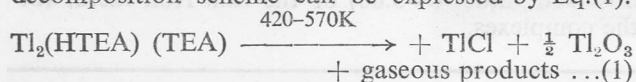


in minimum amount of 2N HCl, with aqueous H₃TEA (30 v/v) till a yellow precipitate formed, just dissolved giving a yellow coloured solution. The solution was extracted with chloroform and the organic extract dried over anhyd. Na₂SO₄. The solvent was removed by blowing air and the solid obtained was dried in a desiccator. (Found : Tl, 64.5; Cl, 5.6; N, 4.8. C₁₂H₂₅N₂ CITl₂ requires Tl, 63.71; Cl, 5.53; N, 4.37%). The X-ray powder diffraction patterns of the complex gave the following d_{hkl} (Å) values : 6.48s, 4.79s, 3.96w, 3.11m, 2.84m, 2.46w, 2.18w.

The thermogravimetric studies were made in air at a heating rate of 6°C per min. The mass change and the temperature curves suggested that there are three distinct stages in the decomposition process. The first stage starts at 420K with a rapid mass loss upto 450K and completes at 570K losing 37% of mass. The second stage begins around 670K and is complete around 780K, registering a mass loss of 64%. The final stage takes place in the temperature range 900-1075K. No residue was left at 1075. In separate experiments, the complex was heated to 570 and 870 K and the residues analysed by chemical and X-ray methods. The product at 570 K contained 43.1% Tl(I) and 43.9% of Tl(III). The X-ray powder patterns gave d_{hkl} (Å) values 3.84, 2.73s, 2.24w, 1.92w, 1.72w corresponding to TlCl (ref. 8a); and 3.04s, 2.64s, 1.87m, 1.60w corresponding to Tl₂O₃ (ref. 8b). Further, the infrared spectrum of the residue did not indicate the presence of any organic moiety. The X-ray patterns and the chemical analysis of the residue at 870 K suggested it to be pure Tl₂O₃. It is also known⁹ that TlCl volatilizes in the temperature range 673-873 K. Thus, the mixture of TlCl and Tl₂O₃ formed during the decomposition, loses TlCl in the second stage of mass loss and Tl₂O₃ in the final stage. The decomposition scheme can be expressed by Eq.(1).



The conductance of the complex in chloroform gave the molar conductivity value of 3.9 mhos cm⁻² suggesting it to be a non-electrolyte. The electronic spectrum in chloroform gave two transitions at 392 (ε = 3 × 10⁴) and 298 nm (ε = 9 × 10⁴) which are ascribed to the charge transfer bands.

The νOH at 3400 observed in the IR spectrum ν_{max} in cm⁻¹ of the free ligand is shifted to 3180 with a reduced intensity in the spectrum of the complex, suggesting bonding of OH group to Tl. It has been reported¹⁰⁻¹⁴ that in chlorothallates νTl-Cl appears in the region 270-300 and the absorption at 275 observed in the present complex is assigned to νTl-Cl. The band at 400 observed is tentatively assigned^{12,13,15} to νTl-O. In several Tl(III) complexes of N-containing ligands νTl-N is reported^{11,14} to appear below 200 which is beyond the range of the spectrophotometer used in the present study.

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Synthesis & Characterisation of Anionic Diaryltetrahalotellurates(IV)

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Diaryltetrahalotellurates(IV) of the type [R₄M]₂[R'₂TeX₄] (where R=Me, Et, Bu, Ph; M=N, P, As or Sb; R'=C₆H₅, *p*-CH₃OC₆H₄; X=Cl, Br) have been obtained by the interaction of diaryltellurium dichlorides and tetraorgano ammonium, phosphonium, arsonium or stibonium halides in aqueous and non-aqueous media. Halogen exchange between a complex anion and silver or alkali metal halides or pseudohalides yields the corresponding pseudohalide or mixed halide-pseudohalide derivative. The ionic nature of the complexes is established through conductance measurements.

ALTHOUGH inorganic penta- and hexa-halo-tellurates(IV) have been reported¹, the anionic organotellurium complexes are less known and except for [Me₃Te]⁺[MeTeI₄]⁻ (ref.2), others are of recent origin³⁻⁶. The preparation and characterisation of a number of tetrahalo- and tetrapseudohalo-diaryltellurates(IV) are reported in this note.

