E-ISSN: 2709-9423
P-ISSN: 2709-9415
JRC 2022; 3(2): 01-05
© 2022 JRC
www.chemistryjournal.net
Received: 03-04-2022
Accepted: 07-05-2022

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Spectral, analytical and biological studies of zinc metal complexes with substituted chalcone thiosemicarbazones

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Abstract

Complexes of Zn have been prepared by reacting metal choride/acetate with chalcone thiosemicarbazone. The transition complexes were derived from the reaction between substituted chalcone thiosemicarbazone with an aqueous solution of transition metal salt. The metal complexes were used in various biological systems, polymers, dyes, anti-inflammatory, analgesic and anti-oxidative action. The Schiff bases and their metal complexes were used in various biological activities such as antimicrobial, antifungal, antiviral, insecticides, and antitumor activity.

Keywords: Spectral, analytical and physical studies, biological activities, chalcone thiosemicarbazones, metal complexes

Introduction

Schiff bases and their coordination complexes have acquired great significance in the field of inorganic research mainly because of their biological Activity [1-5]. Metal complexes play an essential role in agriculture, pharmaceutical and industrial chemistry. The Schiff᾽s base and their metal chelates is effective anticancer, antitumor, anti tuberculosis, antipyretic agent as well as anti fertility. Schiff᾽s base possess industrial application as catalysts, dyes, fiber, perfumes an aesthetic, plant growth inhibitors cosmetics corrosion inhibitors, oxygen absorbents, polymers, lubricating agents, for removing metal impurities of oil and drying accelerators [6-9]. Thiosemicarbazone ligands and their Zn(II) complexes have been screened for antimicrobial activity against some gram (+ve) and gram (-ve) bacterial and fungal species. The Fe ^{II} Cu ^{II} and Zn ^{II} complexes of Schiff bases are also biologically active [10] and they exhibit enhanced activities as compared to their parent ligands.

The chemistry of chalcone thiosemicarbazone and their allied derivative has great interest due to their diverse pharmaceutical activities. Their use as antifungal, 11 antibacterial, 12 antituberculosis [13]. Antimicrobial [14]. Agents. Metal complexes play an essential role in agriculture, pharmaceutical and industrial chemistry. The Schiff base and their metal chelate are effective anticancer, antitumor, ant tuberculosis, antipyretic, agent as well as ant perfumes, polymers, lubricating agent [15-17].

These complexes are colored solids, with sharp melting points and are sparingly soluble in common organic solvents and insoluble in water. These compounds are characterized by their elements analysis and spectral (IR, NMR, MASS,) studies.

The Zn complex showed a wide range of bactericidal activities against the Gram-positive and Gram negative bacteria, were potent than, or similar with commercial antibiotics (Kanamycin and penicillin) [18].

Materials and Methods

The substituted chalcones thiosemicarbazone transition metal complexes were derived from the reaction on aqueous solution of metal salt. The substituted chalcones and thiosemicarbazone ligands were prepared by the reaction of substituted chalcones with thiosemicarbazide in the presence of hot ethanol. All the transition metal-ligand 1:2 complexes isolated in the solid state, were stable in air, and characterized on the basis of their elemental and spectral data. The chalcones thiosemicarbazone ligands and their transition complexes were screened for their IR, NMR, and antifungal and antibacterial studies.

Synthesis of substituted chalcone (1a-e)

It was prepared by method of joshi *et al.* [20-22] by boiling the solution of o-chlorobenzaldehyde (1.40g, 10 mmol) and p-fluoroacetophenone (1.21 ml, 10 m mol) in ethanol (50ml) in a round bottomed flask and heated on a water bath for 5-10 minutes. Then 10% NaOH aqueous solution was added drop wise and stirred for 7-8 hours. After completion of the reaction, the mixture was acidified with ice cold hydrochloric acid and filtered to give crude product which was recrystallized with distilled ethanol.

1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-enone (chalcones)

All the other substituted chalcones were synthesized similarly and analytical, physical data of these compounds are listed in Table 1.

