



Synthesis, Characterization and Fungicide Activity of c-Substitutional Phenoxazine Complexs with Titanium (IV)

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Abstract

We report in this work the synthesis, characterization and fungicide activity of titanium (IV) complexes with Phenoxazine, (3, 7-disulfonylazide) 10H Phenoxazine, (3, 7-disulfonyl triphenyl phosphineimine) 10H Phenoxazine, (3, 7-disulfonyl trimethyl phosphineimine) 10H Phenoxazine and (3, 7-disulfonyl trimethylphosphiteimine).

To determine the ratio of M-L according to Job's method and to compare the fungicidal activity of complexes with ligand, the Phenoxazine derivatives have been reported to be biologically versatile compounds possessing biological activities.

الخلاصة

يهدف هذا البحث الى تحضير معقدات الفينوكسازين ومشتقاتها مع التيتانيوم الرباعي التكافؤ ودراسة نشاطها البيولوجي والطفيلي وقد تم تحضير خمسة معقدات عضوية-فلزية من التيتانيوم مع الفينوكسازين وهي (٧،٣-ثنائي سلفونيل ازيد) فينوكسازين وثلاث من (٧،٣-ثنائي سلفونيل فوسفين ايمين) فينوكسازين وقد تم قياس نسبة المعدن الى اللكند اعتمادا على طريقة جوبس. تمت مقارنة النشاط البيولوجي لهذه المعقدات مع النشاط البيولوجي للكند ووجد انها أعلى منه نشاطا.

Introduction

N-Alkylphenoxazine (NAP) have been reported to be biologically versatile compounds, possessing anticholinergic, antihistamine and antiamebic activities^{1,2}. It is known that the metal complexes have greater activity than the ligands themselves. In view of the importance of metal-phenoxazine complexes as fungicides, it was considered worthwhile to study the titanium (IV)-phenoxazine complexes.

Experimental

Melting points were determined using a Gallen Kamp melting point apparatus and are uncorrected. IR spectra (KBr disc) were recorded on a Pye-Unicam sp-300 and (FT-IR). The conductivity was recorded on (Orign Research) microprocessor ionanalyzer/901.

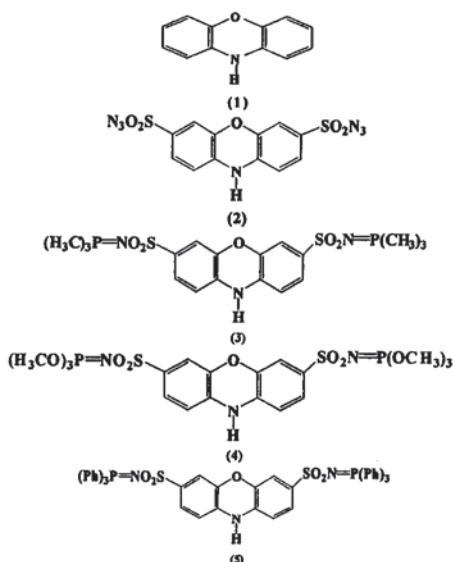
Synthesis of the complexes

Potassium titanyl oxalate dihydrate (1.3 gm, mole) dissolved in 50 mL distilled water, was added with vigorous stirring to a solution of C-

substituted Phenoxazine (1.7 gm, 1mole) in 60 mL distilled water. There was an immediate separation of solid complex. The suspension was set-aside for one hour, filtered washed several times with water and finally with ethanol and dried.

Antifungal studies

The Phenoxazine derivatives⁽¹⁻²⁾ and their corresponding complexes (prepared in 10% DMF) were tested against solution, *Escherichia-coli* and *Staphylocococcus-saureus* at different concentrations. The experiment was conducted by using neutral agar, and the solution of the ligand fungi *Escherichia-coli* and *Staphylocococcus-saureus* were taken in 2 mm dishes for 24 hrs. The incubation was carried out at 22 +2° for 24 hrs. The formula of complexes {Ti(C₂O₄)L}2H₂O; where L=C-substituted Phenoxazines and Phenoxazine



All these complexes possess high melting points. The complexes are insoluble in water and soluble in DMF and dimethyl sulfoxide. The molar conductance in DMF are in the range (10-12) $\text{ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$ at 10^{-3} m concentrations, indicating the non electrolytic nature of the complexes which could be assigned to the disappearance of ionic property the electrolyte complexes table (1).

