSO as solvent and TMS as internal reference. Thermogravimetric analysis (TGA) measurements were made using a DuPont 950 thermobalance. Ten milligram samples were heated at $10^\circ/min$ in a dynamic nitrogen atmosphere ($70 ml/min$); the sample holder was boat-shaped, $10 \times 5 \times 2.5$ mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a $KOH-H_2O_2$ mixture. The halide content was then determined by titration

with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone as an indicator. The molecular structures of the investigated compounds were optimized by HF method with 3-21G basis set. The molecules were built with the Perkin Elmer ChemBio Draw and optimized using Perkin Elmer ChemBio3D software [26]. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}) and HOMO-LUMO energy gap (ΔE) for the investigated molecules were calculated.

Results and Discussion

The ligand 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H_2L) is shown in Scheme 1. The optimized structures of cyclic form (A) and Schiff base form (B) are given in Figure 1. The selected geometrical structures of the investigated ligand (H_2L) [cyclic form (A) and the Schiff base form (B)] were calculated by optimizing their bond lengths and bond angles and listed in Tables 1 and 2. From Table 3 the computed net charges on active centers, it is found that the most negative charges in Schiff base form (B) and cyclic form (A) are N3 and S20.

Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital takes



Bond lengths (Å)			
Cyclic form (A)		Schiff base form (B)	
C19-H32	1.113	S20-H32	1.346
N18-H31	1.047	N18-H31	1.104
C16-H30	1.102	C17-H30	1.103
C15-H29	1.103	C16-H29	1.103
C14-H28	1.103	C15-H28	1.106
C13-H27	1.104	C12-H27	1.093
O11-H26	0.97	O11-H26	0.97
C8-H25	1.103	C8-H25	1.104
C7-H24	1.103	C7-H24	1.103
C6-H23	1.102	C6-H23	1.102
C5-H22	1.102	C5-H22	1.102
C4-H21	1.103	C4-H21	1.103
C4-N3	1.264	C14-C19	1.354
C2-N3	1.269	C18-C19	1.347
C1-C2	1.347	C17-C18	1.34
C10-C2	1.35	C16-C17	1.338
C9-C10	1.351	C15-C16	1.341
C8-C9	1.345	C14-C15	1.354
C7-C8	1.34	C4-N3	1.264
C1-C7	1.342	C2-N3	1.269
C6-C1	1.344	C1-C2	1.347
C5-C6	1.34	C10-C2	1.351
C4-C5	1.34	C9-C10	1.353
C12-C17	1.346	C8-C9	1.348
N18-C17	1.268	C7-C8	1.34
C16-C17	1.34	C1-C7	1.341
C15-C16	1.343	C6-C1	1.344
C14-C15	1.344	C5-C6	1.34
C13-C14	1.344	C4-C5	1.34
C12-C13	1.342	C19-S20	1.832
S20-C12	1.474	C14-N13	1.273
C19-S20	1.792	C12-N13	1.264
N18-C19	1.473	C9-C12	1.353
C19-C9	1.514		

Table 1: Bond lengths for the cyclic form and Schiff base form.

part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO for cyclic form (A) and Schiff base form (B) are shown in Figure 2. The calculated quantum chemical parameters are given in Table 4. Additional parameters such as ΔE , absolute electronegativities, χ , chemical potentials, Pi , absolute hardness, η , absolute softness, σ , global electrophilicity, ω , global softness, S , and additional electronic charge, ΔN_{max} , have been calculated according to the following equations [27-29]:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (1)$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \quad (2)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (3)$$

