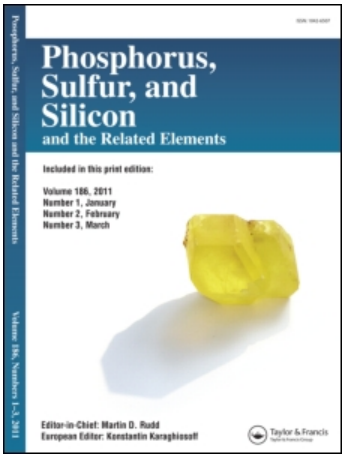

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SYNTHESIS, CHARACTERIZATION AND BIOCIDAL EFFECTS OF TRIORGANOLEAD(IV) COMPLEXES DERIVED FROM THIO-LIGANDS

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SYNTHESIS, CHARACTERIZATION AND BIOCIDAL EFFECTS OF TRIORGANOLEAD(IV) COMPLEXES DERIVED FROM THIO-LIGANDS

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The substitution reactions of heterocyclic thiosemicarbazones with triphenyllead(IV) chloride in 1:1 molar ratio give Ph_3PbL (L = anion of thiosemicarbazone derived from heterocyclic aldehyde or ketone) type of complexes. The elemental analyses, molecular weight determinations, conductivity measurements and spectral (IR, ^1H and ^{13}C NMR) studies have been used to elucidate their penta-coordinated structures. Some representative ligands and their metal chelates have also been screened for their antimicrobial effects against different species of pathogenic fungi and bacteria.

Key words: Triphenyllead(IV) complexes; thiosemicarbazones; spectral studies and antimicrobial studies.

INTRODUCTION

Thiosemicarbazones having heterocyclic ring have attracted much interest among the nitrogen and sulfur donor ligands, since their metal complexes show a remarkable diversity in coordination behaviour depending upon the nature of the central metal atom[1–3] and the reaction conditions. Moreover these complexes also exhibit significant biochemical activity. In the current literature, a number of silicon, germanium and tin complexes of sulfur donor ligands have been reported[4–6] but much remains to be explored regarding the complexing behaviour of thio-ligands towards the organolead(IV) moiety, which is in itself an interesting biologically active species.[7] This fact and our continuing interest in the field of coordination chemistry of organometallic compounds, prompted us to synthesize the triorganolead(IV) complexes with thio-ligands and study their mode of bonding as well as their biological aspects.

RESULTS AND DISCUSSION

Equimolar reactions of triphenyllead(IV) chloride with the potassium salt of monofunctional bidentate thiosemicarbazones (TsczH) in dry methanol lead to the formation of the following type of complexes.

$$Ph_3PbCl + Tscz{\cdot}K \rightarrow Ph_3Pb(Tscz) + KCl\downarrow$$

The resulting complexes are coloured solids, monomeric and non-electrolytic in nature. The mode of bonding of the ligands to the lead(IV) atom has been discussed on the basis of the following spectral studies.

IR Spectra

The IR spectra of all the ligands and their organolead(IV) complexes have been recorded. The disappearance of ν(NH) band in the region, 3300–2900 cm^{-1}, shift-

