"LEAD (II) COMPLEXES OF SCHIFF BASES AS BIOCIDAL AGENTS"

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ABSTRACT

Four Schiff-bases were synthesized by the reaction of 2-amino phenol, 2-amino thiophenol, 2-amino pyridine and 2-amino benzoic acid with 2-acetyl furan and these compounds with reacted with Pb (II) acetate to get their respective complexes. All the compounds and their Pb (II) complexes were characterized by elemental analysis and I.R. spectral studies. They compounds were also screened for their biological, anti-bacterial and antifungal agents.
(Key Words: Schiff-bases, I.R. spectral biocidal studies)

INTRODUCTON

Schiff-bases having azomethine group are found to be quite active against micro organism[1-7]. It is reported[8] that the biocidal activity of a ligand increased having N, O, and S donor sites is several times on being co-ordination with a suitable metal Ion[8-10] in view of above, it was considered to interest screen the reported. Schiff-bases and their Pb (II) complexes against the two bacteria viz. Staphylococcus aureus gram positive bactria) and Escherichia Coli (gram negative becteria) and two fungi *Aspergillus niger* and Candida albicans using by serial dilution method. The result have been reported in the forms of MIC values (MIC = Minimum Inhibitary Concentration)

MATREIAL AND METHODS

All the chemical used were of A.R. grade. The ligands and their complexes were prepared as follows:

(A) SYNTHESIS OF SCHIFF-BASES :

1. 2-Acetyl furanilidine – Anthranilic Acid (A.F.A.A.) :-

2.0 ml (0.02 M) of 2-acetyl furan in minimum volume of dry ethanol was added to 2.74 gm (0.02M) of Anthranilic acid in minimum volume of dry ethanol. This mixture was refluxed for about 6 hours on water bath and then reduced the volume to 1/3 of its original volume. It was filtered, concentrated, cooled and recrystallized from ethanol and dried. The obtained coloured compound was found soluble in ethanol, D.M.F., D.M.S.O., T.H.F. having M.P. 140ºC and molecular formula $C_{13}H_{11}NO_3$.

2. 2-Acetyl furanilidine –o – aminophenol (A.F.A.P.) :-

2.0 ml (0.02 M) of 2-acetyl furan was dissolved in 20ml of dry methanol and 2.18 gm (0.02M) of 2-aminophenol was added to it and mixed together. It was kept on water bath and refluxed for 8 hours, reduced to half of its volume and allowed to stand over night. The obtained product was filtered and washed with dry ethanol and again recrystallised with ethanol to give black crystals. These crystals were found soluble in methanol ethanol, D.M.F., T.H.F., having M.P. 180°C and molecular formula $C_{12}H_{11}NO_2$.

3. 2-Acetyl furanilidine – O – aminothiophenol (A.F.A.T.P.) :-

2.0 ml (0.02 M) of 2-acetyl furan was dissolved in minimum volume of benzene and 2.14 ml (0.02 M) 2-amino thiophenol was dissolved in minimum volume of benzene sepertely. Both the solutions were mixed together. This mixture was refluxed over a water bath for about 7 hours and solution was allowed to stand over night. The obtained product was filtered and washed with alcohol Black coloured solid was found soluble in methanol, benzene, D.M.F., D.M.S.O. and T.H.F. Its M.P. was 142°C and molecular formula ($C_{12}H_{11}NOS$).

4. 2-Acetyl furanilidine –o-aminopyridine (A.F.A.Py.) :-

2.0 ml (0.02 M) of 2-acetyl furan was mixed with 10ml benzene and addedto 1.90 gm (0.02M) 2-aminopyridine in 20 ml benzene. This mixture was refluxed on a water bath for about 5 hours and then allowed to stand for over night. The obtained solid product was filtered and washed with dry ethanol. It was soluble in D.M.F., D.M.S.O., T.H.F. and methanol having melting point 125°C and molecular formula $C_{11}H_{10}N_2O$.

