

Some Diorganotellurium (IV) Bis(salicylaldehyde) Complexes

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Diorganotellurium (IV) bis(salicylaldehyde) complexes, $[R_2Te(O_2C_7H_5)_2]$ ($R = C_6H_5$, CH_3 , $p\text{-CH}_3OC_6H_4$ and biphenylene) have been prepared by the interaction of organotellurium (IV) methoxide with salicylaldehyde. The complexes react with haloacetic acids ($R'COOH$) ($R' = CF_3$, CCl_3 , $CHCl_2$ and CH_2Cl) to give mixed ligand complexes $[R_2Te(O_2C\text{-}H_5)(OCOR')]$. Their possible structures are suggested.

Salicylaldehyde complexes of organo-tin, -lead, -thallium, -antimony & -phosphorus have been reported¹⁻⁴. The corresponding organotellurium complexes do not appear to have been prepared so far. We report herein the preparation and characterisation of diorganotellurium (IV) bis(salicylaldehyde) complexes.

All experiments were carried out under dry nitrogen atmosphere. $(C_6H_5)_2TeCl_2$ (ref. 5) $(CH_3)_2TeI_2$ (ref. 6) $(C_6H_4)_2TeI_2$ (ref. 7) and $(p\text{-CH}_3OC_6H_4)_2TeCl_2$ (ref. 8) were prepared according to established procedures. Other physicochemical studies were made as described earlier⁹. Diorganotellurium (IV) bis(salicylaldehyde) complexes were obtained as follows:

Diorganotellurium (IV) bis(salicylaldehyde) complexes

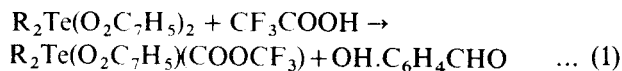
In a typical experiment freshly cut sodium (0.460 g; 20 mmol) was added to absolute methanol (10 ml) and stirred for 1 hr at $-10^\circ C$. A solution of $(C_6H_5)_2TeCl_2$ (3.526 g; 10 mmol) in methanol (50 ml) was added to this solution at the same temperature followed by salicylaldehyde (2.88 g; 20 mmol) in the same solvent (50 ml). The reaction mixture was stirred for 6 hr. Filtration followed by removal of the solvent under reduced pressure yielded $(C_6H_5)_2Te(O_2C_7H_5)_2$ as a solid, which was recrystallised from chloroform pet. ether ($40\text{-}60^\circ$) mixture and dried *in vacuo*.

Identical product was obtained by the reaction of $(C_6H_5)_2TeO$ with a methanolic solution of salicylaldehyde in (1:2) molar ratio.

Reaction of $(C_6H_5)_2Te(O_2C_7H_5)_2$ with $R'COOH$

To a solution of $(C_6H_5)_2Te(O_2C_7H_5)_2$ (5.23 g, 10 mmol) in diethyl ether (50 ml) was added a solution of CF_3COOH (2.28 g; 20 mmol) in the same solvent (50 ml) and the mixture stirred for 2 hr. On standing

overnight in deep freeze, a crystalline solid separated out which was washed with pet. ether ($40\text{-}60^\circ$) and identified as $(C_6H_5)_2Te(O_2C_7H_5)(OCOCF_3)$. Salicylaldehyde was also identified as the product and the reaction occurred in accord with Eq. (1)



The newly synthesised complexes are yellow solids with sharp melting points, feebly sensitive towards atmospheric moisture and turn red on long standing. They are soluble in common organic solvents. The molar conductances of $10^{-3} M$ solutions of the complexes indicate them to be non-electrolytic. In the presence of ethanolic sodium hydroxide the complexes hydrolyse to corresponding R_2TeO .

The IR spectra of the complexes (I to IV; Table 1) exhibit two peaks in the carbonyl region at 1620 and 1590 cm^{-1} which may be typical of a bidentate¹⁰ salicylaldehyde group. An additional medium band at $1680 \pm 5\text{ cm}^{-1}$ may be assigned to the free uncoordinated, but hydrogen bonded¹¹ carbonyl group of the unidentate salicylaldehyde group¹².