Table 1: Analytical and physical data of substituted chalcones

Comp.	Ar-X	Ar-Y	Mol. Formula	Colour	Mol.wt.	m.p.	Yield	Elemental analysis % (cal.) CH
1a.	4-Cl-C_6H_4	4-OH-C_6H_4	$C_{15}H_{11}ClO$	Yellow	242.70	105	84	74.23, 4.57
1b.	2-Cl-C_6H_4	4-F-C_6H_4	$C_{15}H_{10}ClF$	Cream	244.69	95	76	73.63, 4.12
1c.	-C_6H_5	4-OH-C_6H_4	$C_{15}H_{12}O$	Brown	208.26	110	77	86.51, 5.81
1d.	-C_6H_5	4-F-C_6H_4	$C_{15}H_{11}F$	Cream	210.25	95	69	85.69, 5.27
1e	-C_6H_5	-C_6H_5	$C_{15}H_{12}$	Cream	192.26	70	82	93.71, 6.29

Synthesis of substituted chalcone thiosemicarbazones Complexes (2A-E)

1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-ene-1-thiosemicarbazone

1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-ene-1-thiosemi-carbazone was prepared by method of Compaigne and Archer [19]. 1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-enone (5.21g,20 mmol) was dissolved in ethanol(50ml) in a 250 ml round bottom flask and heated on a water bath for 10-15 minutes. This hot solution was treated with hot ethanol solution (50ml) of thiosemicarbazide (1.82g, 20 m mol) and refluxed for 6-7 hrs on water bath. The change in colour from cream to yellow in the solution indicated the formation of 1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-ene-1-thiosemicarbazone. On cooling the reaction mixture was obtained as yellow crystalline product which was filtered under water suction and further recrystallized from absolute ethanol and finally dried over fused cacl$_2$ in vacuum desiccators.

Yield	85%
M.P.	150^{o}C
IR(KBr) υ_{max} cm^{-1}	3400(–NH_2 str.), 3150(–NH str.), 1180(>C=S str.),1540 (>C=C<),3065(Ar-H)
^{1}H NMR δppm ($CDCl_3$)	2.0 (–NH_2), 7.0 (S,–NH), 7.0-7.6 (m, Ar-H) 5.4-6.9(-CH=CH-)

All the other substituted chalcone thiosemicarbazones complexes were synthesized similarly and analytical, physical data of these compounds are listed in Table 2.

Table 2: Analytical and physical data of substituted chalcones thiosemi-carbazones complexes.

Comp.	Ar-X	Ar-Y	Mol. Formula	Colour	Mol. Wt.	M.P.	Yield	Elemental Analysis % CHN S
2a	4-Cl-C_6H_4	4-OH-C_6H_4	$C_{16}H_{14}ClN_3OS$	Yellow	331.8	170	90	57.91, 4.25, 12.66, 16.59
2b	2-Cl-C_6H_4	4-F-C_6H_4	$C_{16}H_{13}ClFN_3S$	Cream	333.8	150	85	57.57, 3.91, 12.59, 9.61
2c	-C_6H_5	4-OH-C_6H_4	$C_{16}H_{15}N_3OS$	Brown	297.3	125	82	64.62, 5.08, 14.13, 10.78
2d	-C_6H_5	4-F-C_6H_4	$C_{16}H_{14}FN_3S$	Cream	299.0	185	86	64.19, 4.71, 14.04, 10.71
2e	-C_6H_5	-C_6H_5	$C_{16}H_{15}N_3S$	Brown	281.0	132	76	68.30, 5.37, 14.93, 11.10

Synthesis of substituted chalcone thiosemicarbazones metal complexes

Bis [1-(4-Hydroxyphenyl)-3-(-4-chlorophenyl) prop-2-ene-1-thiosemi*-carbazone] zinc (II) (3a-d)

1-(4-Hydroxyphenyl)-3-(-4-chlorophenyl) prop-2-ene-1-thiosemi-carbazone (0.698g, 2mmol) was dissolved in ethanol (20ml) and heated on a water bath. This solution was mixed with an aqueous solution of metal salt $ZnCl_2.H_2O$ (0.136g, 1mmol) in 2:1 molar ratio respectively. Then the whole mixture was refluxed on water bath for 2-3 hrs and then left over night to yield the crystalline brown colored complex which was filtered out under suction and washed with water till filtrate became colorless. The product was finally washed with dilute ethanol and dried over fused calcium chloride in vacuum desiccators. All the compounds were prepared by using the same method.

Table 3: Bis [1-(4-Hydroxyphenyl)-3-(-4-chlorophenyl) prop-2-ene-1-thiosemi*-carbazone] zinc (II)

Yield	78%
M.P.	156^{o}C
IR(KBr) υ_{max} cm^{-1}	3320(–NH_2str.),1650(>C=Nstr.),1540 (>C=C<), 3010(Ar-H)
^{1}H NMR δppm ($CDCl_3$)	2.1 (–NH_2), 7.1-7.4 (m, Ar-H) 5.2-6.5(-CH=CH-)

All the other substituted chalcone thiosemicarbazones metal complexes were synthesized similarly and analytical, physical data of these compounds are listed in Table 3.

