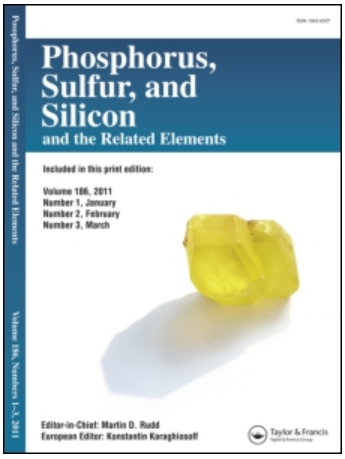

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME FUNGITOXIC ORGANOLEAD(IV) COMPLEXES OF SULFUR AND NITROGEN DONOR LIGANDS

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Some organolead(IV) complexes derived from biologically active sulfur and nitrogen donor ligands have been synthesized and characterized by elemental analyses, molecular weight determinations and conductivity measurements. The trigonal bipyramidal and octahedral geometries for these complexes have been proposed on the basis of electronic, infrared and NMR (^1H and ^{13}C) spectral evidences. The antifungal activity of some of the ligands and their complexes have also been evaluated against *Fursarium oxysporum* Scw. ex Frics f. sp. *Ciceri* (Pedwick) subram.

Key words: Organolead(IV); S-benzyldithiocarbazate, IR spectra; ^1H, ^{13}C NMR spectra; antifungal activity.

INTRODUCTION

The lead and organolead complexes of sulfur, nitrogen or oxygen donor ligands are a topic of interest due to their pronounced biological activity and interesting mode of bonding.[1–5] Our growing interest in the field of coordination chemistry of organolead complexes with biologically active sulfur and nitrogen donor ligands[6–10] has prompted us to synthesize and study the coordination pattern of diphenyllead(IV) complexes with the ligands derived by condensing various heterocyclic aldehydes and S-benzyldithiocarbazate along with their antifungal activity.

RESULTS AND DISCUSSION

The reactions of Ph_2PbCl_2 with the sodium salt of the ligands in 1:1 and 1:2 molar ratios have yielded $(C_6H_5)_2PbCl$ $[N\{C(H)\cdot R\}NCSSCH_2C_6H_5]$ and $(C_6H_5)_2Pb[N\{C(H)\cdot R\}NCSSCH_2C_6H_5]_2$ type of complexes respectively (Table I) (where R = Picolinealdehyde, 2-furaldehyde, 2-thiophenecarboxaldehyde or Indole-3-carboxaldehyde).

These are coloured solids, moisture sensitive, soluble in common organic solvents and monomeric and show non-electrolytic behaviour in DMF. The mode of bonding in these metal chelates has been proposed on the basis of electronic, infrared and NMR (^1H and ^{13}C) spectral evidences.

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TABLE I

Analyses and physical characteristics of lead(IV) complexes

Compound and colour	Melting point (°C)	Yield (%)	Analyses (%) C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	S Found (Calc.)	Pb Found (Calc.)	Mol Fo (C
$H_5)_2PbCl[N\{C(H)C_4H_3S\}NCSSCH_2C_6H_5]$ Dark yellow	d	78	43.23 (43.62)	3.24 (3.05)	3.97 (4.07)	13.48 (13.96)	29.96 (30.13)	66 (68
$H_5)_2PbCl[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]$ Yellow light	d	75	44.41 (44.66)	3.27 (3.13)	3.99 (4.17)	9.18 (9.53)	30.46 (30.85)	65 (67
$H_5)_2PbCl[N\{C(H)C_5H_4N\}NCSSCH_2C_6H_5]$ Yellow	178	86	45.33 (45.70)	3.38 (3.22)	5.86 (6.15)	9.07 (9.38)	30.11 (30.34)	66 (68
$H_5)_2PbCl[N\{C(H)C_8H_6N\}NCSSCH_2C_6H_5]$ Yellow light	104	84	48.06 (48.35)	3.31 (3.20)	5.47 (5.84)	8.47 (8.89)	28.52 (28.79)	69 (72
$H_5)_2Pb[N\{C(H)C_4H_3S\}NCSSCH_2C_6H_5]_2$ Yellowish brown	173	80	48.00 (48.35)	3.47 (3.39)	5.40 (5.94)	19.96 (20.36)	21.58 (21.97)	91 (94
$H_5)_2Pb[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]_2$ White cream	177	95	49.76 (50.04)	3.66 (3.51)	5.81 (6.51)	13.88 (14.05)	22.41 (22.74)	89 (91
$H_5)_2Pb[N\{C(H)C_5H_4N\}NCSSCH_2C_6H_5]_2$ Yellow dark	160	83	50.99 (51.44)	3.86 (3.64)	8.76 (9.00)	13.28 (13.72)	22.00 (22.20)	90 (93
$H_5)_2Pb[N\{C(H)C_8H_6N\}NCSSCH_2C_6H_5]_2$	165	85	54.42 (54.81)	3.68 (3.57)	8.01 (8.34)	12.26 (12.71)	20.18 (20.57)	98 (100

