Twenty eight novel Schiff base metal complexes: A toxicity study with potato tuber moth, *Phthormaea operculella* Zeller, larvae

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الخلاصة

قدرت سميات ثمانية وعشرين مركبا جديدا من المعقدات الفلزية لقواعد شيف ليرقات عثة درنات البطاطا *Phthormaea operculella* Zeller بتعريض يرقات الأعمار الأول والثاني والثالث والرابع كل على انفراد لشرائح بطاطا (قطر ٢.٥ سم وسمك ٠.٢٥ سم) معاملة في أطباق بتري قطر (٢.٥سم). استخدمت مبيدات الحشرات التراسيدين ودلتاماك وسيفن كمركبات قياسية للمقارنة . بينت النتائج ان كل م عقدات قواعد شيف المختبرة سامة بتراكيز معقولة لقتل اليرقات وان بعضها أكثر سمية من البعض الآخر . وبشكل عام تناقصت سمي ة الم‍عقدات مع تعاقب العمر اليرقي. وبينت النتائج أيضاً ان أكثر من نصف ونصف وربع المركبات كانت ذات سمية مساوية أو أكثر سمية من الالتراسيدين ودلتاماك وسيفن على التوالي . وعزيت سمية قواعد شيف الفلزية لليرقات – ولو جزئياً – إلى تطابقها مع موقع التأثير . وللتحقق من فا علية أكثر هذه المركبات سمية كوسائل للمكافحة ينصح بإجراء اختبارات إضافية مختبرية وحقلية مع هذه الحشرة و / أو حشرات أخرى.

Abstract

The toxicities of twenty-eight novel Schiff base metal(II) complexes to potato tuber moth (PTM), ***Phthormaea operculella*** Zeller, larvae were determined by separately exposing 1st, 2nd, 3rd, and 4th instar larvae to treated potato slices in 2.5 cm dia Petri deshis. The insecticides Altracidin, Deltamac, and sevin were used as standards for comparisons. All Schiff base complexes tested were toxic at levels practical for PTM larvae control. However, some of them were much more toxic than others and generally, their toxicities decreased in successive instars. More than 1/2, 1/2, and 1/4 of the complexes were as or more effective than Ultracidin, Deltamac, and Sevin, respectively.The toxicity of the complexes tested could be attributed,at least in part, to their complimentarity with the site of action. Further laboratory and field tests are highly recommendded to fully assess the effectiveness of the most effective complexes as controls for PTM and/or other insects.

Key words: Toxicity, Schiff base metal complexes, potato tuber moth, larvae

Introduction

Insecticides have played a vital role in preventing or reducing the damages caused by most economically important insect pests and for the foreseeable future, they will remain the main weapons of defenses against insect pests. Owing to the problems of residues and resistance most of the existing insecticides can no longer be recommended for insect control in warehouses. Thus, the need of and the search for safer alterna-tive chemicals with a mode of action different from those of conventional insecticides has become imperative, to maintain desired level of insect pest control. Therefore, research groups have made strong efforts to evaluate novel compounds with insecticidal properties. Numerous authors have noted that various metal complex derivatives of Schiff bases possess strong insecticidal properties against representative insect species in the order Lepidoptera, Coleopteran and Orthoptera (Douglas and Pankaja, 1988); American cockroach, *Periplaneta Americana* (Siddiqi et al., 1988; Rajesh and Sanjay, 2003); eggs, larvae, and adult khapra beetle, ***Trogoderma granareum*** (Mukta); and flea (Sanath et al., 2006). However, non of the previous studies has included a comparison of the responses to Schiff base metal complexes versus any of the currently in use insecticides.

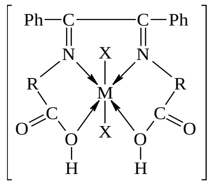
The present study is carried out in the laboratory to evaluate the toxicities of twenty eight novel Schiff base metal complexes to the larvae of potato tuber moth (PTM), ***Phthormaea operculella*** Zeller. Sevin, Deltamac, and Ultracidin, which are recognized as effective insecticides for insect control are included in the study for comparison purpose.