Table 4: Analytical and physical data of substituted chalcones thiosemi-carbazones metal complexes.

Comp. No.	Ar-X	Ar-Y	Mol. formula	Colour	Mol. Wt.	m.p. ^{0}C	Yield %	Elemental analysis % (calcd.) CHNS
3a	4-Cl-C_6H_4	4-OH-C_6H_4	$C_{33}H_{29}Cl_2N_6O_2S_2Zn$	Yellow	742.0	190	82	53.41, 3.94, 11.33, 8.64
3b	2-Cl-C_6H_4	4-F-C_6H_4	$C_{33}H_{27}Cl_2F_2N_6S_2Zn$	Cream	746.0	185	81	53.13, 3.65, 11.26, 8.60
3c	-C_6H_5	4-OH-C_6H_4	$C_{33}H_{31}N_6O_2S_2Zn$	Brown	673.6	176	74	58.88, 4.64, 12.48, 9.53
3d	-C_6H_5	4-F-C_6H_4	$C_{33}H_{29}F_2N_6S_2Zn$	Cream	677.1	185	72	58.53, 4.32, 12.41, 9.47
3e	-C_6H_5	-C_6H_5	$C_{33}H_{31}N_6S_2Zn$	Brown	641.1	168	76	61.82, 4.87, 13.11, 10.00

Results and Discussion

Substituted chalcone

In the IR spectra of substituted chalcone a sharp absorption band from 1740-1680 cm^{-1} is observed due to acetophenone >C=O and at 1620 cm-1 due to >C=C< stretching vibration. In the ^{1}H NMR spectra of substituted acetophenones a sharp singlet at δ7.90 ppm, δ 2.4 ppm and aromatic proton have been observe as multiple in the range δ 6.52-8.2 ppm.

Substituted chalcone thiosemicarbazones

Formation of substituted chalcone thiosemicarbazones was confirmed by the disappearance of intense absorption band at 1670 cm^{-1} due to carbonyl group (>C=O) new absorption bands at 3410-3300,1180-1050 cm^{-1} assigned to –NH_2, >C=S stretching vibrations, respectively appears. Similarly in ^{1}H NMR spectra broad signal δ2.3-3.2 ppm appears due to –NH_2 protons and sharp singlet from δ7.0 ppm due to –NH proton. Aromatic protons are observed as multiple from δ6.8-7.6 ppm.

Metal complexes of substituted chalcone thiosemicarbazones

In IR spectra of metal complexes of substituted chalcone-thiosemicarbazones the presence of absorption band at 3350cm-1 due to –NH_2 (symmetric) and at 3400cm-1due to-NH_2 (asymmetric) modes remain almost unaltered. Sharp absorption band from 3280-2850cm-1 which was due to NH- in ligands disappear in complexes indicating possible deprotonation on the β-nitrogen after complextion with metal ion .A new absorption band in the complexes at 445-432 due to (M-N) confirm the metal nitrogen bond in the complexes. A very strong band at 1650-1590cm-1 due to (>C=N) group. In the IR spectra of ligands in solution, an absorption band is observed at 2500cm-1 which may be assigned to ν (S-H) stretching vibration. The ^{1}NMR spectra of showed sharp signal at δ2.5 ppm due to –NH2 protons and multiplet signals observed at δ 7.0-7.30 ppm are due to aromatic protons.

The IR and ^{1}H NMR data of substituted acetophenone thiosemicarbazone and their metal complexes are summarized in Table-4 and 5.

Table 5: IR of Different complexes

IR (KBr : ν max cm^{-1})									
Comp. no.	>NH_2	>NH	Ar-H	>C=N	>C=C<	M-N	>C=S	C-S	>C=O
1a	-	-	3010	-	1605	-	-	-	1710
1b	-	-	3020	-	1610	-	-	-	1690
1c	-	-	3250	-	1605	-	-	-	1740
1d	-	-	3021	-	1605	-	-	-	1690
1e	-	-	3010	-	1610	-	-	-	1705
2a	3350	3200	3050	1580	1550	-	1150	-	-
2b	3400	3150	3065	1585	1540	-	1180	-	-
2c	3450	3180	3085	1650	1480	-	1105	-	-
2d	3390	3200	3040	1606	1650	-	1150	-	-
2e	3280	3300	3080	1540	1630	-	1140	-	-
3a	3290	-	3000	1580	1560	430	-	1040	-
3b	3310	-	3040	1650	1560	470	-	1060	-
3c	3385	-	3150	1620	1550	440	-	1100	-
3d	3330	-	3080	1650	1660	440	-	1080	-
3e	3240	-	3050	1580	1490	385	-	990	-

