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SOME NEW COORDINATION COMPOUNDS OF TIN (II) AND LEAD (II) WITH SCHIFF BASES REARRANGED FROM BENZOTHIAZOLINES

Arpita Verma, Shilpa Sharma, K.B. Bansal, Manoj Kumar, S. Varshney and A.K. Varshney
Department of Chemistry, University of Rajasthan,Jaipur-302004
*E-mail: anilakv123@rediffmail.com

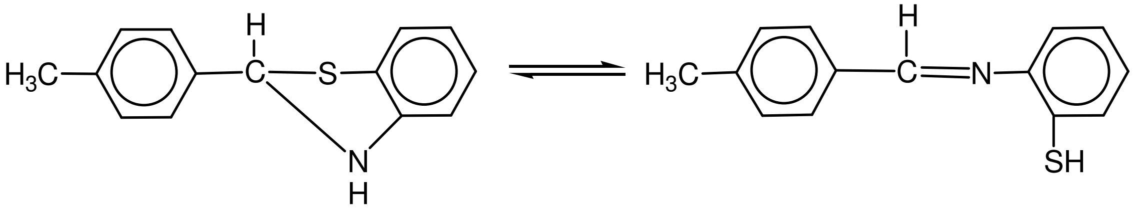
ABSTRACT

The present paper is a report on the synthesis of some new coordination compounds of Sn(II) and Pb(II) by the reactions of tin(II) acetate/lead (II) acetate with sulfur containing ligands. Ligands used in these reactions are benzothiazolines prepared by the reaction of p-tolualdehyde, 4-acetylbiphenyl, 9-anthraldehyde, 4-fluoroacetophenone and 2-acetylfluorene with o-aminothiophenol which on reaction with metal ion rearrange to Schiff bases. Characterization and structure elucidation of the complexes are achieved by elemental analysis, electronic, infrared, ^{1}H, ^{13}C NMR and ^{119}Sn NMR spectral studies. The potency of the synthesized compounds have been assessed by growth inhibiting potential of the complexes against variety of fungal and bacterial strains.

Keywords: Tin (II) acetate; lead (II) acetate; o-aminothiophenol; benzothiazolines ; spectral studies.

INRODUCTION

The condensation of o-aminothiophenol with the carbonyl compounds should form the Schiff base, but we get the benzothiazoline. These benzothiazolines when react with metal salts rearrange into Schiff base with the formation of their coordination compounds.



Metal complexes of such ligands and particularly of sulfur containing ligands are drawing enormous attention mainly due to their practical utility[1-2]. They are active against tuberculosis, cancer, viruses, malaria, smallpox and certain kinds of tumor.

The role of metal chelates in all aspects of biological studies has gained considerable importance as these provide valuable approaches to the metabolic studies, oxidative phosphorylation, trans methylation and principles of chemotherapy. Recently, much interest has been shown in the synthesis of metal chelates of sulfur containing ligands and it is within this particular area that rather significant advances have been made[3]. It was, therefore, considered worthwhile to synthesize such type of complexes by the reactions of tin (II) acetate and lead (II) acetate with benzothiazolines .

EXPERIMENTAL

Analytical methods and physical measurements

Tin and lead were estimated gravimetrically as SnO_2 and lead sulphate respectively. Nitrogen and sulphur were estimated by Kjeldahl's method and Messenger's method, respectively[4-5]. The electronic spectra were taken with a Toshniwal spectrophotometer in methanol. The IR spectra were recorded on FTIR spectrophotometer using a model A-8400S, Shimadzu in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL-300.

Synthesis of ligands

All the ligands were prepared by the condensation of aldehydes / ketones viz. p-tolualdehyde, 4-acetyl biphenyl, 9-anthraldehyde, 4-fluoroacetophenone and 2-acetyl fluorene with o-aminothiophenol in 1 : 1 molar ratio using absolute alcohol as the reaction medium.