$$\sigma = \frac{1}{\eta} \quad (4)$$

$$Pi = -\chi \quad (5)$$

$$S = \frac{1}{2\eta} \quad (6)$$

$$\omega = \frac{Pi^2}{2\eta} \quad (7)$$

$$\Delta N_{max} = -\frac{Pi}{\eta} \quad (8)$$

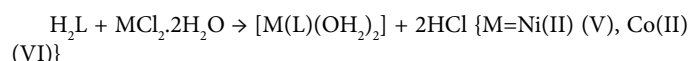
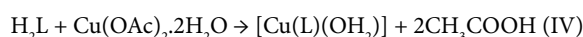
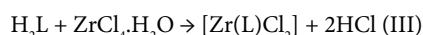
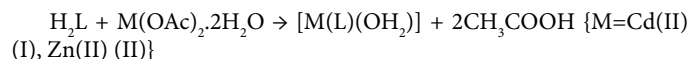
The HOMO–LUMO energy gap, ΔE , which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems [26-29]. The value of ΔE for Schiff base form (B) and cyclic form (A) was found 0.038 and 0.119 a.u., respectively, so the Schiff base form (B) more stable and highly reactive than cyclic form (A).

Structural of the ligand and complexes

The reaction of oxine with 2-aminobenzenethiol afforded a product whose IR spectrum shows a band at 3300 cm^{-1} (assigned to νNH) but no absorption at 2620 cm^{-1} (νSH). Thus the Schiff base (7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol)(H_2L) (B) is ruled out. The sulphur atom of the thiol group tends to form another S–C bond.

Cyclization takes place with the resulting formation of a thiazoline. Complexes of the Schiff base with Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Zr(IV) have been isolated and characterized. The complexes formed are characterized with respect to its composition by elemental analysis and showed agreement with theoretical data. The elemental analysis data listed in Table 5.

The analytical data of the novel complexes prepared agree very well with the compositions $[\text{M}(\text{L})(\text{OH}_2)_n]$ (where $\text{M}=\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cu}(\text{II})$ at $n=1$; $\text{M}=\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ at $n=2$) and $[\text{Zr}(\text{L})(\text{Cl}_2)_2]$. This can be represented by the following equations:



The effervescence of HCl and evolution of ethanolic acid during complex formation was assessed quantitatively by pH titration, a spot test, and by its characteristic odor.

Spectral and thermal properties of the ligand and complexes

The IR spectrum of H_2L exhibits the absence of the bands at $\nu(\text{SH})$ (2500–2600 cm^{-1}) and $\nu(\text{C}=\text{N})$ (1600–1660 cm^{-1}) and the appearance of a broad and strong band which is observed in the region, 3360–3060 cm^{-1} . This band is attributed to $\nu(\text{OH})$ and/or $\nu(\text{NH})$. Also, an intense band at 828 cm^{-1} due to the C–S–C linkage and not Schiff base form [7]. Two bands of medium intensity at 1580 and 1505 cm^{-1} are attributed to thiazoline ring vibration (Table 6).

The ^1H NMR data of uncomplex and diamagnetic complexes [18-20] have been listed in Table 7. The δOH (~12.02 ppm) and δNH (4.18 ppm) proton signals are present in the ligand. These signals disappear upon addition of D_2O .

The phenyl protons are observed in the region $\delta 6.53$ – 7.24 ppm and proton due to –CH shows a marked downfield shift on complex