(B) SNYTHESIS OF SCHIFF – BASE METAL COMPLEXES:

Although the metal complexes of the synthesized Schiff-bases were also tried to prepare by the direct complexation of the metal ion with the legands, but the obtained yield was very poor and the reaction was not successful. Hence the template synthesis method was adopted in the cases.

1. Bis (2-Acetyl furanilidine – Anthranilic Acid) Pb (II) :-

2.30 gm (0.01M) of A.F.A.A. was dissolved in minimum volume of ethanol and added to 50ml ethanolic solution of 1.90 gm (0.005M) lead acetate trihydrte in a round bottom flask. The obtained solution was refluxed over a water bath for about 7 hours and cooled. The obtained coloured product was filtered through suction, washed with ethanol followed by ether and dried under vacuuo over anhydrous $CaCl_2$ in a desicator. M.P. 255°C, molecular formula ($C_{26}H_{20}N_2O_6$) Pb.

2. **Bis (2-acetyl furanilidine – 2 - aminotheophenol Pb(II) $(CH_3COO)_2$:**

1.00ml (0.01M) 2-acetyl furan was added to 40ml ethanolic solution of 1.90 gm (0.005M) lead acetate trihydrate in a round bottom flask. The contents were heated over a water bath for an hour and then 1.07 ml (0.01M) 2-amino-thiophenol in 25ml ethanol was added to it. After refluxing again for two hours the resulting product was allowed to cooled and filtered. It was washed successively with ethanol, ether and dried in vacuuo in a desicator to get a coloured crystalline product M.P. 165°C, molecular formula $(C_{14}H_{13}NO_3S)_2$ Pb_2.

3. Mono (2 – Acetyl furanildine – 2 – aminopyridine) Pb (II) $(CH_3COO)_2.H_2O$.

30 ml ethanolic solution containing 0.94 gm (0.01M) 2-aminopyridine was mixed with an ethanolic solution of 3.80 gm (0.01M) lead acetate trihydrate. The mixture was heated over a water bath and then 1.0 ml (0.01M) of 2-acetyl furan in ethanol was added. After refluxing for 2 hours, the contents were allowed to cool. The solid product thus obtained was filtered and washed successively with dry ethanol ether and dried in vaccum over anhydrous $CaCl_2$ in a disicator M.P. 260°C, molecular formula ($C_{15}H_{18}N_2O_6$).

4. Bis (2-Acetyl furanilidine-2-aminophenol) Ph(II) :

2.00 gm (0.01M) of A.F.A.P. was dissolved is 50ml ethanol and added to 50ml ethanolic solution of 1.90 gm (0.005M) lead acetate trihydate in a round bottom flask. The obtained solution was refluxed over a water bath for about 4 hours and cooled. The obtained coloured product was filtered through suction, washed with ethanol followed by ether and dried in vacuuo over anhydrous $CaCl_2$ in a desicator M.P. 310°C molecular formula ($C_{24}H_{20}N_2O_4$) Pb.

RESULT AND DISCUSSION

Analytical data of the metal complexes indicate that one molecule of (A.F.A.A.) / (A.F.A.T.P.) and (A.F.A.P.) (A.F.A.Py.) is co-ordinated to a metal ion having three water moleculers as determined by thermal studies. The observed values of molar conductance for all the chelates suggest their non-ionic character (Table-1)

M.I.C. values presented in (Table-VI) reveals that antimicrobial activity of the metal chelates in comparison to their respective synthesized organic legands is considerably increased due to their combined activity effect.

Infra Red Spectra

A comparative study of infra-red spectra of ligands and their chelates reveals that certain bands are common in the infra-red spectra of metal chelates and the involved ligands. Infra-red spectra of all the free ligands give bands in the region of 1645-1560 cm^{-1} which may be attributed due to the stretching vibrations of azomethine group (> C = N). This band is shifted upto ~ 60 cm^{-1} towards lower frequency region in the spectra of their respective metal chelates suggesting there by the participation of imine nitrogen in complexation[11-14].