Synthesis of tin (II) and lead (II) complexes

Tin (II) complexes were synthesized by the reaction of tin (II) acetate and benzothiazolines in 1:2 molar ratios in dry methanol as reaction medium. The resulting solution was stirred on magnetic stirrer for about two hours. The solvent was removed under reduced pressure and the product was finally dried in vacuo at 40-50°C. The physical properties and analytical data are recorded in Table-1

Biological activity

The antimicrobial activity of ligands and their corresponding tin (II) and lead (II) complexes are tested against fungi and bacteria (R.phaseoli, *F. oxysporum, S. aureus, E. coli*, *P.fluorescens etc*.). The results also show that the resulting products are lipophilic in nature. The complexes are found to possess higher activity than ligands. The results of these studies show that the metal complexes are more active than the ligands and the data are recorded in Table-5.The fungitoxicity of the compounds increase with increase in concentration.

RESULTS AND DISCUSSION

The reactions of tin (II) acetate and lead (II) acetate with benzothiazolines in 1:2 molar ratio proceed in following manner :

$$1.\quad Sn(CH_3COO)_2 + C_{28}H_{26}\,\overset{\frown}{N\ \ S} \xrightarrow[\text{Molar ratio}]{1\ :\ 2} Sn(C_{28}H_{24}\,\overset{\frown}{N\ \ S}) + 2CH_3COOH$$

$$2.\quad Pb(CH_3COO)_2 + C_{28}H_{26}\,\overset{\frown}{N\ \ S} \xrightarrow[\text{Molar ratio}]{1\ :\ 2} Pb(C_{28}H_{24}\,\overset{\frown}{N\ \ S}) + 2CH_3COOH$$

Where $\overset{\frown}{N\ \ S}$ represents the donor sets of ligands.

Electronic spectra

The electronic spectra of the ligands exhibit two bands near 250 nm and 315 nm consistent with the typical spectrum of a benzothiazoline (cyclic form) moiety[6-7]. These bands may be attributed to the ϕ-ϕ^* and $\pi\rightarrow\pi^*$ benzenoid transitions. In the corresponding tin (II) complexes, an additional band around 410 nm due to $n\rightarrow\pi^*$ transition of the azomethine group is also observed. The formation of this new band may be due to the isomerization of benzothiozoline in to Schiff bases.

Infrared spectra

In the solid state IR spectra of benzothiazoline,the presence of a strong and broad band due to νNH group in the region 3300-3100 cm^{-1} and absence of νSH at ~ 2500-2600 cm^{-1} is indicative of the benzothiazoline rather than the Schiff-base structure .A new band at 1605 cm^{-1} is observed in the spectra of metal complexes due to the presence of ν(C=N) vibrations. The appearance of this band suggests that the complexes are metal Schiff base derivatives as the benzothiazoline ring rearranges to give the Schiff-base derivatives in the presence of metal ion.The data are given in Table-2.

^{1}H NMR spectra

The proton magnetic resonance spectra of benzothiazolines show the N–H proton signals at δ 5.8 ppm which disappear on complexation, indicating that the rearrangement of benzothiazoline form to the Schiff base form has occurred. The ligand shows a complex multiplet in the region δ 7.40-6.40 ppm for the benzene protons and these remains at almost the same position in the spectra of complexes. The data are given in Table-3.

^{13}C NMR spectra

The ^{13}C NMR spectra of ligands and their corresponding tin (II) and lead (II) complexes have been recorded in Table-4. The considerable shifts in position of carbons attached with sulfur and nitrogen clearly indicate the deprotonation of SH group and coordination of azomethine nitrogen to metal atom.The data are given in Table-4.

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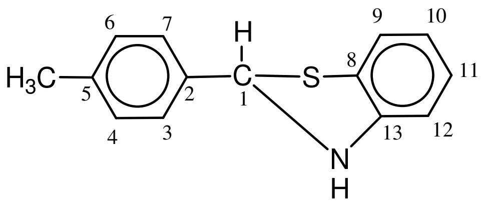

Fig. -1: $C_{14}H_{13}NS$ (L^1H)