Cyclic form (A)				Schiff base form (B)			
Bond angles (°)		Dihedral angles (°)		Bond angles (°)		Dihedral angles (°)	
H29-C15-C16	119.758	C17-N18-C19-C9	118.396	H32-S20-C19	110.219	N13-C14-C19-C18	179.992
H29-C15-C14	119.848	N18-C19-C9-C8	133.06	H31-C18-C19	121.254	N13-C14-C15-C16	179.965
C16-C15-C14	120.394	C2-C10-O11-H26	101.723	H31-C18-C17	117.264	C14-C19-S20-H32	72.327
H28-C14-C15	119.635	C13-C12-C17-N18	179.608	C19-C18-C17	121.482	C15-C14-N13-C12	179.713
H28-C14-C13	119.694	C19-N18-C17-C16	178.568	H30-C17-C18	120.731	C9-C12-N13-C14	179.955
C15-C14-C13	120.67			H30-C17-C16	120.43	C8-C9-C12-N13	179.933
H30-C16-C17	120.688			C18-C17-C16	118.839		
H30-C16-C15	120.399			H29-C16-C17	120.014		
C17-C16-C15	118.912			H29-C16-C15	120.512		
C12-C17-N18	115.06			C17-C16-C15	119.474		
C12-C17-C16	120.83			C14-C19-C18	120.752		
N18-C17-C16	124.11			C14-C19-S20	127.244		
H27-C13-C14	119.24			C18-C19-S20	112.005		
H27-C13-C12	121.781			H28-C15-C16	116.104		
C14-C13-C12	118.979			H28-C15-C14	120.762		
C17-C12-C13	120.214			C16-C15-C14	123.134		
C17-C12-S20	114.008			C19-C14-C15	116.32		
C13-C12-S20	125.777			C19-C14-N13	132.385		
C12-S20-C19	97.185			C15-C14-N13	111.295		
H31-N18-C17	122.202			C14-N13-C12	131.33		
H31-N18-C19	123.005			H27-C12-N13	117.554		
C17-N18-C19	114.764			H27-C12-C9	116.044		
H32-C19-S20	109.889			N13-C12-C9	126.402		
H32-C19-N18	107.338			H26-O11-C10	109.471		
H32-C19-C9	113.911						
S20-C19-N18	98.942						
S20-C19-C9	113.811						
N18-C19-C9	111.791						
H26-O11-C10	109.399						

Table 2: Bond angles and dihydral angles for the cyclic form and Schiff base form.

Atom	Charges	
	Cyclic form (A)	Schiff base form (B)
N3	-0.62	-0.62
N18	-0.8691	-
O11	-0.5325	-0.5325
N 13	-	-0.629
S20	-0.3315	-0.2815

Table 3: Net charges on active centers of the cyclic form and Schiff base form.

formation.

By heating the cyclic form (A) (Scheme 1) at $\geq 210^\circ\text{C}$ an intense-orange yellow crystalline compound is formed, that was supposed to be due to the transformation in 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (D) (Scheme 1) by the loss of a hydrogen molecule from it.

Four significant changes in the IR spectrum of the complexes were observed: (i) the band due to $\nu(\text{NH})$ mode is absent; (ii) three strong bands at 1504, 1436 and 1397 cm^{-1} , and two bands of medium intensity at 1387 and 1530 cm^{-1} (benzene and thiazol ring vibrations) [30,31]; (iii) a strong band at 828 cm^{-1} assignable to the C-S-C linkage; (iv) the $\nu\text{C}=\text{N}$ band is observed in the oxidized product at 1595 cm^{-1} . In the electronic spectrum of the ligand, two bands are observed at ~ 39850 and 28580 cm^{-1} . They are fully support the typical spectrum of cyclic form of benzothiazoline and may be attributed to $\sigma\text{-}\sigma^*$ and $\pi\text{-}\pi^*$ benzenoid transitions. The position of this band remains unchanged with pH. On the other hand, in the corresponding complexes, an additional band

