

signal due to aromatic fluorine atom at δ 71.0 ppm (2F), δ 179.0 (1F) and δ 88.0 (2F).

In all the above compounds the absorption band due to Ar. C-F stretching vibration appear between 1260-1200 cm^{-1} .

The antibacterial activity of all synthesized compounds given in table 1 was studied against gramnegative bacteria *Escherichia coli* (table 2). The results indicated that only a few compounds possess prominent activity. Compound Nos. 5, 6, 7 possess maximum activity.

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DIPHENYL LEAD (IV) DIODIDE COMPLEXES WITH SUBSTITUTED 2-AMINOTHIAZOLES

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ORGANO lead(IV) compounds have generated considerable interest^{1,2}. The synthesis and spectral studies on organo lead(IV) complexes of dithiocarbamates³, triphenylphosphin oxide⁴, 1-chloro-1,2,3-benzotriazoles⁵, acetylacetone⁶ have been reported. The spectral studies on five coordinate diorganolead(IV) complexes of ONO and SNO donor ligands have been documented⁷. The organo lead(IV) complexes with ONNO tetradentate ligands have been studied by DiBianca *et al.*⁸. However, attempts have not been made on complexes of diorganolead(IV) with aminothiazoles. The present communication deals

with the preparation and spectral properties of diphenyl lead(IV) diiodide complexes of substituted 2-aminothiazoles.

All chemicals used were of BDH grade. The ligands 2-amino-4-phenylthiazole (apt)⁹, 2-amino-4-ethyl-5-methylthiazole (aemt)¹⁰, 2-amino-4,5,6,7-tetrahydrobenzothiazole (athbt)¹¹, 2-amino-4-methyl-5-carbethoxythiazole (amct) and diphenyl lead(IV) diiodide¹² were synthesized according to published methods.

The complexes were prepared by mixing diphenyl lead(IV) diiodide and the appropriate ligand solutions in 1,2-dichloroethane in the ratio of 1:2 moles. The mixture was refluxed for 2 hrs and concentrated to a small volume. The yellowish orange coloured complex was isolated by the addition of petroleum ether (40-60°). The solid complex was filtered, washed with aliquots of 1,2-dichloroethane followed by dry petroleum ether. It was dried under vacuum.

The complexes were analysed for the metal, nitrogen, sulphur and iodine by standard procedures. The analytical data agreed with the calculated values of the complexes within the limits of experimental errors. The molar conductance measurements of the complexes in acetonitrile at a concentration $\sim 1 \times 10^{-3}$ M were taken on ELICO conductivity bridge. Infrared spectra (4000-400 cm^{-1}) of ligands and their complexes were recorded on Carl-Zeiss UR-10 spectrophotometer. The NMR spectra were taken on a Varian T-60 spectrometer in CDCl_3 using TMS as internal standard.

The complexes are crystalline and yellowish orange in colour and have $\text{Ph}_2\text{PbL}_2\text{I}_2$ stoichiometry. The molar conductance in acetonitrile solution lies in the range 12-17 mhos $\text{cm}^2 \text{mole}^{-1}$. The low conductance accounts for the non-electrolytic nature of all the complexes. An attempt to determine the molecular weight of these complexes failed due to poor solubility of the complexes in common organic inert solvents.

2-Aminothiazoles can coordinate to central metal through sulphur, ring nitrogen or amino nitrogen. Recent studies on the complexes of Co(II), Ni(II), Cu(II) and Ti(IV) with the above ligands, have indicated coordination through amino nitrogen of ligand molecule.¹³⁻¹⁶ However, metal sulphur bonding in Ag(I)¹⁷ and metal ring nitrogen bonding in Co(II), Cu(II) and Hg(II) complexes of 2-aminobenzothiazoles have been reported.¹⁸ This makes it interesting to ascertain the coordination of substituted 2-aminothiazoles to diorganolead(IV). The infrared band assignment for the major bands is presented in table 1.

The solution spectra of ligands exhibit bands at $\sim 3500 \text{ cm}^{-1}$ and $\sim 3400 \text{ cm}^{-1}$ whereas solid phase spectra show in the range 3450-3350 cm^{-1} and 3300-3100 cm^{-1} . These bands are assigned to ν_{NH} vibrations of NH_2 group. Thus the difference about

TABLE I

Infrared frequencies and their assignments (cm^{-1})

Compound	Phase	ν_{NH}	$\delta(\text{NH}_2)$	Exocyclic $\nu_{\text{C-N}}$	
(apt)	CHCl_3	3510s	3410s	1615s	1346ms
	Nujol	3450ms	3272ms	1610s	1350sbr
$\text{Ph}_2\text{Pb}(\text{apt})_2\text{I}_2$ aemt	Nujol	3300wbr	3170wbr	1618sbr	1355sbr
	CHCl_3	3500s	3405s	1612vs	1346w
	Nujol	3448s	3275ms	1616s	1343ms
$\text{Ph}_2\text{Pb}(\text{aemt})_2\text{I}_2$ athbt	Nujol	3300wbr	—	1632ms	1355ms
	CHCl_3	3505s	3406vs	1615vs	1312vs
	Nujol	3385s	3295ms	1615vs	1320s
$\text{Ph}_2\text{Pb}(\text{athbt})_2\text{I}_2$ amct	Nujol	3270ms	3160ms	1630s	1352ms
	CHCl_3	3416s	3286ms	1615s	1324ms
	Nujol	3312ms	3100br	—	1332ms
$\text{Ph}_2\text{Pb}(\text{amct})_2\text{I}_2$	Nujol	—	3100br	1668ms	1332ms

s = sharp; m = medium; br = broad; w = weak.