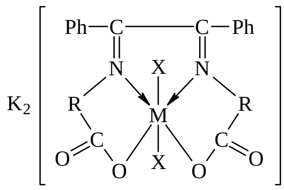
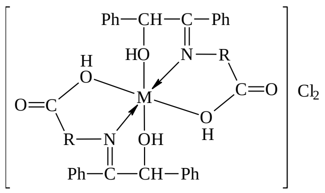
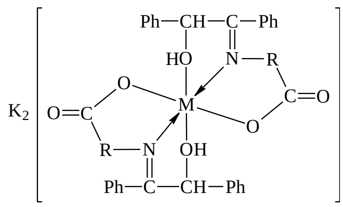
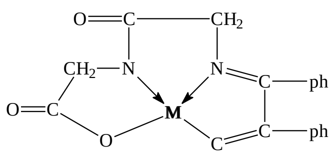
Materials and Methods

Chemicals

The nomenclature and structure of the 28 Schiff base metal complexes examined are given in Figure 1. These compounds were synthesized by the third author (Al-Shaheen, 1998, 2000, 2001, 2004). Samples used in this study were of purity greater than 98%. The insecticides Ultracidin (Methidathion®) 40% EC, Carbaryl (Sevin®) 85% WP, and Deltamac (Deltamethrin®) 2.5% EC were included in the study for comparison purposes. An aqueous stock solution of each compound was prepared. Dilutions were made with distilled water to obtain the amount of compound (1,2,3,4, and 5 μl of Ultracidin and Deltamac and 1,2,3,4 and 5 μg of Sevin and the Schiff base metal complexes/potato slice) needed in 250 μl aliquots. A glass microsyringe was used to dispense the solution evenly on the surface of each potato slice (Ca. 2.4 cm dia. and 0.25 cm thick).

Figure 1: Chemical formula and chemical name of the Schiff base metal complexes used in this study



Comp. No.	Chemical formula	R	X	M	Chemical Name
I	$C_{18}H_{16}O_4N_2CoCl_2$	CH_2	Cl	Co	Dichlorobenzilidene diglycine cobalt (II)
II	$C_{22}H_{24}O_4N_2NiCl_2$	$(CH_2)_3$	Cl	Ni	Dichlorobenzilidene dibutyric acid nickel (II)
III	$C_{22}H_{24}O_4N_2CuCl_2$	$(CH_2)_3$	Cl	Cu	Dichlorobenzilidene dibutyric acid copper (II)
IV	$C_{24}H_{24}O_4N_2CoCl_2$	$CH(CH_2)_2CO_2H$	Cl	Cu	Dichlorobenzilidene diglutamic acid copper (II)
V	$C_{24}H_{24}O_{10}N_4Ni$	$(CH_2)_3$	NO_3	Ni	Dinitratobenzilidene dibutyric acid nickel (II)
VI	$C_{22}H_{24}O_{10}N_4Co$	$(CH_2)_3$	NO_3	Co	Dinitratobenzilidene dibutyric acid cobalt (II)
VII	$C_{18}H_{16}O_4N_2NiCl_2$	CH_2	Cl	Ni	Dichlorobenzilidene diglycine nickel (II)
					
VIII	$K_2C_{18}H_{16}O_4N_2CoCl_2$	CH_2	Cl	Co	Potassium dichlorobenzilidene diglycinato cobalt (II)
IX	$K_2C_{22}H_{22}O_4N_2NiCl_2$	$(CH_2)_3$	Cl	Ni	Potassium dichlorobenzilidene dibutyrato acid nickelate(II)
X	$K_2C_{22}H_{22}O_4N_2CuCl_2$	$(CH_2)_3$	Cl	Cu	Potassium dichlorobenzilidene dibutyrato acid copprate(II)
XI	$K_2C_{24}H_{22}O_8N_2CuCl_2$	$CH(CH_2)_2CO_2H$	Cl	Cu	Potassium dichlorobenzilidene diglutamato acid cuppate(II)
XII	$K_2C_{22}H_{22}O_{10}N_4Ni$	$(CH_2)_3$	NO_3	Ni	Potassium dinitratobenzilidene dibutyrato acid nickelate (II)
XIII	$K_2C_{22}H_{22}O_{10}N_4Co$	$(CH_2)_3$	NO_3	Co	Potassium dinitratobenzilidene dibutyrato acid cobaltate (II)
XIV	$K_2C_{18}H_{14}O_4N_2NiCl_2$	CH_2	Cl	Ni	Potassium dichlorobenzilidene diglycinato nickelate (II)
					