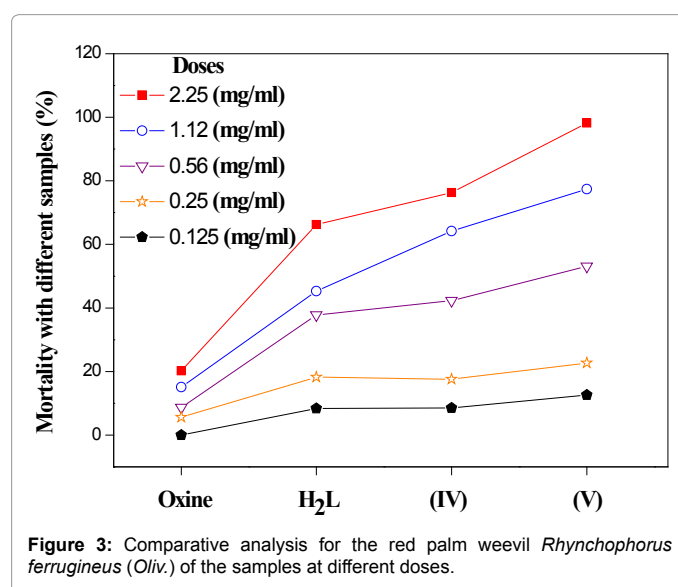


Figure 3: Comparative analysis for the red palm weevil *Rhynchophorus ferrugineus* (Oliv.) of the samples at different doses.

around $\sim 24400 \text{ cm}^{-1}$ is also observed. This new band may be assigned to either $n\text{-}\pi^*$ transitions [7,32] or $\pi\text{-}\pi^*$ transition [7,32] of the double of the azomethine group.

Rearrangement of the ligand in the presence of metal ions

The reaction of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-

Compound	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	ΔE (a.u.)	χ (a.u.)	η (a.u.)	σ (a.u.) ⁻¹	Pi (a.u.)	S (a.u.) ⁻¹	ω (a.u.)	ΔN_{max}
Cyclic form (A)	-0.211	-0.092	0.119	0.151	0.059	16.731	-0.151	8.365	0.192	2.532
Schiff base form (B)	-0.231	-0.148	0.083	0.189	0.042	24.041	-0.189	12.021	0.095	4.558

Table 4: The calculated quantum chemical parameters for H₂L.

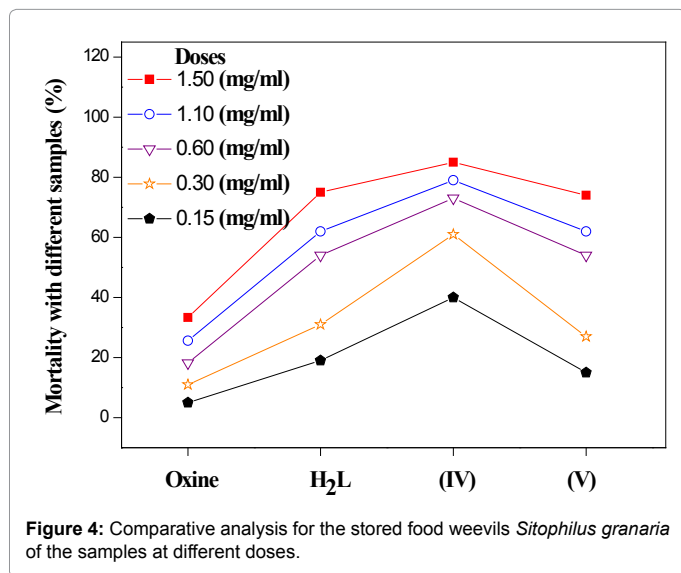


Figure 4: Comparative analysis for the stored food weevils *Sitophilus granaria* of the samples at different doses.

Complex ^a	Found (Calc.)%			
	C	H	N	S
[Cd(L)(OH ₂) ₂] (I)	47.1 (47.0)	3.0 (2.9)	7.2 (6.9)	7.0 (7.8)
[Zn(L)(OH ₂) ₂] (II)	53.1 (53.1)	3.2 (3.3)	8.1 (7.8)	9.1 (8.9)
[Zr(L)Cl ₂] (III)	(41.7) 41.8	2.6 (2.7)	5.8 (6.1)	6.8 (7.0)
[Cu(L)(OH ₂) ₂] (IV)	53.7 (53.8)	3.5 (3.4)	8.3 (7.9)	8.7 (9.0)
[Ni(L)(OH ₂) ₂] (V)	48.8 (48.9)	3.6 (3.6)	6.9 (7.1)	7.8 (8.1)
[Co(L)(OH ₂) ₂] (VI)	48.9 (48.9)	3.5 (3.6)	7.4 (7.1)	8.4 (8.1)

Table 5: Microanalytical data of the complexes. ^aMicroanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes [for molecule structures see Schemes 2-4].

