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Oxy-Ti(IV) Dicarboxylates

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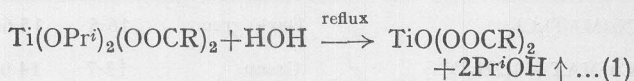
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Oxy-titanium(IV) carboxylates of composition $TiO(OOCR)_2$ have been synthesized by controlled hydrolysis of dialkoxy titanium dicarboxylates. These are obtained as viscous liquids, semisolids or solids, depending upon the chain length of carboxylic acids. Their refractive indices, melting points, molecular weights, thermal decomposition and IR data are reported.

TITANYL compounds possess different types of metal-oxygen linkages¹⁻³ depending upon the routes of their synthesis and molecular association. Some of these derivatives find extensive industrial applications⁴. The possibility of the formation of oxycarboxylates has been indicated by Mehrotra

and Pandey⁵ during their attempts to synthesize titanium tetra soaps. In the present note we report the synthesis of some oxy-titanium dicarboxylates. Their refractive indices, melting points, molecular weights, IR spectra and thermal decomposition data are also being reported.

Oxy-titanium dicarboxylates were synthesized by controlled hydrolysis of dialkoxy-titanium dicarboxylates in benzene solution (Eq. 1).



Pr^iOH produced in the reaction was removed azeotropically using benzene and estimated quantitatively. The excess solvent was distilled out under reduced pressure and the products obtained were finally dried at $50^\circ/0.5$ mm.

The products are viscous liquids, semisolids or solids depending upon the number of carbon atoms in the carboxylic acid chain. The liquid derivatives have very little difference in their refractive indices (Table 1).

The ebullioscopic and osmometric molecular weight determinations in benzene solution show little tendency of association. The molecular complexities fall in the range 1.2-1.4. The plot of the weight of compound added to a measured quantity of benzene against the change in resistance is always linear showing that the molecular complexity is independent of concentration of the solute within the measured range.

The IR spectra of $TiO(OOCR)_2$ derivatives (in nujol or neat) show the presence of two types of

TABLE 1 — ANALYTICAL AND PHYSICO-CHEMICAL DATA OF OXY-TITANIUM CARBOXYLATES

Reactants (g)	Isopropanol (g) Found (calc.)	Product	Yield (g) Found (calc.)	Ti (%) Found (calc.)	Mol. wt. Found (calc.)
$Ti(OPr^i)_2(OOCC_7H_{15})_2$ (2.10) H_2O (0.10)	0.24 (0.28)	$TiO(OOCC_7H_{15})_2^*$ $\eta_D^{35} = 1.4975$	1.70 (1.63)	13.52 (13.68)	451 (350)
$Ti(OPr^i)_2(OOCC_{11}H_{23})_2$ (3.36) H_2O (0.11)	0.30 (0.33)	$TiO(OOCC_{11}H_{23})_2^*$ $\eta_D^{35} = 1.4902$	2.82 (2.73)	10.05 (10.35)	592 (462)
$Ti(OPr^i)_2(OOCC_{13}H_{27})_2$ (1.36) H_2O (0.04)	0.10 (0.13)	$TiO(OOCC_{13}H_{27})_2^*$ $\eta_D^{35} = 1.4882$	1.23 (1.14)	9.02 (9.23)	662 (519)
$Ti(OPr^i)_2(OOCC_{15}H_{31})_2$ (4.21) H_2O (0.20)	0.36 (0.37)	$TiO(OOCC_{15}H_{31})_2^\dagger$	3.69 (3.58)	8.23 (8.34)	733 (575)
$Ti(OPr^i)_2(OOCC_{17}H_{35})_2$ (5.51) H_2O (0.14)	0.43 (0.45)	$TiO(OOCC_{17}H_{35})_2^*$ $\eta_D^{35} = 1.4978$	4.72 (4.74)	7.78 (7.65)	751 (626)
$Ti(OPr^i)_2(OOCC_{17}H_{35})_2$ (4.41) H_2O (0.12)	0.33 (0.36)	$TiO(OOCC_{17}H_{35})_2^\ddagger$ (m.p. $58-9^\circ$)	3.85 (3.79)	7.50 (7.59)	857 (630) (886)§
$Ti(OPr^i)_2(OOCC_{21}H_{43})_2$ (3.04) H_2O (0.07)	0.21 (0.22)	$TiO(OOCC_{21}H_{43})_2^\ddagger$ (m.p. $65-6^\circ$)	2.81 (2.68)	6.38 (6.45)	908 (743) (1038)§

*Viscous liquid.