Table 6: NMR of different complexes

^{1}H NMR spectral data(δ,ppm)						
Compd. no.	Mol. formula	Ar-H (m)	NH(s,1H)	- NH_2	CH=CH-	-OH
1a	$C_{15}H_{11}ClO$	6.5-8.2	-	-	7.3-8.1	-
1b	$C_{15}H_{10}ClF$	7.0-7.8	-	-	7.2-8.0	-
1c	$C_{15}H_{12}O$	7.0-7.6	-	-	7.1-8.0	-
1d	$C_{15}H_{11}F$	7.0-7.8	-	-	7.2-8.0	-
1e	$C_{15}H_{12}$	7.0-7.4	-	-	7.3-8.1	-
2a	$C_{16}H_{14}ClN_3OS$	6.8-7.4	7.0	2.0	6.6	6.0
2b	$C_{16}H_{13}ClFN_3S$	7.0-7.6	7.0	2.0	5.4-6.9	-
2c	$C_{16}H_{15}N_3OS$	6.8-7.4	7.0	2.0	5.6-6.6	6.0
2d	$C_{16}H_{14}FN_3S$	7.0-7.6	7.0	2.0	5.6-6.6	-
2e	$C_{16}H_{15}N_3S$	7.3-7.6	7.0	2.0	5.6-6.6	-
3a	$C_{33}H_{29}Cl_2N_6O_2S_2Zn$	6.0-7.3	-	2.0	6.0-7.3	5.1
3b	$C_{33}H_{27}Cl_2F_2N_6S_2Zn$	7.1-7.5	-	2.0	5.4-6.3	-
3c	$C_{33}H_{31}N_6O_2S_2Zn$	6.0-7.3	-	2.0	5.3-6.4	5.0
3d	$C_{33}H_{29}F_2N_6S_2Zn$	7.0-7.4	-	2.0	5.6-6.4	-
3e	$C_{33}H_{31}N_6S_2Zn$	7.1-7.3	-	2.0	5.6-6.3	

Antibacterial and antifungal activities

Representative Chalcone thiosemicarbazone ligands and their metal complexes were screened for their antibacterial activity and antifungal activity at 60, 80, and 100 ppm concentrations.

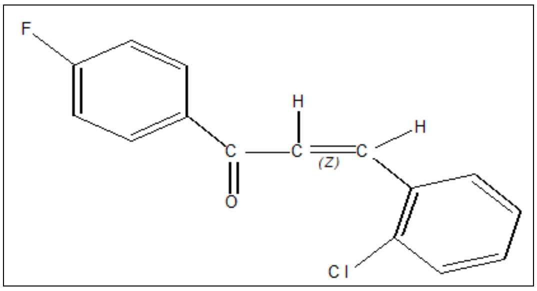


Fig 1: 1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-enone (chalcones)