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{Aromatic vib.})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
H ₂ L ^b	c	-	1272	-	-	-
(I)	1585	1508, 1464	1274	360	510	450
(II)	1583	1508, 1456	1270	365	515	455
(III)	1577	1509, 1458	1273	363	518	460
(IV)	1575	1510, 1460	1275	1370	520	410
(V)	1572	1512, 1462	1340	1375	525	465
(VI)	1574	1512, 1459	1344	1377	528	463

Table 6: Characteristic IR bands (cm⁻¹) of the Schiff base and its metal complexes^a. ^aThe serial number corresponds to that used in Table 5. ^b $\nu(\text{C}-\text{S}-\text{C})$ link. vib. = 828 cm⁻¹, ^cCyclic form.

ol (H₂L) with the metal ions investigated in this work are invariably accompanied with the opening of the thiazoline ring and the rearrangement of the ligand to the Schiff base 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (B) (Scheme 1). Thus the complexes obtained were of the form [M(L)(OH₂)_n] (where M=Cd, Zn, Cu at n=1;

Compound	-OH	-C ₆ H ₄
Scheme 1 A	12.02	6.53-7.24
(I)	12.12	6.33-7.44
(II)	11.92	6.30-7.46

Table 7: ¹H NMR data of ligand^a and its complexes^a. ^aThe serial number corresponds to that used in Table 5. ^{*}No signals even weak, of the open ring tautomer (Scheme 1B) can be detected. Note: NH proton signal is observed at 4.18 ppm (Scheme 1A).

M=Co, Ni at n=2) and [Zr(L)(Cl)₂]. L stands for the conjugate anion of the Schiff base (H₂L) (B).

Reaction of a solution of (A) in DMF:Ethanol (2:1) with M(CH₃COO)₂ (M=Zn or Cd), ZrCl₄ and MCl₂ (M=Cu, Co, Ni) with stirring at room temperature yields a dark crystalline complexes (Schemes 2-4). The IR spectra of this complexes show absorptions at ~1590, 1510 and 1460 cm⁻¹ (Table 6) which can be ascribed to imine and aromatic ring vibrations. On the other hand, no C-S-C linkage band (characteristic of the closed ring structure) appears. These results indicate that the metal complexes of the tautomeric Schiff base were obtained.

Important IR bands of the ligand and the complexes have been compared in order to find out bonding sites of the ligand. A broad and strong band at 3360–3060 cm⁻¹, attributable to νOH and/or νNH disappears altogether in the complexes, indicating bond formation between metal and phenolic oxygen atom after deprotonation. This is also supported by the disappearance of a series of bands in the vicinity of 2960 cm⁻¹ due to intramolecular hydrogen bonding (Scheme 1) [11,13,33]. However, new bands appear at ~1595, ~3430, and 795–815 cm⁻¹, possibly due to $\nu\text{C}=\text{N}$, $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$ of the coordinated azomethine and water molecules in the complexes. The disappearance, in the spectra of all complexes of a peak due to $\nu(\text{S}-\text{H})$, indicates the deprotonation of thiolic proton on complex formation [34]. The participation of phenolic oxygen and thiolic sulphur in coordination to the metal ion is further supported by an upward shift [34] in $\nu(\text{C}-\text{O})$ (phenolic) to extent of 20–30 cm⁻¹ and a downward shift [17-19,34] in $\nu(\text{C}-\text{S})$ in all the complexes. The major shift of $\nu(\text{C}-\text{O})$ (phenolic) to higher energy by ~30 cm⁻¹ in the case of Ni(II) and Co(II) complexes certainly indicates the presence of phenoxo bridge [35]. The new medium to strong absorption bands at 510–530, 440–470, 360–385 and ~300 cm⁻¹ are assigned to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{S})$ and $\nu(\text{Zr}-\text{Cl})$ modes [36], respectively.