†Semisolid.

‡White solid.

§Molecular weight determined by osmometry.

carboxylate groups. A band at $\sim 1730\text{ cm}^{-1}$ which has been assigned to $\nu\text{C}=\text{O}$ in metal carboxylates^{6,7}, where carboxylic acid behaves as a unidentate ligand, was found to be present in all these derivatives. Two other bands present at ~ 1560 and $\sim 1450\text{ cm}^{-1}$ may be assigned to $\nu_a\text{COO}^-$ and $\nu_s\text{COO}^-$ respectively. These indicate the bidentate⁸ nature of carboxylate groups.

No bands are observed in the regions ~ 3500 , ~ 1130 and $1100\text{--}900\text{ cm}^{-1}$ corresponding to hydroxy, isopropoxy and $\text{Ti}=\text{O}$ stretching⁹⁻¹¹ respectively, indicating the absence of any free acid or $\text{Ti}(\text{OPr}^i)_2(\text{OOCR})_2$ species. However, a broad band around 835 cm^{-1} observed in these derivatives may be assigned to $\text{Ti}=\text{O}\rightarrow\text{Ti}$ type of linkage¹². As the molecular weight data are not in agreement with polymeric or dimeric structures, it may be suggested that the coordination between terminal oxygen and titanium atoms is destroyed in solution giving rise to monomeric species and consequently the molecular weight falls corresponding to the molecular complexity 1.3.

These derivatives have no tendency of adduct formation with nitrogen containing ligands like pyridine.

The compounds are thermally stable up to 200° above which temperature these decompose slowly, giving CO , CO_2 , H_2O and leaving TiO_2 as the residue. About 80% of its decomposition is completed around 300° .

This mode of decomposition of $\text{TiO}(\text{OOCR})_2$ derivatives is different from that of other metal carboxylates^{13,14} in which the decomposition proceeds with the formation of a ketone as an intermediate product.

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Pentacoordinated Ti(IV) Chloride & Sn(IV) Bromide & Iodide Complexes with Acridine & Piperazine

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Donor-acceptor type complexes of TiCl_4 , SnBr_4 and SnI_4 with acridine and piperazine have been prepared and characterized on the basis of conductance and IR data. A pentacoordinated trigonal bipyramidal structure has been proposed for all the complexes. The $(\text{TiCl}_4)_2$ -piperazine complex has been found to be binuclear.

IN continuation of our earlier work^{1,2} on the complexes of acridine and piperazine with SnCl_4 and GeCl_4 , the preparation and characterization of TiCl_4 , SnBr_4 and SnI_4 complexes with these donor molecules are reported in this note. The possibility of the formation of a binuclear complex with piperazine has also been considered. Molecular addition compounds of group (IV) halides have extensively been studied³⁻⁸.

Acridine (Fluka AG, m.p. 108°) was recrystallized from alcohol. Piperazine hexahydrate (E. Merck, m.p. 56°) was used as such without further purification. Anhydrous Ti(IV) chloride (BDH) was used whereas Sn(IV) bromide and iodide were prepared according to standard methods⁹.

Acridine complexes—A solution of Sn(IV) bromide/iodide in ethanol-chloroform mixture was added to an ethanolic solution of acridine in approximately equimolar quantity. Sn(IV) bromide yielded a greenish yellow crystalline substance but Sn(IV) iodide gave a gelatinous mass which dissolved on stirring. However, this solution later yielded a yellowish orange compound. Ethanolic solutions of Ti(IV) chloride and excess of acridine when left overnight after mixing yielded needle-shaped crystals. All the solids obtained were washed with ethanol and dried *in vacuo*.

Piperazine complexes—These were also prepared as above but the complex formation was rapid in the case of Sn(IV) iodide and Ti(IV) chloride whereas with Sn(IV) bromide a granular product was obtained after a few minutes.

The melting points and analyses of the complexes are given in Table 1. All the addition compounds formed with acridine and piperazine are of the type $\text{MX}_4\cdot\text{L}$, except the adduct of TiCl_4 with piperazine which is of $(\text{MX}_4)_2\cdot\text{L}$ type.

The molar conductances (Systronix conductivity bridge) of approximately 10^{-3} millimolar solutions of the adducts of acridine in nitromethane at room temperature fall well below the range for a univalent electrolyte¹⁰, indicative of non-ionic nature of these adducts.

Acridine exhibits two strong bands in its IR spectrum at 1515 and 1555 cm^{-1} attributable to $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$ respectively. Its adducts with TiCl_4 , SnBr_4 and SnI_4 exhibit $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$