A strong band in the region 1740-1620 cm^{-1} has been observed in the I.R. spectra of A.F.A.A., A.F.A.P., A.F.A.Py. legands which is due to the presence of stretching vibration of carbonyl group (>C=O). Co-ordination through this carbonyl oxygen to the central metal ion is confirmed by a negative shift in this frequency in the spectra of corresponding metal chealates[15-16].

I.R. Spectra of A.F.A.T.P. display a weak band at 2840-2630 cm^{-1}, a diagnostic of SH group which disappears in the spectra of respective metal chealates, indicating thereby the co-ordination of ligand to metal ion as a consequence of deprotonation of thiol group[17].

The presence of co-ordinated water molecules in Pb(II) complexes of A.F.A.Py. is indicated by a broad-band at 3320-3370 cm^{-1} followed by an other band at 840-830 cm^{-1} which are probably due to the stretching and rocking vibrations of –OH respectively.

BIOLOGICAL SCREENING

The antibacterial and anti-fungal activity of ligands and their metal chelates have been given in terms of Minimum Inhibitory Concentration (M.I.C.) value (Table-VI) A perusal of the value indicates an increase in the activity of the metal chelate in comparison to their respective synthesized organic ligands. A special class of Schiff-bases is known to strong antimicrobial activity.

Table-I

(% Analysis : Found Calculted)

S. No.	Compound	Colour	Dip/mp °C	C	H	N	S	Metal	Molar Conductance Ohm^{-1} $Mole^{-1}$	F.W. Calcul-ated	Molecular Formula	Mol. Wt.
1.	A.F.A.A.	Green	140	68.40 (68.12)	4.98 (4.80)	6.37 (6.11)	-	-	-	-	$C_{13}H_{10}NO_3$	229
2.	A.F.A.P.	Black	180	71.90 (71.64)	5.65 (5.47)	6.75 (6.97	-	-	-	-	$C_{12}H_{11}NO_2$	201
3.	A.F.A.T.P.	Black	142	66.56 (66.35)	5.00 (5.06)	6.24 (6.45)	14.55 (14.74)	-	-	-	$C_{12}H_{11}NOS.$	217
4.	A.F.A.Py.	Dark Brown	125	70.75 (70.96)	5.25 (5.37)	14.92 (15.65)	-	-	-	-	$C_{11}H_{10}N_2O$	186

Contd. ……

5.	Pb $(AFAA)_2$	Dark Yellow	225	47.12 (47.05)	3.50 (3.01)	4.44 (4.22)	-	31.85 (31.25)	8.25	663	$(C_{26}H_{20}N_2O_6)$ Pb	680
6.	Pb $(AFAP)_2$	Dark Brown	310	46.50 (47.44)	2.98 (3.29)	3.88 (4.61)	-	34.94 (34.13)	7.21	607	$(C_{24}H_{20}N_2O_4)$ Pb	620
7.	Pb $(AFATP)_2$	Black	165	33.11 (34.85)	2.85 (2.69)	2.80 (2.90)	-	43.11 (42.98)	9.10	964	$(C_{14}H_{13}NO_3S)_2$ Pb_2	988
8.	Pb (AFAPy) Ac_2H_2O	Dark Brown	260	34.50 (34.02)	3.64 (3.40)	5.82 (5.29)	-	40.11 (39.16)	5.75	529	$(C_{15}H_{18}N_2O_6)$ Pb	540