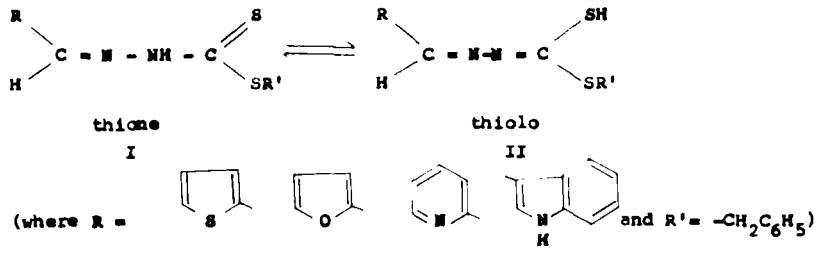
-decomposed.

ELECTRONIC SPECTRA

In the electronic spectra, a band at ca. 218 nm assigned to 1B band of the phenyl ring in the ligands shows red shift in the corresponding complexes. The ligand chromosphore, $\rangle C{=}N$ (at ca. 285 nm) shifts to the higher wavelength (ca. 300 nm) in the complexes suggesting the involvement of this group in bonding.

IR SPECTRA

The infrared spectra of these ligands in solid and solution forms indicate that the ligand exists in the tautomeric forms as indicated below:



A broad band at ca. 3100–3300 cm^{-1} due to ν NH disappears in the solution spectra and the appearance of a new band at ca. 2500 cm^{-1} may be ascribed to ν SH clearly supported the tautomeric equilibrium between the two forms of the ligands.[11]

The absence of ν SH/NH in the solid and solution spectra of the complexes shows the deprotonation of this group during complexation (Table II). A strong band observed at ca. 1635 cm^{-1} in both the solution and solid state spectra of all the complexes may be due to ν C=N mode[12] and its shifting (ca. 20 cm^{-1}) towards the higher region in comparison to the corresponding ligands (ca.

TABLE II

IR data (in cm^{-1}) of the ligands and their corresponding complexes

Compound	NH	C=N	Pb—N	Pb—S
$C_5H_4N{\cdot}C(H){:}NNHC(=S)SCH_2C_6H_5$	3100–3300	1605	—	—
$Ph_2PbCl[N\{C(H)C_5H_4N\}NCSSCH_2C_6H_5]$	—	1628	540	445
$Ph_2Pb[N\{C(H)C_5H_4N\}NCSSCH_2C_6H_5]_2$	—	1630	535	450
$C_4H_3O{\cdot}C(H){:}NNHC(=S)SCH_2C_6H_5$	3120–3300	1600	—	—
$Ph_2PbCl[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]$	—	1630	540	440
$Ph_2Pb[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]_2$	—	1635	545	450
$C_4H_3S{\cdot}C(H){:}N{\cdot}NHC(=S)—S—CH_2C_6H_5$	3100–3300	1605	—	—
$Ph_2PbCl[N\{C(H)C_4H_3S\}NCSSCH_2C_6H_5]$	—	1620	545	445
$Ph_2Pb[N\{C(H)C_4H_3S\}NCSSCH_2C_6H_5$	—	1625	540	440

1605 cm^{-1}) indicates the participation of the azomethine nitrogen in bonding. Further, some additional new bands in the ca. 600–400 cm^{-1} region in the complexes may be assigned to ν(Pb—S) and ν(Pb—N) vibrations.[13]

