

firmed from the deshielding of the phenyl protons. The phenyl protons resonate between 6.93 and 7.86 in the SO_2 insertion compounds.

The SO_2 insertion products of phenyllead chelate were not sufficiently soluble in common solvents for molecular weight determinations. Their mass spectra could not be recorded due to poor volatility.

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Acceptor Behaviour of 2-Chloroethoxytitanium(IV) Trichloride & Bis (2-chloroethoxy) titanium(IV) Dichloride Towards Some Nitrogen Donors

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Adducts of 2-chloroethoxytitanium(IV) trichloride and bis (2-chloroethoxy)titanium (IV) dichloride with piperidine, morpholine, α , β and γ -picolines, ethylenediamine, N,N,N',N' -tetramethylethylenediamine and N,N -dimethylhydrazine have been prepared and some of their physical properties reported. The IR spectra indicate six-coordinate titanium for all these complexes and the alkoxy bridged frame work [originally present in bis(2-chloroethoxy)titanium(IV) dichloride] breaks down on complex formation.

ACCEPTOR properties of metal alkoxides have been less investigated than those of the metal halides and this seems to be mainly due to the polymeric nature which precludes complex formation. We report here, the preparation and characterization of the complexes of 2-chloroethoxytitanium (IV) trichloride and bis (chloroethoxy) titanium(IV) dichloride with some nitrogen donors such as piperidine, morpholine, α , β and γ -picoline, ethylenediamine (en), N,N,N',N' -tetramethyl-ethylenediamine (tmen) and N,N -dimethylhydrazine (dmh).

All the reagents used were purified by standard methods before use. 2-Chloroethoxytitanium (IV) trichloride(I) and bis(2-chloroethoxy)titanium (IV) dichloride (II) were prepared as described by Paul *et al.*^{1,2} and their purity checked.

Solid complexes of I and II were obtained by mixing appropriate quantities of their precooled solutions

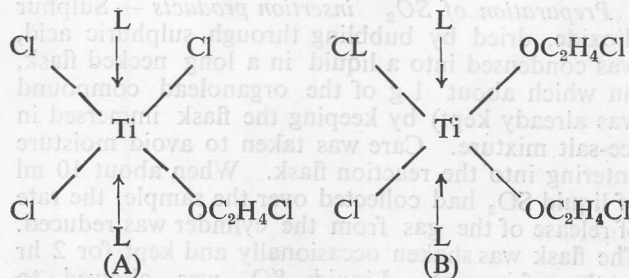
in benzene with those of the ligands in the same solvent. The viscous complexes obtained initially with en turned into solids on washing with dichloromethane. All the complexes were filtered under anhydrous conditions, washed with dry benzene, dry ether and dried *in vacuo*, yield 60-70%.

Titanium and chlorine contents of the complexes were determined gravimetrically^{3,4}. Molar conductance values of the complexes in nitromethane (10^{-3} M solutions) were measured on a Toshniwal (India) Conductometer, Infrared spectra of the complexes were recorded in nujol mull using NaCl and polythene plates on Perkin Elmer 337 and 621 spectrophotometers.

The complexes of piperidine, morpholine, α - β - and γ -picolines and en with I and II have 2:1 composition, whereas the complexes of tmen and dmh have 1:1 stoichiometry. Most of the complexes decompose on storage even in sealed tubes. Some of the complexes are soluble in nitromethane and their molar conductance values in the same solvent (10^{-3} M solutions) indicate that they are predominantly covalent in nature ($\Delta_M \sim 2.0 - 25.0 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$). Very low solubility of these complexes in benzene or nitrobenzene precludes their molecular weight determination.

The IR data* of the ligand and their corresponding complexes reveal following characteristic features. The $\nu(\text{C} \dots \text{C})$ and $\nu(\text{C} \dots \text{N})$ of α -, β -, and γ -picolines shift ($\Delta\nu$ 10-45 cm^{-1}) to higher spectral region and the C-H out-of-plane deformation vibration shifts ($\Delta\nu$ 15-60 cm^{-1}) to lower spectral region in their complexes. The $\nu(\text{N-H})$ of morpholine, piperidine and dmh present at 3440, 3290 and 3298 respectively shift to lower spectral region by 60 cm^{-1} in morpholine complexes, ~ 90 -100 cm^{-1} in piperidine complexes and by 50-70 cm^{-1} in dmh complexes. The $\nu(\text{N-H})$ of en shifts to lower spectral region by $\sim 170 \text{ cm}^{-1}$ while the (N-H) bending vibration present at 1605 splits into two bands (1650 and 1590) in its complexes. The $\nu(\text{CN})$ in tmen shifts to lower spectral region by 45-160 cm^{-1} in its complexes. These observations indicate the coordination of these ligands⁶⁻¹⁴ to titanium through their nitrogen atom(s) The bands due to Ti-O-(R) group appear ~ 1065 -1130 in these complexes.