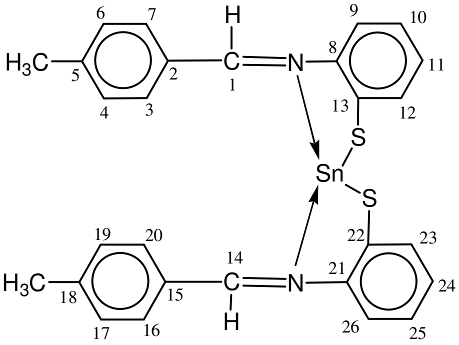

Fig.- 2: Sn.$C_{28}H_{24}NS$

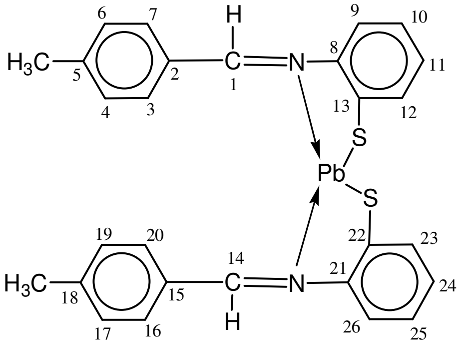

Fig.- 3: Pb.$C_{28}H_{24}$NS

Table -1: Reactions of tin (II) acetate and lead (II) acetate with benzothiazolines.

S. No.	Compounds	Ligands	Molar ratio	Product colour & state	Melting point (°C)	Analysis: Found (Calcd.) %			Molecular weight: Found (Calcd.)
						Pb/Sn	N	S	
1.	$Sn(CH_3COO)_2$	$C_{14}H_{13}NS$	1:2	$Sn(C_{28}H_{24}NS)$ Yellowish cream solid	195°	19.57 (20.77)	4.88 (4.90)	10.10 (11.22)	561.33 (571.31)
2.	$Sn(CH_3COO)_2$	$C_{20}H_{17}NS$	1:2	$Sn(C_{40}H_{32}NS)$ Yellow solid	105°	15.20 (16.40)	3.75 (3.87)	8.80 (8.86)	703.52 (723.51)
3.	$Sn(CH_3COO)_2$	$C_{21}H_{15}NS$	1:2	$Sn(C_{42}H_{28}NS)$ Yellow solid	115°	15.56 (15.96)	3.66 (3.76)	8.30 (8.62)	743.30 (743.49)
4.	$Sn(CH_3COO)_2$	$C_{14}H_{12}NSF$	1:2	$Sn(C_{28}H_{22}NSF)$ Yellow solid	110°	19.10 (19.54)	4.40 (4.61)	10.25 (10.55)	607.10 (607.29)
5.	$Sn(CH_3COO)_2$	$C_{21}H_{15}NS$	1:2	$Sn(C_{42}H_{28}NS)$ Cream solid	110°	15.70 (15.96)	3.56 (3.76)	8.31 (8.62)	743.20 (743.49)
6.	$Pb(CH_3COO)_2$	$C_{14}H_{13}NS$	1:2	Pb $(C_{28}H_{24}NS)$ Yellow solid	145°	30.90 (31.40)	3.99 (4.24)	9.70 (9.71)	654.82 (659.81)
7.	$Pb(CH_3COO)_2$	$C_{20}H_{17}NS$	1:2	Pb $(C_{40}H_{32}NS)$ Cream solid	90°	25.01 (25.51)	2.98 (3.44)	7.08 (7.89)	802.10 (812.01)
8.	$Pb(CH_3COO)_2$	$C_{21}H_{15}NS$	1:2	Pb $(C_{42}H_{28}NS)$ Yellow solid	118°	24.40 (24.90)	3.26 (3.36)	7.40 (7.70)	831.80 (831.99)
9.	$Pb(CH_3COO)_2$	$C_{14}H_{12}NSF$	1:2	Pb $(C_{28}H_{22}NSF)$ Yellow solid	113°	29.56 (29.77)	3.91 (4.02)	8.92 (9.21)	695.50 (695.79)

Table-2: Antimicrobial activity of benzothiazolines and their corresponding tin (II) and lead (II) complexes.