Diphenyltellurium dichloride⁷, bis(*p*-methoxyphenyl)tellurium dichloride⁸, tetraphenylphosphonium bromide, tetraphenylarsonium chloride⁹ and tetraphenylstibonium chloride⁹ were prepared by reported methods. Tellurium and halogens or pseudohalogens were determined volumetrically and gravimetrically respectively^{10,11}.

Preparation of anionic complexes — Tetraorgano ammonium, phosphonium, arsonium and stibonium complexes of tetrahalodiaryltellurates(IV) were prepared as follows: diaryltellurium dichloride (2mmol) was refluxed with a solution of the corresponding onium salt (4 mmol) in chloroform or ethanol (30 ml) for 4-5 hr. Concentration of the solution followed by the addition of ethyl acetate to the reaction mixture afforded the complexes which were recrystallised from dichloromethane-ethyl acetate (1:1)

or methyl cyanide-ethyl acetate (1:1). The characterization data of the complexes are listed in Table 1. All the compounds were crystallised as needles in yields between 80 and 100%.

Preparation of tetrachlorodiphenyltellurate(IV) in aqueous media — Diphenyltellurium dichloride

TABLE 1 — CHARACTERISATION DATA OF TETRAHALODIARYL-TELLURATES(IV)

Compd	[R ₄ M] ₂ [R' ₂ TeCl ₂ X ₂]			Colour (m.p. °C)	Found (calc.) (%)	
	R	M	X		Te	X
					FOR R' = C ₆ H ₅	
I	Me	N	Cl	White (145)	23.00 (22.32)	24.59 (24.79)
II	Et	N	Cl	White (87-90)	18.58 (18.65)	20.95 (20.72)
III	Bu	N	Br	Yellow (105)	13.12 (12.79)	23.09 (22.13)
IV	Ph	P	Cl	White (230-35)	11.36 (11.57)	12.60 (12.36)
V	Ph	P	Br	White (187-89)	10.08 (10.71)	18.58 (19.36)
VI	Ph	As	Cl	White (198-200)	10.62 (10.71)	11.89 (11.91)
VII	Ph	Sb	Cl	White (>240)	9.40 (9.93)	11.00 (11.04)
					FOR R' = <i>p</i> -CH ₃ OC ₆ H ₄	
VIII	Me	N	Cl	White (165)	20.41 (20.19)	23.05 (22.43)
IX	Et	N	Cl	White (105)	17.00 (17.15)	18.98 (18.05)
X	Et	N	Br ^(a)	Yellow (117-20)	13.68 (13.79)	34.88 (34.89)
XI	Ph	P	Cl	White (247-48)	11.00 (10.97)	12.00 (12.19)
XII	Ph	P	Br	White (>240)	9.87 (10.19)	18.98 (18.47)
XIII	Ph	As	Cl	White (222-25)	10.21 (10.20)	10.68 (11.34)
XIV	Ph	Sb	Cl	White (>240)	8.90 (9.49)	9.99 (10.55)

(a) In this reaction the reactant was (*p*-CH₃OC₆H₄)₂TeI₂ instead of the dichloride.

(0.705 g, 2 mmol) was taken in 6*N* HCl and a solution of tetraphenylphosphonium chloride (1.4 g, 4 mmol) in water (25 ml) added to it with constant stirring. The complex that precipitated out in quantitative yield was filtered off. The product was identical with that obtained by the above method. The complex [(C₆H₅)₄P]₂[(*p*-CH₃OC₆H₄)₂TeCl₄] was obtained following the same procedure.

Pseudohalogen exchange reactions — To convert tetrachloro tellurate into tetracyanatotellurate(IV), bis(tetraphenylphosphonium)tetrachlorobis(*p*-methoxyphenyl) tellurate (1.162 g, 1 mmol) was stirred with silver cyanate (0.6 g, 4 mmol) in chloroform (30 ml) for 2 hr and then refluxed for 3-4 hr. The precipitated silver chloride was rejected and the filtrate on evaporation gave tetracyanatobis(*p*-methoxyphenyl)tellurate(IV), yield-92%, m.p. 230-31°.