TABLE I

Physical properties and analyses of triphenyllead(IV) complexes

Reactants		Product formed and Colour	M.P. (°C)	Elemental analyses(%)			Mol.Wt.
Starting material (g)	Ligand (g)			N Found (Calcd.)	S Found (Calcd.)	Pb Found (Calcd.)	Found (Calcd.)
Ph_3PbCl	$C_7H_8N_4S$	$C_{25}H_{22}N_4SPb$	360	9.33	5.40	33.25	640.50
(0.62)	(0.24)	Reddish brown		(9.07)	(5.19)	(33.54)	(617.73)
Ph_3PbCl	$C_6H_7N_3SO$	$C_{24}H_{21}N_3SOPb$	282	7.18	5.07	34.55	590.71
(0.74)	(0.26)	Dark brown		(6.93)	(5.28)	(34.15)	(606.71)
Ph_3PbCl	$C_6H_7N_2S_2$	$C_{24}H_{21}N_3S_2Pb$	276	6.48	10.64	32.93	600.81
(0.70)	(0.27)	Dark brown		(6.75)	(10.30)	(33.26)	(622.77)
Ph_3PbCl	$C_{10}H_{10}N_4S$	$C_{28}H_{24}N_4SPb$	227	8.35	4.63	31.92	677.13
(0.79)	(0.36)	Chockolate		(8.54)	(4.89)	(31.59)	(631.76)
Ph_3PbCl	$C_8H_{10}N_4S$	$C_{26}H_{24}N_4SPb$	165	8.54	5.35	32.31	654.22
(0.65)	(0.27)	Lemon yellow		(8.87)	(5.07)	(32.79)	(631.76)
Ph_3PbCl	$C_7H_9N_3SO$	$C_{25}H_{23}N_3SOPb$	224	6.65	5.32	33.13	647.85
(0.72)	(0.28)	Dark brown		(6.77)	(5.16)	(33.37)	(620.74)
Ph_3PbCl	$C_7H_9N_3S_2$	$C_{25}H_{24}N_3S_2Pb$	252	6.83	10.31	32.90	660.55
(0.52)	(0.22)	Yellowish green		(6.59)	(10.07)	(32.54)	(636.81)
Ph_3PbCl	$C_{11}H_{12}N_4S$	$C_{29}H_{26}N_4SPb$	264	8.56	4.47	30.58	644.70
(0.40)	(0.20)	Green		(8.38)	(4.78)	(30.93)	(669.81)

Satisfactory carbon and hydrogen analyses have been obtained.

TABLE II

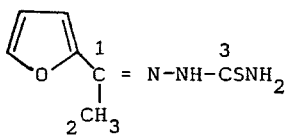
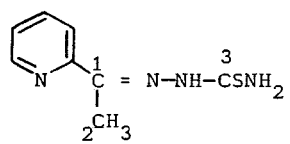
^{1}H NMR spectral data (δ, ppm) of ligands and their corresponding triphenyllead(IV) complexes

Compound	-NH	$-NH_2$	N=C(H)-/-C(CH$_3$)=N	Aromatic	Pb-C_6H_5
Fur.TsczH	10.74	2.83	8.68	8.06-6.85	-
Thiop.TsczH	10.63	2.93	8.65	8.44-7.18	-
Pyd.TsczH	10.91	2.86	8.72	8.58-7.29	-
2-AcFur.TsczH	11.54	2.84	2.37	7.93-7.11	-
2-AcThiop.TsczH	10.78	2.66	1.75	8.69-7.38	-
2-AcPyd.TsczH	10.85	2.69	1.91	8.83-7.42	-
Ph_3Pb (Fur.Tscz)	-	2.85	8.92	8.44-7.06	6.85
Ph_3Pb (Thiop.Tscz)	-	2.96	8.87	8.75-7.23	7.05
Ph_3Pb (Pyd.Tscz)	-	2.88	8.90	8.62-7.33	*
Ph_3Pb (2-AcFur.Tscz)	-	2.87	2.65	8.36-7.2	7.16
Ph_3Pb (2-AcThiop.Tscz)	-	2.69	1.91	8.83-7.42	6.92
Ph_3Pb (2-AcPyd.Tscz)	-	2.92	2.00	8.94-7.68	7.05

* = Overlapped with aromatic protons.