Taking into consideration the previous reports [37] we have attributed a band of medium intensity appearing around 290 cm⁻¹ to $\nu(\text{Zr}-\text{Cl})$ vibration. The appearing of only one medium intensity band in the above region makes us to corroborate that chlorine atoms in the complex occupy the Trans position. The ligand acts as tridentate and dibasic coordinating to the metal atom via the nitrogen atom of the azomethine group, sulphur and oxygen atoms of thiazoline as evidenced by their spectral data.

Magnetic moments

The magnetic moments of the complexes (Table 8) were measured at room temperature. On the basis of the magnetic and spectral evidence

Complex	Band Position (cm ⁻¹)	Assignment	Dq (cm ⁻¹)	B (cm ⁻¹)	β	u ₂ /u ₁	LFSF (KJmol ⁻¹)	μ _{eff.} ^b (B.M)	Geometry
IV	-	-	1960.6	-	-	-	140.71	1.92	Tetrahedral
V	9520	³ A _{2g} → ³ T _{2g} (F)	952.2	966	0.92	1.72	136.7	3.1	Octahedral
	16390	³ A _{2g} → ³ T _{1g} (F)							
	26665	³ A _{2g} → ³ T _{1g} (P)							
VI	8695	⁴ T _{1g} → ⁴ T _{2g} (F)	869.5	819.3	0.84	1.97	83.2	4.46	Octahedral
	17100	⁴ T _{1g} → ⁴ A _{2g} (F)							
	21270	⁴ T _{1g} → ⁴ T _{1g} (P)							

Table 8: Electronic spectral bands, assignments ligand field parameters for complexes^a. ^aThe serial number corresponds to that used in Table 5. ^bPer metal ion and measured at room temperature

Complex	g	g _⊥	g _{iso}	A ^b	A _⊥	G	f	K	K _⊥	α ²
IV	2.41	2.07	2.19	168	25	5.7	143	0.64	0.53	0.98

Table 9: ESR parameter of Cu(II) complexa. ^aThe serial number corresponds to that used in Table 5. ^bHyperfine parameters are given in 10 cm⁻¹.

the Cu(II) complex shows the presence of one unpaired electron (1.92 B.M.). The relatively higher 1.92 B.M. value seems to suggest the relatively high tetrahedral distortion from square planar geometry.

Electron spin resonance

The ESR spectrum of solid Cu(II) complex at room temperature is characteristic of a monomer, d⁹, configuration. The ESR spectrum shows g_{||}>g_⊥>2.0023, suggesting a d_{x²-y²} ground state, which is characteristic of a tetrahedral geometry [24]. The g-values are related by the expression [24], G=(g_{||}-2)/(g_⊥-2). If G<4.0, significant exchange is present. Copper(II) complex shows G>4.0, indicating the presence of distribution from square planar towards tetrahedral configuration.

The g-values of Cu(II) complex with a ²B_{1g} ground state (g_{||}>g_⊥) may be expressed [24,38] by:

$$g_{||} = 2.0023 - (8K_{||}^2 \lambda_o / \Delta E_{xy}) \quad (9)$$

$$g_{\perp} = 2.0023 - (2K_{\perp} \lambda_o / \Delta E_{xz}) \quad (10)$$

where K_{||} and K_⊥ are the parallel and perpendicular components respectively of the orbital reduction factor (K). λ_o is the spin-orbit coupling constant for the free copper. ΔE_{xy} and ΔE_{xz} are the electron transition energies of ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_g. From the above relations, the orbital reduction factor (K_{||}, K_⊥, K), which are a measure of covalency [24,38] can be calculated. For an ionic environment, K=1 and for a covalent environment K<1, the lower the value of K, the greater is the covalent character. Kivelson and Neiman [39] noted that, for an ionic environment, g_{||}>2.3 and for a covalent environment g_{||}<2.3. Approximate metal-ligand σ-bond coefficients (α²), which is defined as the fraction of unpaired electron density located on the copper ion, for this complex was, calculated (Table 9). The empirical factor f=g_{||}/A_{||} cm⁻¹ value was considered as a diagnostic of stereochemistry. The g_{||}/A_{||} cm⁻¹ value (Table 9) shows that the complex (IV) has a tetrahedral geometry, and this is further confirmed by the Symons plot [40].