Halogen exchange reactions — In a typical experiment an aqueous solution of KI (excess) was added to a solution of bis(tetraphenylarsonium) tetrachlorodiphenyltellurate (IV) (1.19 g, 1 mmol) in 4*N* HCl with constant stirring. The corresponding iodo compound obtained in quantitative yield, was filtered, washed with water and dried, m.p. 290(d).

Halogen exchange reactions of complex anions afford new complexes (Table 2) not accessible by previous methods. The stability and insolubility of complex anions increase in the order, [R₂TeCl₄]²⁻ < [R₂TeBr₄]²⁻ < [R₂TeI₄]²⁻, due to which tetrachloro or dichlorodibromotellurates are irreversibly converted to the tetraiodo derivatives in aqueous media. The tetrapseudohalotellurates were also prepared in a similar fashion in non-aqueous medium.

The molar conductances (10⁻³*M* solution) are in the ranges 160-200, 240-300 and 52-60Ω⁻¹ mol⁻¹ cm² in methanol, acetonitrile and nitrobenzene, respectively. These values correspond to 2:1 electrolytes¹². This is further supported by the observed value (~3.00) of the vant Hoff factor for the complexes.

TABLE 2 — ANIONIC COMPLEXES OBTAINED BY HALOGEN EXCHANGE REACTIONS

Compd*	Reactant*	[R ₄ M] ₂ [R' ₂ TeX ₂ Y ₂]			Colour (m.p., °C)	Found (calc.) (%)				
		R	M	R'		Te	(X+Y)	C	H	N
						X=I; Y=I				
XV	IV	C ₆ H ₅	P	C ₆ H ₅	Yellowish orange (225d)	8.70 (8.69)	34.29 (34.57)	49.04 (49.08)	3.48 (3.43)	—
XVI	VI	C ₆ H ₅	As	C ₆ H ₅	Red brown (290d)	8.52 (8.19)	32.00 (32.62)	—	—	—
XVII	XI	C ₆ H ₅	P	<i>p</i> -CH ₃ OC ₆ H ₄	Red brown (>240)	8.56 (8.52)	32.99 (32.94)	—	—	—
XVIII	XIII	C ₆ H ₄	As	<i>p</i> -CH ₃ OC ₆ H ₄	Red brown (246)	7.90 (8.05)	32.04 (32.01)	—	—	—
						X=SCN; Y=SCN				
XIX	IV	C ₆ H ₅	P	C ₆ H ₅	Pink (170-72)	9.89 (10.69)	19.07 (19.47)	64.48 (64.43)	4.00 (4.22)	4.64 (4.69)
XX	XIII	C ₆ H ₅	As	<i>p</i> -CH ₃ OC ₆ H ₄	White (140)	9.35 (9.74)	16.86 (17.74)	60.22 (60.56)	4.08 (4.15)	4.38 (4.28)
						X=CNO; Y=CNO				
XXI	XI	C ₆ H ₅	P	<i>p</i> -CH ₃ OC ₆ H ₄	White (230-31)	10.07 (11.03)	—	68.88 (68.53)	4.78 (4.70)	4.98 (4.84)

*Compounds listed in Table 1.

Infrared absorption frequencies due to fundamental modes of vibration, $\sqrt{C-N}$, $\sqrt{C-X}$ and $\delta N CX$ ($X=O,S$), of the pseudohalide groups are listed in Table 2. Out of these the $\sqrt{C-X}$ has been reliably used to distinguish between the normal and the iso form of the pseudohalide groups. The position of these absorptions for the complexes reported herein indicate their iso-structure ($Te-N CX$)¹³. The NMR spectra of $[(C_6H_5)_4P]_2 [(C_6H_5)_2 TeCl_4]$ was recorded at room temperature. Two multiplets are observed at τ 2-2.6 and τ 7.45 due to phenyl ring protons and methoxy protons respectively. The spectrum, including the integrations, corresponds to the proposed formulation of the compound.