In the far infrared region $\nu(\text{Ti-Cl})$ vibration is observed in the region 410-360 as one or more bands and this is the region where six coordinate titanium absorbs¹⁵. The $\text{TiCl}_3(\text{OC}_2\text{H}_4\text{Cl})_2\text{L}$ and $\text{TiCl}_2(\text{OC}_2\text{H}_4\text{Cl})_2\text{L}$ (where L = ligand) complexes, thus apparently seem to have coordination number six as shown in structures (A) and (B)



*IR ν_{max} in cm^{-1}

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES OF 2-CHLOROETHOXYTITANIUM(IV) TRICHLORIDE AND BIS-(2-CHLOROETHOXY)TITANIUM (IV) DICHLORIDE WITH NITROGEN DONORS

Complex	Colour	m.p. (°C)	Cl (%)		Ti (%)	
			Found	Calc.	Found	Calc.
A. 2(piperidine)	White	242	34.1	35.1	—	11.8
A. 2(morpholine)	White	128-30(d)*	33.9	34.8	10.8	11.7
A. 2(α -picoline)	Light brown	126-28	34.6	33.8	11.4	11.9
A. 2(β -picoline)	Pale Yellow	64-67	34.7	33.8	11.8	11.9
A. 2(γ -picoline)	Pale Yellow	105-10	33.1	33.8	11.6	11.9
A. 2(en)	White	260	40.1	40.9	13.0	13.5
A. tmen	White	140(d)	41.0	40.6	13.4	13.7
A. dmh	White	168-70	47.9	48.3	—	16.3
B. 2(piperidine)	White	240-42	30.9	31.7	—	10.7
B. 2(morpholine)	White	240	30.7	31.4	10.5	10.6
B. 2(α -picoline)	White	95-96	30.1	30.6	10.0	10.2
B. 2(β -picoline)	Dirty white	112-14	30.2	30.6	10.0	10.2
B. 2(en)	White	280	35.0	35.7	11.7	12.0
B. tmen	White	280	36.0	36.0	12.4	12.1
B. dmh	Yellow	180-82	41.7	42.0	—	14.2

*A = $\text{TiCl}_3(\text{OC}_2\text{H}_4\text{Cl})$, B = $\text{TiCl}_2(\text{OC}_2\text{H}_4\text{Cl})_2$.

However, the $\text{TiCl}_3(\text{OC}_2\text{H}_4\text{Cl})_2\text{L}'$ and $\text{TiCl}_2(\text{OC}_2\text{H}_4\text{Cl})_2\text{L}'$ complexes (where $\text{L}' = \text{tmen}$ and dmh) seem to acquire coordination number six ($\nu\text{Ti}-\text{Cl}$ bands observed in most of the complexes are $\sim 365\text{s}$, 340s) without forming chloride or alkoxy bridging, as no bands corresponding to $\text{Ti}-\text{Cl}\rightarrow\text{Ti}$ vibration^{16,17} and $\text{Ti}-\text{O}\rightarrow\text{Ti}$ vibration¹⁸ are observed in these complexes. The ligands tmen and dmh, therefore, appear to act as chelate bidentate ligands in these complexes.

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Organic Tellurium Derivatives: Part II—Telluracyclopentane Halides, Pseudohalides & Carboxylates

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Some telluracyclopentane derivatives of the formulae $\text{C}_4\text{H}_8\text{TeX}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{NCO}, \text{NCSe}, \text{NCS}, \text{N}_3, \text{CH}_2\text{COO}, \text{CCl}_2\text{COO}, \text{C}_6\text{H}_5\text{COO}$) have been prepared metathetically and characterised on the basis of elemental analyses, molecular weights, IR, NMR, conductance and dipole moment measurements. TGA and biocidal activity of a few representative compounds have also been studied.

THE interaction of organic dihalides with elemental tellurium to give tellurium heterocycles has been reviewed¹. Compared to the organic tellurium halides¹⁻³ the corresponding pseudohalide derivatives have received little attention¹. It was, therefore, of interest to prepare a number of telluracyclopentane dipseudohalides and study the mode of bonding of the pseudohalide groups. While this work was in progress, triphenyltellurium pseudohalides⁴ and more recently diaryltellurium dithiocyanates were reported^{5,6}.

In addition we have prepared and characterised three telluracyclopentane dicarboxylates mainly to examine their biocidal activity.

Telluracyclopentane-1,1-diiodide⁷ was synthesised by heating finely powdered tellurium metal (200 mesh) with 1,4-diiodobutane.

Telluracyclopentane-1, 1-dibromide — Telluracyclopentane 1,1-diiodide (1g, 2.28 mmol) was stirred (1 hr) with a suspension of freshly prepared silver bromide (0.09 g, 4.78 mmol) in dry acetone (40 ml) at room temperature. The precipitated silver iodide (and excess silver bromide) was filtered off