TABLE III

^{13}C NMR spectral data (δ, ppm) of ligands and their corresponding triphenyllead(IV) complexes

Compound	1	2	3	Aromatic / C_6H_5-Pb
	155.47	13.81	179.86	151.20, 146.63, 127.44, 127.68
Ph_3Pb(2-AcFur.Tscz)	150.26	12.15	171.24	151.88, 146.92, 128.08, 128.44, 129.27, 130.41, 132.82, 134.33
	154.23	13.68	178.24	147.67, 147.54, 135.62, 123.14, 119.94
Ph_3Pb(2-AcPyd.Tscz)	145.32	12.08	168.52	147.85, 147.83, 136.11, 123.65, 120.36, 133.25, 134.56, 135.83, 137.42

ing of azomethine vibration band to the lower wave number side from 1600 ± 10 to 1590 ± 5 cm^{-1} in the corresponding lead complexes and the appearance of new bands in the complexes in the region, 400–600 cm^{-1} due to ν(Pb—S)[8] and ν(Pb ← N)[9] vibrations clearly indicate the formation of lead chelates. Further, medium to strong intensity bands at ca. 230 and 210 cm^{-1} may be attributed to $\nu(Pb—C_6H_5)_{as}$ and $\nu(Pb—C_6H_5)_s$ vibrations,[10] respectively.

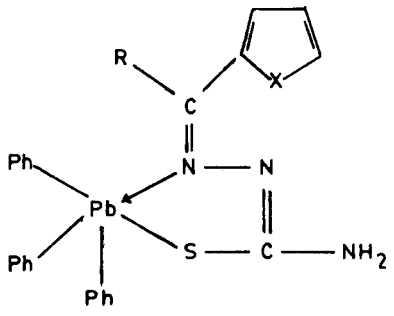
^1H NMR Spectra

To substantiate further the mode of bonding in these complexes, the ^1H NMR spectra of some ligands and their corresponding metal complexes have been recorded and the chemical shift values are enlisted in Table II. The signal due to NH proton in the ligands is found to be absent in the spectra of lead complexes indicating the chelation of ligand moiety through the replacement of proton from the functional group. Further, signals due to the azomethine and aromatic protons in the ligands show downfield shifting on complex formation.

^{13}C NMR Spectra

The ^{13}C NMR spectral data for three ligands (Thiop·TsczH, 2-AcFur·TsczH and 2-AcPyd·TsczH) along with their corresponding organolead(IV) complexes have also been recorded (Table III) to provide an additional evidence for the complex formation discussed above. The shifting in the position of resonance of carbon attached to sulfur atom suggests the bonding of sulfur with the lead atom in thiosemicarbazone derivatives. Further, the shifting of the azomethine (>C=N) carbon signal in the spectra of complexes as compared to the ligands, also confirms the involvement of nitrogen of azomethine group in coordination.

Thus on the basis of the above studies, it becomes clear that the ligands are behaving in a monofunctional bidentate manner coordinating through azomethine nitrogen and thiolic sulfur. Therefore a pentacoordinated structure (I) may be proposed for the resulting triphenyllead(IV) complexes. However, repeated efforts to grow single crystals of all of the above described organoderivatives by using various solvent combinations have been unsuccessful.



(R=H or CH_3 and X=O or S)

I

TABLE IV

Antifungal activity of ligands and their corresponding triphenyllead(IV) complexes

Compound	Average percentage inhibition after 7 days							
	Alternaria brassicae Conc. (ppm)		Alternaria tenuis Conc.(ppm)		Aspergillus niger Conc. (ppm)		Fusarium oxysporum Conc. (ppm)	
	200	400	200	400	200	400	200	400
2-AcPyd.TsczH	30	36	29	34	37	44	23	31
2-AcFur.TsczH	24	31	21	28	32	37	22	27
2-AcThiop.TsczH	35	39	31	38	41	47	36	24
Ph_3Pb (2-AcPyd.Tscz)	78	89	81	89	75	87	60	72
Ph_3Pb (2-AcFur.Tscz)	71	80	61	76	68	79	78	87
Ph_3Pb (2-AcThiop.Tscz)	81	90	88	94	80	95	74	88

TABLE V

Antibacterial activity of ligands and their corresponding triphenyllead(IV) complexes

Bacteria	Diameter of inhibition zone (mm)			
	1	2	3	4
E.coli	19	9	16	14
B.subtilis	16	12	19	17
S.aureus	13	10	18	15