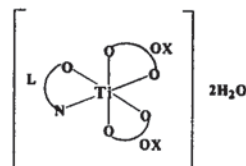
Table (1) values of molar conductivity of complexes

Complexes	$\Delta m (\Omega^{-1} \cdot \text{mole}^{-1} \cdot \text{cm}^2 \text{ in DMF})$
7	10.11
8	12.35
9	12.43
10	11.92
11	9.87

The electronic spectra⁽³⁻⁶⁾ of all complexes showed band in the region 441 nm, which may be assigned to charge-transfer with $(n-1) d^n$ electronic configuration of Titanium. The band at λ_{max} 239-310 nm found in the 3,7-disulfonyl

phosphineimine phenoxazine and the corresponding complexes may be attributed to $\pi \rightarrow \pi^*$ transition, the band found in the region 300-320 nm in the phosphineimine may be assigned to the $n \rightarrow \pi^*$ transition. This band is found slightly shifted toward higher energy region in the spectra of the corresponding titanium (IV)-disulfonyl phosphineimine complexes evidently due to coordination.

The toxicity of the complexes can be explained on the basis of chelation theory⁽⁷⁻⁹⁾. It has been suggested that the chelation reduces the polarity of the metal ion considerably because of the positive charge is partially shared with donor atoms and π -electron delocalisation over the lipophilic character of the metal chelate which favors its permeation through lipid layers of the fungus membrane.



Structure

The selected IR frequencies of titanium (IV) Phenoxazine complexes are given in table (2) showed a shift in the band attributed to the ligand themselves. This phenoxazine indicate that the metal coordinates with the (NH) of the phenoxazine nucleus, and show characteristic absorption bands in the region of $(1720-1679 \text{ cm}^{-1})$ asymmetric (COO) vibration bands due to ν (Ti-N) appeared $(520-550 \text{ cm}^{-1})$ and at $(320-350 \text{ cm}^{-1})$ for γ (Ti-O)⁽¹⁰⁾.

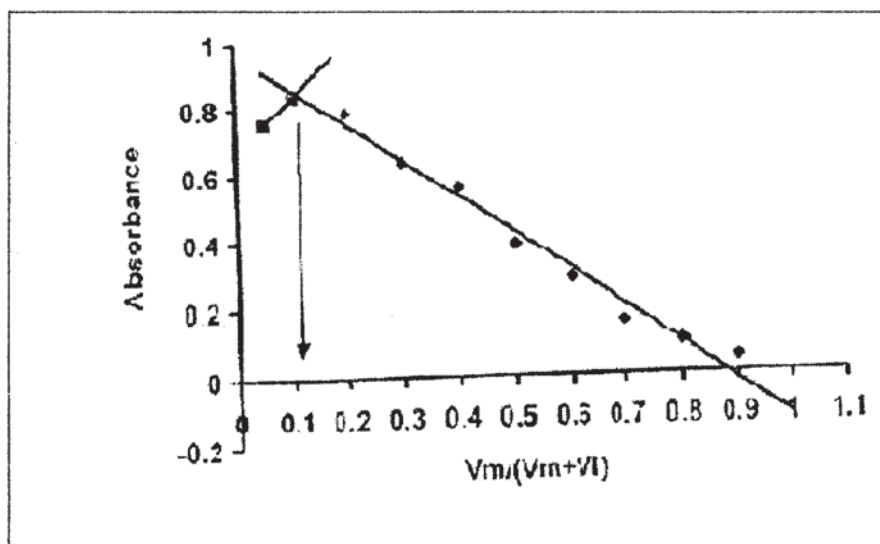
The IR-spectrum of complex (2) showed shifted band 2131 cm^{-1} to 2100 cm^{-1} due to (N_3) , while IR spectrum of (3,4,5) showed a shift for $(\text{P}=\text{N})$ group to lower wave number, that was indicate to the metal coordinates two stretching bands at 1368 cm^{-1} 1164 cm^{-1} due to SO_2 group.

Table (2) λ_{max} values ligands and Ti (IV) complexes.

Fig. No.	L	$\lambda_{\text{max}} \text{ L}$ 10^{-3} M	color	complexes	λ_{max} complexes Ti (IV)	color
1	1	239,318	colorless	7	224,302,402	Deep Yellow
2	2	310,441,523	Deep blue	8	301,437,518,851	Violet
3	3	309,436,540	Red	9	301,433,526,816	Violet
4	4	312	Yellow	10	306,404,529	Deep blue
5	5	292,364	Light Yellow	11	284,358,550	Deep blue

Table (3) characteristic infrared absorption bands in cm^{-1} of the complexes.