XV	$C_{32}H_{30}N_2O_6CoCl_2$	CH_2	-	Co	Dichloro bis(benzoinlidene glycine) cobalt (II)
XVI	$C_{32}H_{30}N_2O_6NiCl_2$	CH_2	-	Ni	Dichloro bis(benzoinlidene glycine) nickel (II)
XVII	$C_{32}H_{30}N_2O_6CuCl_2$	CH_2	-	Cu	Dichloro bis(benzoinlidene glycine) copper (II)
XVIII	$C_{36}H_{38}N_2O_6CoCl_2$	$(CH_2)_3$	-	Co	Dichloro bis(benzoinlidene butyric acid) cobalt (II)
XIX	$C_{36}H_{38}N_2O_6NiCl_2$	$(CH_2)_3$	-	Ni	Dichloro bis(benzoinlidene butyric acid) nickel (II)
XX	$C_{36}H_{38}N_2O_6CuCl_2$	$(CH_2)_3$	-	Cu	Dichloro bis(benzoinlidene butyric acid) copper (II)
					
XXI	$K_2C_{32}H_{26}N_2O_6Co$	CH_2	-	Co	Potassium bis(benzoinlidene glycinato) cobaltate (II)
XXII	$K_2C_{32}H_{26}N_2O_6Ni$	CH_2	-	Ni	Potassium bis(benzoinlidene glycinato) nickelate (II)
XXIII	$K_2C_{32}H_{26}N_2O_6Cu$	CH_2	-	Cu	Potassium bis(benzoinlidene glycinato) copperate (II)
XXIV	$K_2C_{36}H_{34}N_2O_6Co$	$(CH_2)_3$	-	Co	Potassium bis(benzoinlidene butyrato acid) cobaltate (II)
XXV	$K_2C_{36}H_{34}N_2O_6Ni$	$(CH_2)_3$	-	Ni	Potassium bis(benzoinlidene butyrato acid) nickelate (II)
					
XXVI	$C_{18}H_{14}O_4N_2Co$	-	-	Co	(Benzoinlidene glycinato) cobalt (II)
XXVII	$C_{18}H_{14}O_4N_2Ni$	-	-	Ni	(Benzoinlidene glycinato) nickel (II)
XXVIII	$C_{18}H_{14}O_4N_2Cu$	-	-	Cu	(Benzoinlidene glycinato) copper (II)

Larvae of PTM ***P. operculella*** Zeller, used in the study were obtained from laboratory cultures reared individually on potato tubers at room temperature (22-26°C). Batches of 10 1st, 2nd, 3rd and 4th instar larvae were separately confined on treated potato slices in 2.5 cm dia. glass Petri deshis. At least three replicates were tested per concentration. The control larvae were similarly confined on untreated slices (distilled water only). After 24 hr the replicate batches were examined under low-powered microscope and the number of dead larvae was scored. A larvae was considered dead if it did not move after being prodded.

Data were corrected for control mortality with Abbott's (1925) formula. Data were then used to calculate concentration mortality lines by the method of Litchfield and Wilcoxon (1949) method.

Results and Discussion

Table 1 shows the toxicity of the Schiff base metal complexes and the three insecticides to the four instars PTM larvae. Although all the Schiff base complexes examined are toxic to the larvae, some are much more toxic than others. Generally speaking, the Dichloro or Dintrato-benzilidene diamino acid metal (II) analogues (I-VII) are as toxic to the larvae as the potassium dichloro or Dinatrato-benzilidene diamino acid metal (II) analogues (VIII-XIV). With the exception of complexes XV and XVIII in the Dichloro-bis(benzoinlideneaminoacid) metal (II) analogues (XV-XX), compound XXI in the potassium bis(benzoinlidene amino acidato) metal (II) analoques (XXI-XXV), and complex XXVI in the benzoinlidene glycylglycinato metal (II) analogues, which were as toxic as the aforementioned complexes, the remaining complexes are much less toxic (Table 1).

Table 1 : Toxicity of 28 Schiff base metal complexes and 3 insecticides to the larvae of potato tuber moth at 24h in the laboratory