1. 2-AcThiop. TsczH
2. 2-AcFur. TsczH
3. Ph_3Pb(2-AcThiop.Tscz)
4. Ph_3Pb(2-AcFur.Tscz)

FUNGICIDAL AND BACTERICIDAL SCREENING

The ligands and their corresponding triphenyllead(IV) complexes have been screened for their antifungal activity against *Alternaria brassicae*, *Alternaria tenuis*, *Aspergillus niger* and *Fusarium oxysporum* at 200 and 400 ppm concentrations. These have also been tested at 1000 ppm concentration against *E. coli*, *B. subtilis* and *S. aureus* for their bactericidal activity. The experimental results show that all the metal complexes are much more toxic than the chelating ligands. However, the toxicity of 2-AcThiop·TsczH and its triphenyllead(IV) complex is somewhat higher than other ligands and their complexes, possibly due to the difference in sulfur content. Further, the toxicity increases on increasing the concentration of the test compounds (Tables IV and V).

The antimicrobial activity of these ligands and their complexes can be ascribed in terms of chelation theory[11] and hydrogen bond formation between the nitrogen (>C=N) atom of the compounds and some bioreceptors in the cells of the fungi and bacteria, which in turn block the synthesis of proteins in them by inhibiting the movement of ribosome along mRNA inhibiting the synthesis of DNA in the cell nucleus.

EXPERIMENTAL

To maintain strictly anhydrous conditions for all the reactions, the chemical and solvents were dried and purified by standard methods before use.

Preparation of Thio-Ligands. The thiosemicarbazones (listed below) were prepared by the reported method.[12]

(1) Furan-2-carboxaldehyde thiosemicarbazone ($C_6H_7N_3SO$) = Fur·TsczH
(2) Thiophene-2-carboxaldehyde thiosemicarbazone ($C_6H_7N_3S_2$) = Thiop·TsczH
(3) Pyridine-2-carboxaldehyde thiosemicarbazone ($C_7H_8N_4S$) = Pyd·TsczH
(4) Indole-3-carboxaldehyde thiosemicarbazone ($C_{10}H_{10}N_4S$) = Indol·TsczH
(5) 2-Acetylfuran thiosemicarbazone ($C_7H_9N_3SO$) = 2-AcFur·TsczH
(6) 2-Acetylthiophene thiosemicarbazone ($C_7H_9N_3S_2$) = 2-AcThiop·TsczH
(7) 2-Acetylpyridine thiosemicarbazone ($C_8H_{10}N_4S$) = 2-AcPyd·TsczH
(8) 3-Acetylindole thiosemicarbazone ($C_{11}H_{12}N_4S$) = 3-AcIndol·TsczH

Preparation of Organolead(IV) Complexes. The potassium salt of the ligands was added to the calculated quantity of triphenyllead chloride in the medium of dry methanol. The contents were refluxed over a fractionating column for 10–12 hours. The contents were cooled and then filtered to separate the precipitated potassium chloride. The excess of solvent from the filtrate was removed under vacuum. The resulting products so obtained were repeatedly washed with a mixture of dry methanol and cyclohexane (1:1) and finally dried under reduced pressure for 3–4 hours. The details of these reactions along with the physical properties are enlisted in Table I.

Analytical Methods and Physical Measurements. The analytical methods and procedures of physical measurements are the same as reported earlier.[13]

Antifungal Screening. The fungi were grown in Czapeks Agar medium (sucrose 30 gm, KH_2PO_4, $NaNO_3$, $FeSO_4$, $MgSO_4$, KCl, Agar-agar and 1000 ml water) at 28 ± 2°C and the compounds after being dissolved in methanol at 200 and 400 ppm concentrations were mixed in the medium. The linear growth of the fungus was obtained by measuring the diameter of colony in petri-dishes after 7 days and the percentage inhibition was calculated by the following relationship.

$$\% \text{ inhibition} = \frac{(C - T) \times 100}{C}$$

C and T are the diameters of the fungus colony in control and test plate, respectively.

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