The electronic spectrum of Co(II) complex showed three absorption bands which may be attributed to the three spin-allowed transitions 8695 cm⁻¹ [⁴T_{1g}(F) → ⁴T_{2g}(F)(v₁)], 17100 cm⁻¹ [⁴T_{1g}(F) → ⁴A_{2g}(F)(v₂)] and 2127 cm⁻¹ [⁴T_{1g}(F) → ⁴T_{1g}(v₃)]. Ni(II) complex exhibited three intense bands which are assigned to 9520 cm⁻¹ [³A_{2g}(F) → ³T_{2g}(v₁)], 16390 cm⁻¹ [³A_{2g}(F) → ³T_{1g}(F)(v₂)] and 26665 cm⁻¹ [³A_{2g}(F) → ³T_{1g}(P)(v₃)] transition [41].

The ligand field parameters like ligand field splitting energy (10Dq),

Racah inter-electronic repulsion parameter (B), covalent factor (β) and ligand field stabilization energy (LFSE) has been calculated [42] and values compiled in Table 8. The calculated Dq and CFSE values of all complexes except Zr(III), Zn(II) and Cd(II) complexes, as well as the B and β-values have been calculated only for Co(II) and Ni(II) complexes following standard equation [42,43]. The B-values are lower than the free ion values, thereby indicating the orbital overlap and delocalization of d-orbitals. The β-values obtained are less than unity commensurate considerable amount of covalent character of the metal-ligand bands [42,43].

Stereochemistry of zirconyl complex

All these observation were taken together with the wide range of coordination numbers ranging from four to eight, envisages that in the complex (III) exhibit coordination number five.

However, it is known from the available data that the complex (III) belonging to d⁰, d⁸ and d¹⁰ systems have trigonal bipyramidal configuration and only a few have square pyramidal configuration. In view of this finding for the zirconium complex it may be suggested that this complex may exist in trigonal bipyramidal structure.

Thermal analysis

The temperature range for the dehydration process shows a strong relationship with the binding mode of the water molecules of the respective metal complexes. The elimination of water occurs in two steps. The first step can be attributed to the release of the hydration water molecules in the temperature range 45-55°C [44]. In the second step, except for the complex (III), all complexes lose coordinated water at temperature 130-145°C [27,44]. The thermal decomposition of the anhydrous complexes starts in the temperature range 330-370°C and is complete at temperature 560-750°C. The final decomposition products are metal oxides [13,27]. As results of the dehydration and decomposition, the observed weight losses for all complexes are in good agreement with the calculated values.

Effect of compounds on the red palm weevil *Rhynchophorus ferrugineus* (Oliv.)

Listed data in Table 10 concluded that the different novel compounds have been produced lethal effect on the newly emerged adult of the red palm weevil *Rhynchophorus ferrugineus*. The highest mortality was 98.2%, which obtained due to effect of complex (V). Synchronize the lower percent mortality was 5.2% after treatment adult

Doses mg/ml	Mortality with different samples (%)			
	Oxine	H ₂ L	(IV)*	(V)*
2.25	20.2	66.2	76.3	98.2
1.12	15.1	45.3	64.2	77.4
0.56	8.7	37.8	42.3	53.1
0.25	5.6	18.2	17.6	22.7
0.125	-	8.4	8.5	12.6
Control	-	-	-	-

Table 10: Effect of some new biologically active chemical compounds on the red palm weevil *Rhynchophorus ferrugineus* (Oliv.). *The serial number corresponds to that used in Table 5.