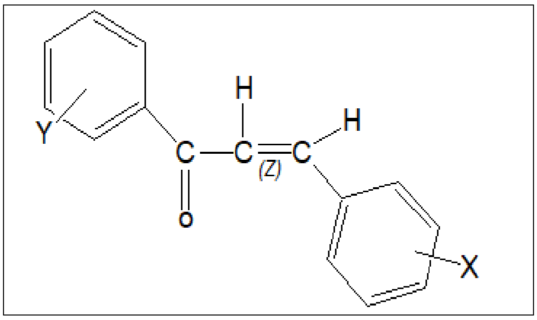


Fig 2: substituted chalcones

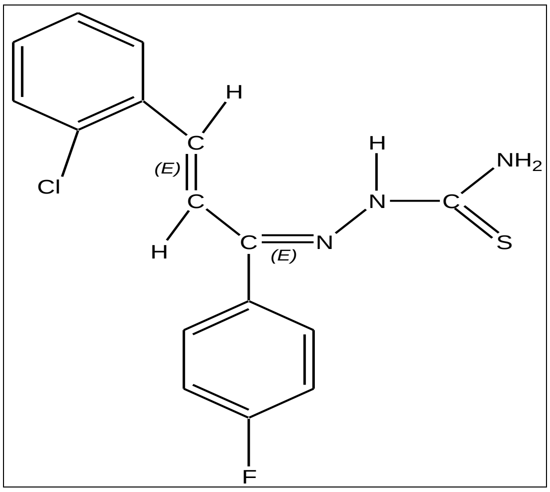


Fig 3:1-(4-Fluorophenyl)-3-(-2-chlorophenyl) prop-2-ene-1-thiosemicarbazone

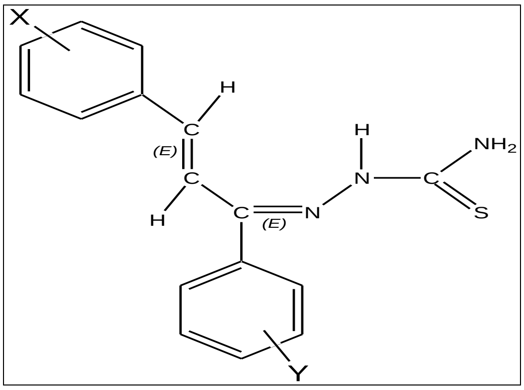


Fig 4: Substituted chalcones thiosemi-carbazones complexes

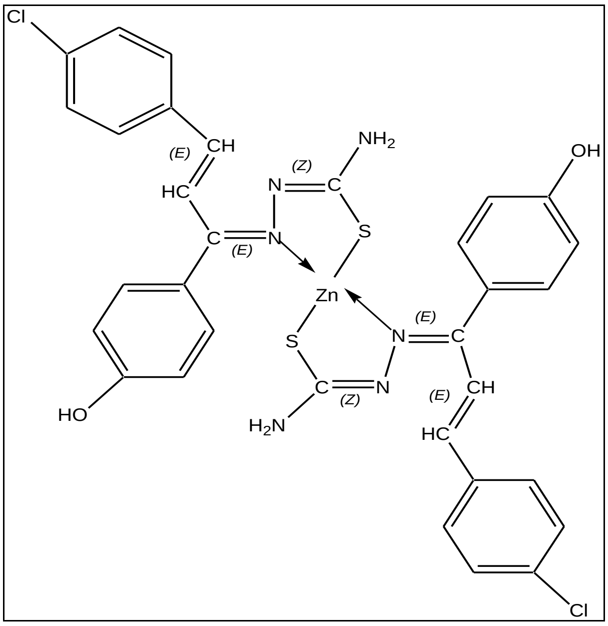
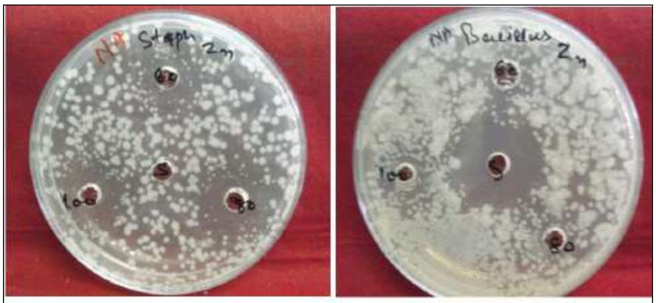


Fig 5: Bis [1-(4-Hydroxyphenyl)-3-(-4-chlorophenyl) prop-2-ene-1-thiosemi*-carbazone] zinc (II)

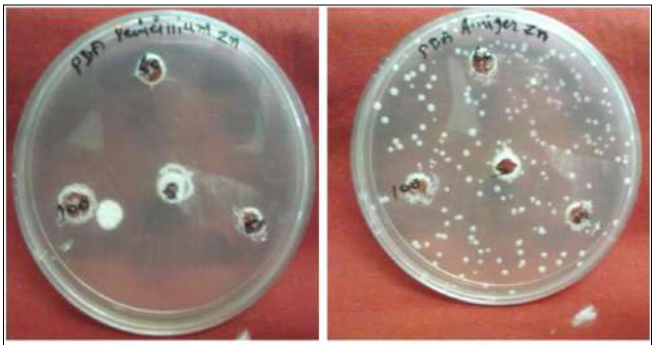


Antibacterial species *Streptocous aureus*

Antibacterial species *Bacilles cereus*

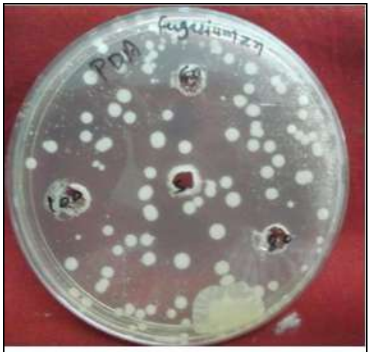
Antibacterial species *Streptomycis*

Antibacterial species *E.coli*



Antifungal species *Penicilium*

Antifungal species *A.niger*



Antifungal species
Fusarium

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