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Boron Complexes of Schiff Bases Derived from *o*-Hydroxyacetophenone & Alkylamines or Arylamines†

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Boron derivatives of the type $B(OC_2H_5)_{3-n}(SB)_n$ [where $n = 1, 2, 3$ and SB^- represents the anion of monofunctional bidentate schiff base, SBH] have been prepared. Monofunctional bidentate schiff bases have been prepared by the condensation of *o*-hydroxyacetophenone with *n*-propylamine, isopropylamine or aniline. The ethoxyboron schiff base derivatives undergo exchange reactions with *t*-butanol and give the corresponding *t*-butoxy derivatives. The resulting compounds have been characterized by their elemental analyses, molecular weight determinations, conductance measurements and IR spectral studies.

A survey of the literature revealed that except for a few ketiminoboranes¹⁻³ and simple

adducts⁴, schiff base complexes of boron have received scanty attention. Boron derivatives of monofunctional bidentate schiff bases have now been synthesised and characterised on the basis of molecular weights, analytical data, molar conductances and IR data.

All the reactions were carried out under strictly anhydrous conditions. Benzene (BDH) and dimethylformamide (E. Merck) were dried by the usual methods. Triethoxyborane was prepared by reacting boric acid with ethanol in benzene medium and simultaneous removal of water liberated during the reaction azeotropically⁵. It was freshly distilled before use.

Schiff bases were prepared by the reactions of *o*-hydroxyacetophenone with *n*-propyl-, isopropylamine or aniline in equimolar proportions in benzene medium⁶ using a water separator. The excess of solvent was removed and the products purified by distillation under reduced pressure. The schiff bases are yellow in colour and have low melting points.

Preparation of boron schiff base derivatives — Triethoxyborane was dissolved in dry benzene and the calculated amount of the schiff base added to it. No appreciable heat was produced. The contents were refluxed over a fractionating column and the ethanol liberated in the reaction collected azeotropically. After the reaction was complete the excess solvent was distilled off and the products dried *in*

TABLE 1 — PRODUCTS FORMED IN THE REACTIONS OF TRIETHOXYBORANE WITH THE SCHIFF BASES OR *t*-BUTANOL

Product	Found (calc) (%)		Mol. wt found (calc.)
	B	N	
$B(OC_2H_5)_2(C_{11}H_{14}NO)$	3.86 (3.90)	5.11 (5.05)	268 (277)
$B(OC_2H_5)(C_{11}H_{14}NO)_2$	2.59 (2.65)	6.81 (6.86)	392 (408)
$B(C_{11}H_{14}NO)_3$	1.98 (2.01)	7.69 (7.78)	524 (539)
$B(OC_2H_5)_2(C_{11}H_{14}NO)^*$	3.87 (3.90)	4.98 (5.05)	269 (277)
$B(OC_2H_5)_2(C_{11}H_{14}NO)_2^*$	2.61 (2.65)	6.88 (6.86)	389 (408)
$B(C_{11}H_{14}NO)_3^*$	2.07 (2.01)	7.73 (7.78)	522 (539)
$B(OC_2H_5)_2(C_{14}H_{12}NO)$ m.p. 178°	3.42 (3.48)	4.59 (4.50)	298 (311)
$B(OC_2H_5)(C_{14}H_{12}NO)_2$ m.p. 118°	2.31 (2.27)	5.88 (5.90)	460 (476)
$B(C_{14}H_{12}NO)_3$ m.p. 101°	1.71 (1.67)	6.50 (6.55)	627 (641)
$B(O-t-C_4H_9)_2(C_{11}H_{14}NO)$	3.19 (3.25)	4.16 (4.20)	325 (333)
$B(O-t-C_4H_9)(C_{11}H_{14}NO)_2$	2.44 (2.48)	6.36 (6.41)	426 (436)
$B(O-t-C_4H_9)_2(C_{11}H_{14}NO)^*$	3.22 (3.25)	4.15 (4.20)	322 (333)
$B(O-t-C_4H_9)(C_{11}H_{14}NO)_2^*$	2.45 (2.48)	6.38 (6.41)	429 (436)
$B(O-t-C_4H_9)_2(C_{14}H_{12}NO)$ m.p. 164°	2.93 (2.95)	3.88 (3.81)	351 (367)
$B(O-t-C_4H_9)(C_{14}H_{12}NO)_2$ M.P.106°	2.12 (2.15)	5.45 (5.55)	487 (504)

*Schiff base derived from isopropylamine

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