Doses mg/ml	Mortality with different samples (%)			
	Oxine	H ₂ L	(IV)*	(V)*
1.5	33.3	75	85	74
1.1	25.6	62	79	62
0.6	18.2	54	73	54
0.3	11	31	61	27
0.15	5	19	40	15
Control	-	-	-	-

Table 11: Effect compounds on the stored food weevils *Sitophilus granaria*. *The serial number corresponds to that used in Table 5.

with the compound oxine with concentration 0.25 mg/ml. Meanwhile the higher dose (2.2 mg/ml) was produced 20.2, 66.2 and 76.3% of adult mortality after adult was treated with the novel compounds oxine, H₂L and complex (IV) respectively. On the other hand the adult mortality was dose dependent, where the mortality percent was increased by increasing dose. In descending order of toxicity the novel compounds were (V), (IV) complexes, H₂L, and oxine, respectively.

The mode of action of these compounds was neurotoxin effect on the nerve cells of the red palm weevil, *Rhynchophorus ferrugineus*.

Comparative analysis for the red palm weevil *Rhynchophorus ferrugineus* (Oliv.) of the samples by using five doses are shown in Figure 3, it is observed that the complex (V) was more biologically active chemical than the other compounds. So it can be concluded that the some complexes exhibits higher biologically active chemical than the free ligand [45].

Effect of compounds on the stored food weevils *Sitophilus granary*

The recorded results in Table 11 revealed that different mortality percentage were occurred after adult treatment with other doses from the different novel compounds. Where the higher percent of adult mortality was 33.3, 75.0, 85.0, 74% after adult was treated with dose 1.6 of oxine, H₂L, complex (IV) and complex (V), respectively. The lower adult mortalities were 5.0, 19.0, 42.0, 40.0 and 15% when adult of weevil was treated with the doses, 0.15 mg/ml by the same previous novel compounds, respectively. In order of toxicity effect in descending manner the chemical compounds were (IV) followed by H₂L, complex (V) and finally oxine.

Many of the new chemical the mode of action of these compounds was neurotoxin effect on the nerve cells of the weevil, *Sitophilus granaria*.

Comparative analysis for the stored food weevils *Sitophilus granaria* of the samples by using five doses are shown in Figure 4, it is observed that the complex (IV) was more biologically active chemical than the other compounds.

Conclusions

In this work, synthesis and characterization of 7-(2,3-dihydro-1,3-benzothiazol-2-yl)quinolin-8-ol (H₂L) and its Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Zr(IV) complexes have been isolated and characterized. The analytical and physicochemical analysis confirmed the composition and the structure of the newly obtained compounds. The results obtained can be summarized as follows:

- Elemental analysis, IR and molar conductivity data are used to proof the stoichiometry and formulation of the complexes. All complexes are 1:1 (metal:ligand) stoichiometry and except (I)-(III), the H₂O molecule(s) are coordinated to the metal ion. The data suggest that the Co(II) and Ni(II) complexes are binuclear and octahedral dimmers, while the rest are monomeric with square planar/tetrahedral geometries, based on the magnetic data, spectral (ESR and visible) and thermal studies.
- The molecular and electronic structures of the investigated ligand (H₂L) [cyclic form (A) and the Schiff base form (B)] have been discussed.
- It was found that the Schiff base form (B) more reactive than cyclic form (A).
- The spectral studies of the isolated complexes showed that the rearrangement of the benzothiazoline to the Schiff base had occurred.
- ESR calculations support the characterization of the structures of the complexes geometries.
- The lowest mortality was 5.6% which obtained due to effect of oxine after adult was treated with dose of 0.25 mg/ml.

The mode of action of these compounds was neurotoxin effect on the nerve cells of the red palm weevil, *Rhynchophorus ferrugineus*.

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