Table-II

I.R. Spectral Data (in cm^{-1}) of A.F.A.A. and its metal (II) chelates

S.No.	A.F.A.A.	Pb(II) A.F.A.A.	Probable assignments
1.	3350 (M)	—	–OH stretching vibration of COOH group
2.	2900 (ms)	2900 m	–CH stretching of Furan ring
3.	1730 (s)	1630 (m)	C = 0 stretching vibration
4.	1620 (m)	1560 (mb)	> C = N stretching vibration
5.	1590 (ms)	1565 (m)	Asymmetrical structure of COO^-
6.	1440 (b)	1440 (ms)	Furan ring breathing vibration
7.	1360 (m)	1350 (s)	Symmetrical structure of COO^-
8.	1260 (s)	1230 (s)	> C = N azomethine stretching
9.	1140 (s)	1140 (s)	In plane C-H deformation
10	—	885 (m)	M-O-C stretching deformation
11.	740 (s)	740 (ms)	Out of plane C–H bending
12	—	540 (s)	M-O stretching
13.	—	440 (s)	M-N stretching

Abbrebiation Used S = Sharp, b = Broad, m = Medium, w = Weak

Table-III

I.R. Spectral Data (in cm^{-1}) of A.F.A.P. and its metal (II) chelates

S.No.	A.F.A.P.	Pb(II) A.F.A.P.	Probable assignments
1.	3600 (s)	—	–OH (Phenolic) stretching
2.	3260 (s)	3260 (s)	CH stretching of Furan ring
3.	2850 (s)	2850 (s)	Symmetric NH_2 stretching
4.	1620 (s)	1580 (s)	> C = N azomethine stretching)
5.	1440 (s)	1440 (s)	Aromatic C = C stretching vibration
6.	1365 (s)	1365 (s)	Furan ring breathing vibration
7.	—	540 (s)	M-O stretching
8.	—	440 (s)	M-N stretching

Table-IV

I.R. Spectral Data (in cm^{-1}) of A.F.A.T.P. and its metal (II) chelates

S.No.	A.F.A.T.P.	Pb(II) A.F.A.T.P.	Probable assignments
1.	3250 (s)	3250(s)	OH stretching of Furan ring
2.	2840 (m)	2860 (ms)	Symmetric NH_2 stretching
3.	2630 (w)	—	–SH stretching
4.	1740 (s)	1720 (ms)	> C = O stretching
5.	1645 (s)	1585 (ms)	> C = N azomethine stretching
6.	1460 (s)	1460 (s)	Furan ring brething vibration
7.	—	575 (s)	Bridging acetate group
8.	—	—	M=Cl bridging Vibration
9.	—	540(s)	Bridging $CH_3\ COO^-$ group

Table-V

I.R. Spectral Data (in cm^{-1}) of A.F.A.Py. and its metal (II) chelates

S.No.	A.F.A.Py.	Pb(II) A.F.A.Py.	Probable assignments
1.	—	3320 (mb)	Co-ordinated water molecules
2.	2860(s)	2850 (s)	CH stretching of furan ring
3.	1720 (ms)	1690 (s)	> C = 0 stretching vibration
4.	1635 (s)	1560 (s)	> C = N stretching
5.	1475 (s)	1470 (s)	Furan ring breathing modes
6.	—	—	M-Cl stretching
7.	—	835 (mb)	Co-ordinated H_2 molecule
8.	—	540 (s)	M-O stretching
9.	—	450 (m)	M–N stretching

Table-VI

Minimum inhibitory Concentration (M.I.C.) in ug/ml of organic ligands and their metal complexes
Temp = 37°C Temp used = 28°C

S.No.	Compound	Bacteria		Fungi	
		S. aureus	E.colo	A. Niger	E. Albicans
1.	A.F.A.A.	4.1	4.1	2.0	2.0
2.	A.F.A.P.	4.2	3.2	4.3	2.1
3.	A.F.A.T.P.	3.5	2.3	2.3	3.5
4.	A.F.A.Py.	2.6	1.9	1.3	2.6
5.	Pb (A.F.A.A.)	2.6	1.4	1.4	0.7
6.	Pb (A.F.A.P.)	1.4	1.4	1.4	0.7
7.	Pb (A.F.A.T.P.)	2.6	1.5	1.4	0.6
8.	Pb (A.F.A.Py.)	3.5	1.5	1.3	0.7

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