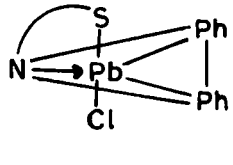
^{1}H NMR SPECTRA

In the ^{1}H NMR spectra of the ligands the signals observed at δ 9.96(1), 9.99(4) ppm and δ 3.32(1), 3.36(4) ppm may be ascribed to NH and SH protons respectively and which have been further supported by the deuterium exchange technique. The absence of these signals in the spectra of their complexes tentatively suggests their deprotonation.[14] In the spectra of the ligands for the signal for azomethine proton has been found to be overlapping with the multiplets of aromatic protons, whereas, it is observed at δ 8.84–8.96 ppm in the spectra of two corresponding complexes. The downfield shift in the azomethine proton indicates the involvement of C=N group in bonding (Table III).

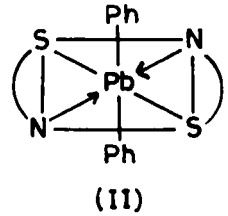
^{13}C NMR SPECTRA

Further, the mode of bonding in these complexes has been substantiated by ^{13}C NMR spectral data. The marked shifting (ca. δ 4–6 ppm) in the positions of carbons attached to S and N atoms clearly indicates that both thiolic sulfur and azomethine nitrogen are participating in complexation (Table IV).

On the basis of above spectral evidences the trigonal bipyramidal (**I**) and octahedral geometries (**II**) around the lead atom may be proposed.



(I)



(II)

TABLE III

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

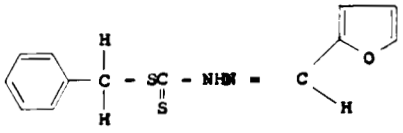
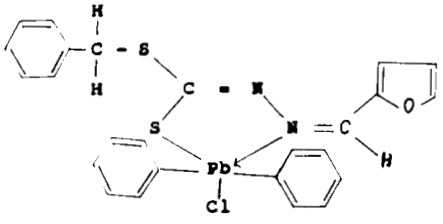
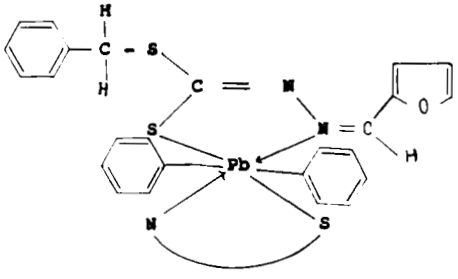
S. No.	Compound	NH	SH	H—C=N	Aromatic	S—CH_2—Ar
1.	$C_4H_3S{\cdot}C(H)NNHCSSCH_2C_6H_5$	9.96s	3.32bs	*	8.55–7.47m	1.33s
2.	$(C_6H_5)_2PbCl[N\{C(H)C_4H_3S\}NCSSCH_2C_6H_5]$	—	—	8.96s	8.62–7.52m	1.27s
3.	$(C_6H_5)_2Pb[N\{C(H)C_4H_3S\}NCSSCH_2C_6H_5]_2$	—	—	8.88s	8.60–7.49m	1.29s
4.	$C_4H_3O{\cdot}C(H)NNHCSSCH_2C_6H_5$	8.99s	3.36bs	*	8.48–7.34m	1.46s
5.	$(C_6H_5)_2PbCl[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]$	—	—	8.84s	8.64–7.66m	1.38s
6.	$(C_6H_5)_2Pb[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]_2$	—	—	8.86s	8.58–7.57m	1.39s

Note: s = singlet; bs = broad signal; m = multiplet.

* = merged with aromatic protons.

TABLE IV

^{13}C NMR (δ, ppm) spectral data for ligand and its corresponding 1:1 and 1:2 lead(IV) complexes

Compound	Chemical shift values
	C_1, 164.751; C_2, 135.670; C_3, 128.129; C_4, 127.261; C_5, 131.704; C_6, 166.159; C_7, 16.3; C_8, 127.479; C_9, 126.937; C_{10}, 126.287; C_{11}, 125.831
	C_1, 161.067; C_2, 135.605; C_3, 128.454; C_4, 127.804; C_5, 131.379; C_6, 162.643; C_7, 16.75: C_8, 127.371; C_9, 126.829; C_{10}, 126.287; C_{11}, 125.371; C_{12}, 128.761; C_{13}, 127.567; C_{14}, 125.867
	C_1, 160.78; C_2, 135.05; C_3, 128.365; C_4, 128.96; C_5, 130.61; C_6, 161.97; C_7, 16.98; C_8, 126.54; C_9, 126.118; C_{10}, 125.17; C_{11}, 125.867; C_{12}, 127.77; C_{13}, 127.36; C_{14}, 124.76