100 cm^{-1} in the position of ν_{NH} frequency of ligands in solution and solid phase indicates the presence of strong N-H . . . N and N-H . . . S type of intermolecular hydrogen bonding. Similar types of hydrogen bonding have been observed in simple 2-amino-thiazole.¹⁴⁻¹⁵ In order to compensate the effect of hydrogen bonding, the spectra of the complexes have been compared with the solution phase spectra of the ligands. The negative shift of the order of 200 cm^{-1} in ν_{NH} frequencies and a positive shift ($50\text{--}10\text{ cm}^{-1}$) in $\delta(\text{NH}_2)$ indicate the coordination through nitrogen atom of amino group.¹³ The ring stretching and skeletal vibrations observed in the range $1590\text{--}1385\text{ cm}^{-1}$ and $1120\text{--}885\text{ cm}^{-1}$ respectively of ligands practically remain unaffected on complexation which suggest coordination of amino nitrogen. The positive shift ($40\text{--}10\text{ cm}^{-1}$) of exocyclic $\nu_{\text{C-N}}$ is further an evidence in favour of bonding through amino nitrogen.¹⁴⁻¹⁶ In the case of free ligands, a medium strong band observed in the range $730\text{--}690\text{ cm}^{-1}$ is assigned to ν_{CS} vibrations.¹⁴ A positive shift ($30\text{--}10\text{ cm}^{-1}$) with the increase in intensity of this band in all complexes rules out the possibility of coordination through ring sulphur.

The NMR spectra of substituted 2-aminothiazoles exhibit a broad amino proton signal in the region $5.02\text{--}5.50\text{ ppm}$. The down field shift ($\sim 0.25\text{ ppm}$) of this band on complexation indicates the participation of amino group in coordination and the existence of Pb-N bond in CDCl_3 solution. The presence of a single amino proton signal in the case of complexes, clearly implies that all the ligands are centrosymmetrically disposed around the central metal ion.

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POLAROGRAPHIC DETERMINATION OF Pd(II) USING CATALYTIC H-WAVES

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LITERATURE records many attempts to determine Pd(II) by D. C. Polarography¹⁻⁵. With one exception⁶, the lower limits of estimation had hardly been 10 ppm and this exception has a prior concentration step of an extraction procedure before final estimation. It is well known that metal complexes of thiosemicarbazide (TS) give catalytic waves some of which have been analytically useful⁷⁻¹⁰ Pd(II) at pH 1.5, in presence of TS, produces a catalytic hydrogen-wave with a large sharp maximum at potentials 170 mV more positive than the normal hydrogen-wave. The I_{max} at the peak potential is found to be proportional to the concentration of Pd(II) in the range, 0.5 – 11.0 ppm.

Polaritor P03 pen recording type polarograph, with a built-in saturated calomel anode is used. The characteristic of the capillary is $2.069 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ at $h_{Hg} = 30 \text{ cm}$ at zero applied potential. Elico pH meter model LI 10 is used for adjusting the pH values correct to ± 0.1 pH.

Unless otherwise stated, all the chemicals are of reagent grade. PdCl₂ (John-Matthey) is dissolved in the minimum quantity of 4NHCl, made up to 100 ml with deionised water and standardised gravimetrically¹¹. This solution (0.0948 M) is diluted appropriately for different studies. TS (Loba-Chemie) is prepared in deionised water to make a stock solution of 0.1 M. Sodium perchlorate is used as the supporting electrolyte to maintain a constant ionic strength of 0.6 M. Before subjecting to polarography the final solution is deoxygenated for 10 min in a stream of oxygen-free nitrogen.

Pd(II) in NaClO₄ medium, at pH 1.5, produces wave $E_{1/2} = +0.06 \text{ V}$ vs SCE due to mercurous

ions¹² liberated chemically by Pd²⁺ ions and an additional wave due to H⁺ reduction with a small maximum at -1.67 V vs SCE. In the presence of TS, the peak potential at -1.67 V shifts to more positive values. With large excess of TS (0.02 M), the maximum at -1.50 V ceases its further shift. Under these conditions addition of even a small amount of Pd(II) increases the I_{max} to about 3-fold compared to the increase of the limiting current. The maximum is however completely suppressed by 0.001% gelatin.

The fact that the pre-wave is catalytic in nature is clear from its independent behaviour with h_{Hg} at high TS concentration and its low temperature coefficient (0.4 %°K). Further the positive shift in potential of the hydrogen reduction wave by the complex also confirms the catalytic nature of the process. That the protons are involved in the reduction process is confirmed by the hydrogen evolution during the macroelectrolysis controlled at -1.60 V vs SCE with a Hg pool cathode under polarographically identical conditions. Also any alteration in H⁺ has a marked influence on the I_{max} at the peak potential. The relationship between I_{max} and Pd(II) concentration, is found to be proportional in the range 0.5 – 11.0 ppm with an accuracy of $\pm 2\%$.

In order to assess the possible analytical applicability of the above method, the effect of other noble metals in the estimation of 2.2 ppm of Pd(II) has been studied, an error of $\pm 2\%$ in the analysis being considered tolerable. The limits of interference are 1 ppm of Ir, 4 ppm of Rh, 10 ppm of Pt and 20 ppm of both Ru and Os. This method has been found to be quite satisfactory for the estimation of Pd(II) in synthetic mixtures simulating the compositions of jewellery metal¹³, electrical standard resistors¹⁴ and catalyst¹⁵ containing Pd(II) and other noble metals.

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