Microorganisms		L^1H		Sn.$C_{28}H_{24}$NS		Pb.$C_{28}H_{24}$NS		L^2H		Sn.$C_{40}H_{32}$NS		Pb.$C_{40}H_{32}$NS	
		50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm
F. oxysporum	IZ (AI)	8 (`0.50)	18 (0.69)	12 (0.75)	22 (0.84)	14 (0.87)	22 (0.84)	8 (0.50)	14 (0.53)	12 (0.75)	18 (0.69)	14 (0.87)	18 (0.69)
R.phaseoli	IZ (AI)	6 (0.37)	12 (0.50)	10 (0.62)	16 (0.66)	12 (0.75)	16 (0.66)	10 (0.62)	18 (0.75)	10 (0.62)	18 (0.75)	10 (0.62)	18 (0.75)
P. fluorescens	IZ (AI)	4 (0.25)	12 (0.46)	8 (0.50)	16 (0.61)	10 (0.62)	16 (0.61)	14 (0.87)	20 (0.76)	14 (0.87)	20 (0.76)	14 (0.87)	20 (0.76)
E.coli	IZ (AI)	8 (0.44)	14 (0.53)	12 (0.66)	18 (0.69)	14 (0.77)	18 (0.69)	14 (0.77)	18 (0.69)	18 (1.00)	22 (0.84)	16 (0.88)	20 (0.76)
S. aureus	IZ (AI)	6 (0.42)	14 (0.77)	10 (0.71)	18 (1.00)	10 (0.71)	24 (1.33)	12 (0.85)	24 (1.33)	16 (1.14)	28 (1.55)	14 (0.87)	26 (1.44)

IZ = Inhibition zone (diameter in mm); AI = Activity index (Inhibition zone of test compounds/Inhibition zone of standard)
$L^1H = C_{14}H_{13}NS$; $L^2H = C_{20}H_{17}NS$

Table-3: Some important IR spectral data of benzothiazolines and their corresponding tin (II) and lead (II) complexes.

S. No.	Compounds	νC=N	νNH/OH	νSn□N / νPb□N
1.	L^1H ($C_{14}H_{13}NS$)		3300	-
2.	Sn ($C_{28}H_{24}NS$)	1590	-	410
3.	Pb ($C_{28}H_{24}NS$)	1570	-	525w
4.	L^5H ($C_{20}H_{17}NS$)		3300	-
5.	Sn($C_{40}H_{32}NS$)	1610	-	405
6.	Pb($C_{40}H_{32}NS$)	1590	-	550w

w = weak

Table-4: ^{13}C NMR spectral data (δ ppm) of benzothiazolines and their corresponding tin (II) and lead (II) complexes.

	Chemical shifts in δ ppm												
Compounds	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}
$C_{14}H_{13}NS(L^1H)$	163.7	138.0	127.8	129.2	136.1	129.2	127.8	119.4	127.4	117.1	125.7	112.5	141.6
Sn.$C_{28}H_{24}NS$	165.4	126.0	128.0	129.0	138.0	129.0	128.0	129.0	129.0	125.0	129.0	129.0	132.0
Pb.$C_{28}H_{24}NS$	165.4	126.0	128.0	129.0	138.0	129.0	128.0	129.0	129.0	125.0	129.0	129.0	132.0

Table-5: Nuclear magnetic resonance data for the benzothiazoline and the corresponding tin and lead complexes in δ ppm.

Compound	–NH	H–C=N	NH_2	Aromatic protons
L^1H ($C_{14}H_{13}NS$)	12.36	8.22	3.40	7.80-6.85
Sn ($C_{28}H_{24}NS$)	-	9.25	3.50	7.75-6.70
Pb ($C_{28}H_{24}NS$)	-	9.58	3.42	6.85-6.20
L^1H ($C_{20}H_{17}NS$)	13.20	8.25	3.85	7.75-7.10
Sn ($C_{40}H_{32}NS$)	-	9.50	3.80	7.70-7.15
Pb ($C_{40}H_{32}NS$)	-	9.40	3.80	7.75-7.05
L^1H ($C_{21}H_{15}NS$)	12.50	8.80	3.50	7.85-7.10
Sn ($C_{42}H_{28}NS$)	-	9.00	3.85	7.95-7.40
Pb ($C_{42}H_{28}NS$)	-	9.10	3.50	7.40-6.80

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