ANTIFUNGAL ACTIVITY

The antifungal activity of the ligand and its corresponding complexes has been evaluated on *Fusarium oxysporum* Scw. ex Fries f. sp. *Ciceri* (Pedwick) Subram. It is quite clear from the fungicidal screening data that the metal chelates are more fungitoxic than the ligand itself. However, the results (Table V) show that the fungitoxicity of the ligand and its complexes decreases on lowering the concentrations. On the basis of screening data it has been concluded that the

TABLE V

Fungicidal activity of 2-furaldehyde-S-benzylthiocarbazate and its complexes (temperature = 25 ± 1°C)

Compound	Average percentage inhibition after 5 days		
	Fusarium oxysporum conc. used (in ppm)		
	50 ppm	100 ppm	150 ppm
$C_4H_3O{\cdot}C(H){\cdot}NNHCSSCH_2C_6H_5$	5.50	5.50	22.84
$(C_6H_5)_2PbCl[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]$	10.34	17.84	27.51
$(C_6H_5)_2Pb[N\{C(H)C_4H_3O\}NCSSCH_2C_6H_5]_2$	15.75	24.40	38.57

organolead complexes are not very active even in the presence of two sulfur atoms probably due to their lesser solubility and bigger size in comparison to other IV B group elements.[15-18]

EXPERIMENTAL

All the manipulations were carried out under anhydrous conditions and the chemicals used were of reagent grade.

The ligands were prepared by the condensation of heterocyclic aldehydes (i) Picolinaldehyde, (ii) 2-furaldehyde, (iii) 2-thiophenecarboxaldehyde, (iv) Indole-3-carboxaldehyde) with S-benzyldithiocarbazate in equimolar ratio in alcohol. These were characterized by elemental analyses, melting point, IR and NMR spectral studies. The physical chracteristics of these ligands are given below:

	Ligands	Colour	State	m.p. °C
a.	$C_{14}H_{13}N_3S_2$	Dark yellow	semisolid	—
b.	$C_{13}H_{12}N_2S_2O$	White cream	solid	145
c.	$C_{13}H_{12}N_2S_3$	Yellow brown	solid	107
d.	$C_{17}H_{15}N_3S_2$	Light brown	solid	115

The sodium salt of these ligands were prepared by refluxing the ligands with sodium methoxide.

Preparation of the complexes

A methanolic solution of Ph_2PbCl_2 (0.01 mol) was added to a methanolic solution of sodium salt of picolinaldehyde-S-benzyldithiocarbazate (0.02 mol) and reaction mixture was refluxed for 6 h. The sodium chloride so formed was filtered off and on removing the solvent under reduced pressure a coloured solid separated out.

It was repeatedly washed with dry cyclohexane so as to ensure its purity and dried over pump. The rest of the complexes were prepared by similar methods.

Analytical Method and Physical Measurements

Carbon and hydrogen analyses were carried out at the microanalytical laboratory of this department, whereas lead and sulfur were estimated gravimetrically.[3] Nitrogen was estimated by the Kjeldahl's method.

Molar conductivity was measured by the Systronics conductivity bridge model 305 and molecular weights were determined by the Rast Camphor method.

Electronic spectra of ligands and complexes were recorded in methanol on a Perkin–Elmer 202 and IR spectra were scanned as KBr pellets or nujol mulls and in chloroform solution on a Perkin–Elmer 577 spectrophotometer. However, ^1H and ^{13}C NMR spectra were recorded on a Jeol FX90 Q spectrometer in $CDCl_3$ and $DMSOd_6$ solutions respectively using TMS as an internal reference.

The antifungal activity of the representative ligand and its corresponding lead(IV) complexes were evaluated against *Fusarium oxysporum* by agar plate technique at 25, 100 and 150 ppm concentrations. The number of replications were three in each case. The inhibition percentage (Table IV) was calculated by the formula.

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

where C = diameter of the fungus colony in control plate after five days; T = diameter of the fungus colony in test plate in the same time.

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