Complexes No.	$\nu\text{N-H}$ Phenoxazine	$\nu\text{C-H}$ Aromatic	$\nu\text{C-H}$ Aliphatic	$\nu\text{C}=\text{c}$ Aromatic	νSO_2 Asym Sym	$\nu\text{Ti-H}$	$\nu\text{Ti-O}$	νCOO	Other Bands
7	3393 M	3096 VW	-	1600 S		522 W	335 M	1713 S 1400 M	
8	3358 S	3085 VW	-	1599 M	1355 W 1160 W	532 M	323 M	1720 S 1390 S	(N ₃) 1100
9	3382 S	3080 M	-	1591 M	1368 M 1164 W	546 M	347 W	1710 S 1380 M	(N=P) 742, 1080, 1103
10	3375M	3092 W	2877 W 2939 M	1591 W	1331 M 1132 M	530 W	321 W	1675 M 1400 S	(N=P) 746, 1050, 1105
11	3284 S	3039 W	2875 W 2950 W	1598 M	1317 M 1163 W	523 W	325 W	1679 M 1392 M	(N=P) 754, 1050, 1113

Fig (1) Job's plot of [phenoxazine-Ti(IV)] complex at $\lambda_{\text{max}} = 600 \text{ nm}$

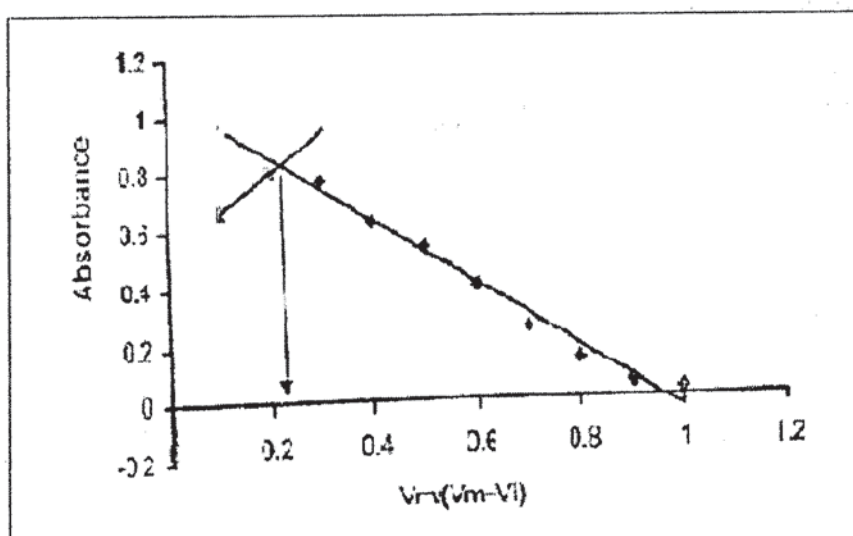


Fig (2) Job's plot of [3,7-disulfonyl azide-Ti(IV)] complex at $\lambda_{\max} = 600$ nm

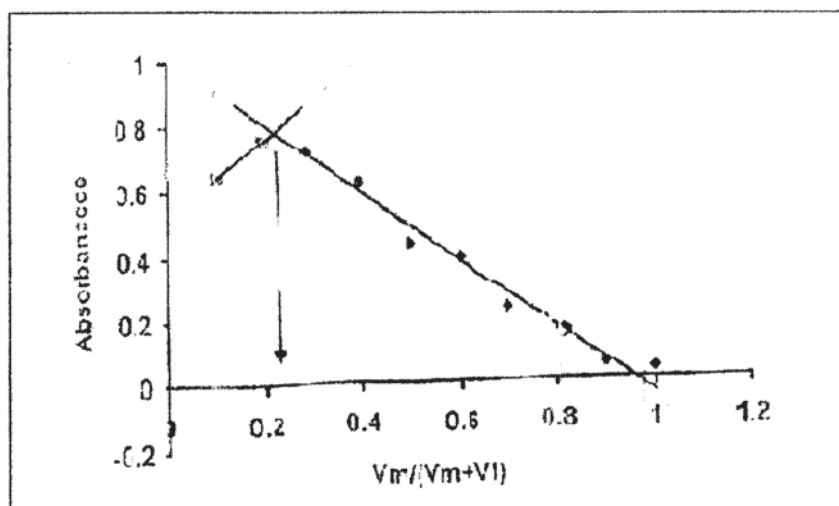


Fig (3) Job's plot of [3,7-disulfonyl phosphineimine-Ti(IV)] complex at $\lambda_{\max} = 600$ nm

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