	LC50 µg/ps					LC50 µg/ps			
	Larval instar					Larval instar			
Comp. No.	**1st**	**2nd**	**3rd**	**4th**	**Comp. No.**	**1st**	**2nd**	**3rd**	**4th**
I	0.7	1.1	1.4	1.6	**XVII**	1.7	2.0	2.3	2.5
II	1.8	2.3	2.7	3.0	**XVIII**	1.0	1.1	1.3	1.7
III	1.2	1.8	2.2	2.5	**XIX**	2.0	2.5	3.0	3.6
IV	1.1	1.5	1.8	2.3	**XX**	1.8	2.3	2.7	3.2
V	2.0	2.5	3.1	3.7	**XXI**	1.0	1.3	1.5	1.8
VI	0.9	1.5	1.9	1.9	**XXII**	2.1	2.9	3.6	4.2
VII	1.6	2.0	2.4	2.8	**XXIII**	2.4	3.5	4.6	5.5
VIII	0.8	1.3	1.5	1.8	**XXIV**	1.5	1.8	2.0	2.3
IX	2.3	2.6	3.1	3.9	**XXV**	3.5	4.5	5.1	5.8
X	1.5	1.5	1.7	2.1	**XXVI**	1.3	1.8	2.1	2.3
XI	0.9	1.5	1.7	2.0	**XXVII**	3.8	4.5	5.2	5.8
XII	2.1	2.5	2.8	3.0	**XXVIII**	3.5	4.0	5.2	5.4
XIII	0.6	0.9	1.2	1.5	**Sevin**	0.8	1.1	1.3	1.7
XIV	1.5	1.7	1.9	2.5	**Deltamac***	1.1	1.6	1.9	2.4
XV	1.0	1.3	1.3	1.5	**Ultracidine**	1.6	2.2	2.5	3.1
XVI	2.5	3.0	3.5	4.0					

The structure-activity relationship indicate specific requireme-nts for substituents on the amino acids for high activity. Maximum insect-icidal activity is associated with complex I where R is CH_2, X is Cl and M is Co(II); complex VI where R is $(CH_2)_3$, X is NO_3, and M is Co(II) complex VIII where R is CH_2, X is Cl^-, and M is Co(II) complex XI where R is $CH(CH_2)_2CO_2H$, X is Cl^- and M is Cu(II); complex XIII where R is $(CH_2)_3$, X is $N\bar{O}_3$ and M is Co(II); Complex XV where R is CH_2 and M is CO (II); Complex XVIII where R is $(CH_2)_3$ and M is CO(II); and complex XXI where R is CH_2 and M is Co(II); The most toxic complexes have LC_{50} values in the range of 0.6 to 2.0 μg/PS, while for the least toxic complexes these values ranged between 2 and 6 μg/PS. Two possible explanations exist for the high toxicity of the most toxic complexes: (1) these complexes could be more difficult for the larvae to metabolize or (2) there may be a structural difference at the site of action such that the most toxic complexes fit that site better than the less toxic ones. It would be logical to predict that complimentarity with the site of action is the more likely reason.

Base-line toxicity data, established by dosage-mortality regres-sion analyses, are used to compare the relative toxicity of 28 Schiff base metal complexes to the Ultracidin, Deltamac, and Sevin standards. The toxicity of each Schiff base metal complex to the larvae of each instar of PTM is compared with each insecticide by a toxicity index based on LC_{50} values (Sun, 1959). The toxicity index values indicated that complex XIII is only slightly more toxic; complexes I, VI, VIII, XI, XV, XVIII, and XXI are as toxic; complexes III, IV, and X are slightly less toxic; and the remaining 17 complexes are moderately to greatly less toxic than Sevin.

When compared with Deltamac complexes VIII, XVIII, and XXI are only slightly more toxic; complexes I, XII, and XV are modera-tely more toxic; complexes III, IV, VI, X, XI, XIV, XXIV and XXVI are as toxic; complexes XVII is only slightly less toxic, and the remaining 13 complexes are moderately to greatly less toxic. In comparison with the least toxic insecticide, Ultracidine, complexes XIV, XXI, XXIV, and XXVI are only slightly less toxic; complexes I, VI, VIII, XI, XIII, XV, and XVIII are moderately more toxic; complexes II, III, VII, XII, XVII and XX are as toxic; complexes IV, V, IX, X, XVI, XIX and XXI are only slightly less toxic and with the exception of complex XXIII the remaining complexes are greatly less toxic.

This study presents for the first time a comparison of the insecticidal activity of Schiff base metal complexes with well known effective insecticides (Sevin, Deltamac and Ultracidine). In the limited structure-activity relationship data obtained in the present study, it is observed that all the Schiff base complexes are toxic at levels which could be considered practical for controlling PTM larvae. Many of the complexes are as toxic or superior to the standard insecticides and show promise as practical insecticides.

In conclusion, our results show that many of the Schiff base complexes tested are of great potential as insecticides and it seems conceivable to assume that other insects are also affected. However, it should be noted that additional studies are necessary to assess their mammal toxicity. Generally, research on new compounds for insect control is becoming of growing interest in view of health hazard to man, environmental insecurity as well as occurrence of insect resistance accounting for conventional insecticides. Based on their great potential as insecticides, pest control programs using these complexes might be feasible and further laboratory and field tests with this and/or other insects are highly recommended in this respect.

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