The presence of two bands at 905 and 890 cm^{-1} in the IR spectrum of I-IV suggests¹² the presence of one unidentate and the other bidentate salicylaldehyde group. In complexes (V to XI) where one of the salicylaldehydes (i.e. the one unidentately bonded) has been replaced by a haloacetate group¹³, the $\nu C=O$ modes appear at 1620 ± 5 and $1590 \pm 5\text{ cm}^{-1}$ and the aldehydic C-H deformation mode at 905 cm^{-1} indicating the presence of chelated, salicylaldehyde group.

In the complexes $[R_2Te(O_2C_7H_5)(OCOR')]$ the $\nu_{as} OCO$ and $\nu_s OCO$ appear at 1700 ± 10 and $1390 \pm 10\text{ cm}^{-1}$ and their difference at $(310 \pm 10\text{ cm}^{-1})$ ($-\Delta\nu OCO = \nu_{as} OCO - \nu_s OCO$) compares favourably with those of $R_2Te(OCOR')_2$ (ref. 9) and other haloacetate compounds whose X-ray are reported¹⁴, indicating unidentate nature of the haloacetate group.

The PMR spectrum of the complex $(p\text{-CH}_3OC_6H_4)_2Te(O_2C\text{-}H_5)_2$ in $CDCl_3$ at 90 MHz displays the absence of $-OH$ proton indicating the presence of ligand in their deprotonated form. The aldehydic protons ($-CHO$) appear downfield, in comparison to that of the free ligand, as two distinct signals of equal intensity at $\delta 9.93$ and 10.23 respectively, probably due to deshielding effect by carbonyl group coordinated to tellurium. The aromatic protons appear as a multiplet in the region $6.4\text{-}8.0$ and $-OCH_3$ protons as a singlet at $\delta 3.7$. The

Table 1—Characterisation Data of $R_2Te(O_2C_7H_5)_2$ and Their Derivatives

Complex	m.p. (°C)	Found (%) (Calc.)		
		Te	C	H
$(CH_3)_3Te(O_2C_7H_5)_2$ (I)	182d	31.90 (31.93)	47.99 (48.04)	4.11 (4.00)
$(C_6H_5)_2Te(O_2C_7H_5)_2$ (II)	65	24.30 (24.36)	59.50 (59.58)	3.70 (3.81)
$(p-CH_3OC_6H_4)_2Te(O_2C_7H_5)_2$ (III)	74	24.24 (24.37)	59.58 (59.88)	3.23 (3.45)
$(C_6H_4)_2Te(O_2C_7H_5)_2$ (IV)	186	21.80 (21.86)	57.40 (57.57)	4.07 (4.11)
$(C_6H_5)_2Te(O_2C_7H_5)(OCOCF_3)$ (V)	110	24.44 (24.84)	—	—
$(C_6H_5)_2Te(O_2C_7H_5)(OCOCCH_3)$ (VI)	143	22.54 (22.58)	44.55 (44.59)	2.60 (2.65)
$(C_6H_5)_2Te(O_2C_7H_5)(OCOCHCl_2)$ (VII)	115	23.88 (24.04)	47.30 (47.49)	2.86 (3.01)
$(C_6H_5)_2Te(O_2C_7H_5)(OCOCH_2Cl)$ (VIII)	140	25.41 (25.72)	50.34 (50.80)	3.30 (3.42)
$(p-CH_3OC_6H_4)_2Te(O_2C_7H_5)(OCOCF_3)$ (IX)	110	22.04 (22.24)	—	—
$(p-CH_3OC_6H_4)_2Te(O_2C_7H_5)(OCOCH_2Cl)$ (X)	102	22.47 (22.94)	49.31 (49.64)	3.64 (3.77)
$(C_6H_4)_2Te(O_2C_7H_5)(OCOCF_3)$ (XI)	126	25.12 (25.14)	—	—
$(C_6H_5)_2Te(O_2C_7H_5)Cl$ (XII)	180	28.80 (29.13)	51.86 (52.05)	3.17 (3.42)
$(C_6H_4)_2Te(O_2C_7H_5)Cl$ (XIII)	189	29.22 (29.27)	52.24 (52.28)	2.86 (2.99)

position and integration of signals are consistent with the proposed stoichiometry.

Though it is difficult to assign appropriate geometry for the presently synthesised complexes, on the available data, however, it seems that organotellurium (IV) derivatives form more stable pentacoordinate complexes as compared to hexacoordinated. Further in these complexes one of the salicylaldehydes is unidentately bonded while the other is bidentately bonded to tellurium. Such behaviour is also observed in organotellurium (IV) oxinates and their derivatives¹⁵.

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