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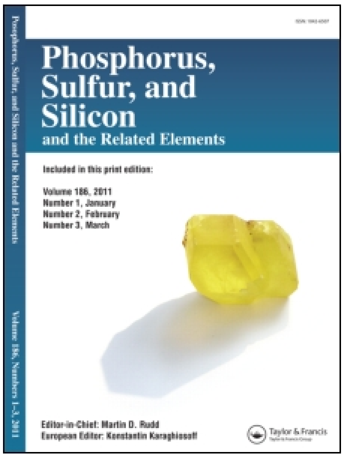

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SYNTHESIS AND CHARACTERIZATION OF ORGANOTELLURIUM(IV) CHLOROSULPHATES

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A variety of diorganotellurium(IV) chlorosulphate $R_2Te(SO_3Cl)_2$ [$R=C_6H_5$, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, $4C_2H_5OC_6H_4$, $(4\text{-}C_2H_5OC_6H_4)C_6H_5$] have been prepared by the metathetical reaction of organotellurium diacetates with HSO_3Cl. The UV spectra in MeCN exhibit bands characteristic of excitations from a nonbonding to an antibonding σ molecular orbitals [$\eta(5px)-\sigma^*(4a_1,3b_2)$]. The proton resonances observed in ^1H NMR spectra of these compounds in d_6-DMSO are considerably deshielded from that observed for the corresponding diacetates indicating the drainage of the non-bonding electrons at tellurium towards SO_3Cl^- group.

Keywords : Organotellurium(IV) chlorosulphates; anion acceptors

INTRODUCTION

It has been established that HSO_3Cl may act as medium as well as chlorosulphonating agent for synthesis of variety of metal chlorosulphates[1], mixed metal chlorosulphates[2,3] oxychlorosulphates[4] and organotellurium chlorosulphates[5]. Conductometric studies in HSO_3Cl have shown that alkali metals, alkaline earth metals[6] and tin(II)chlorides[7] act as strong electrolytes and undergo complete ionization in solution. The ability of $R_2Te(SO_3Cl)_2$ compounds to behave as SO_3Cl^- anion acceptors has been established[8] by synthesis of monomeric complexes of the type $M_2[R_2Te(SO_3Cl)_4]$ (M=Na and K) and $Sn[R_2Te(SOP_3Cl)_4]$.

Results and Discussion

The compounds $R_2Te(SO_3Cl_2)$ were prepared by the metathetical reactions of diorganotellurium(IV) diacetates with HSO_3Cl as shown below.

$$R_2Te(COOCH_3)_2 + 2HSO_3Cl \rightarrow R_2Te(SO_3Cl)_2 + 2CH_3COOH$$
$$[R=C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}CH_3OC_6H_4,\ 4\text{-}C_2H_5OC_6H_4,$$
$$(4\text{-}C_2H_5OC_6H_4)C_6H_5]$$

The observed molar conductivities of these compounds in methylcyanide, a high dielectric ionising solvent are low enough to indicate a covalent linkage of SO_3Cl^- group in $R_2Te(SO_3Cl)_2$.

The IR spectra of the compounds (See Table II) exhibit bands corresponding to the chlorosulphate group may reasonably be assigned by comparing the spectra of the free SO_3Cl^- anion (as in $CsSO_3Cl$)[9]. A positive shift in SO_3 symmetric stretch ν_1 (A) and splitting of doubly degenerate (E modes) suggest an appreciable

TABLE I Analytical data and molar conductivity values of the compounds

	Found (Calc) %					Λ_m
Compounds	Cl	S	Te	C	H	$\Omega^{-1}cm^2mol^{-1}$
$(C_6H_5)_2Te(SO_3Cl)_2$ (1)	13.81 (13.85)	12.45 (12.48)	24.90 (24.89)	28.05 (28.09)	1.92 (1.95)	25
$(4\text{-}CH_3C_6H_4)_2Te(SO_3Cl)_2$ (2)	13.10 (13.13)	11.80 (11.83)	23.57 (23.60)	31.05 (31.07)	2.56 (2.58)	31
$(4\text{-}CH_3OC_6H_4)_2Te(SO_3Cl)_2$ (3)	12.36 (12.39)	11.15 (11.17)	22.25 (22.28)	29.35 (29.33)	2.41 (2.44)	40
$(4\text{-}C_2H_5OC_6H_4)_2Te(SO_3Cl)_2$ (4)	11.79 (11.82)	10.63 (10.65)	21.20 (22.24)	31.94 (31.96)	2.97 (2.99)	35
$[(4\text{-}C_2H_5OC_6H_4)C_6H_5]_2Te(SO_3Cl)_2$ (5)	9.38 (9.40)	8.45 (8.48)	16.86 (16.90)	44.50 (44.52)	3.66 (3.71)	20

TABLE II IR spectra of the compunds (cm^{-1})

Possible Assignments	1	2	3	4	5
$\nu_6(E)$	300m	315m	305m	310m	305m
	330m	330m	335m	335m	335m
$\nu_2(A)$	435m	450m	440m	450m	445m
$\nu_3(A)$	565s	560s	560s	565s	565m
$\nu_5(E)$	635s	630s	625s	635s	625s
	670s	665s	670s	660s	660s
$\nu_1(A)$	1070vs	1070vs	1080vs	1075vs	1080s
$\nu_4(E)$	1180s	1175s	1165s	1175s	1190s
	1270s	1260s	1265s	1285s	1275s
ν (Te-C)	540s	545s	525s	535s	520s

covalent interaction existing between the SO_3Cl^- anion and R_2Te^{2+} cation. This covalent interaction lowers the symmetry of the chlorosulphate group from C_{3v} expected to exist in ionic $CsSO_3Cl$ to C_s symmetry[1-3].

The ^1H NMR spectra of the compounds $R_2Te(SO_3Cl)_2$ have been recorded in DMSO-d_6 at room temperature. Compounds (2), (3), (4) and (5) show vibration at around 6.80 ppm corresponding to the phenyl ring vibrations. There was a sharp singlet around 2.10 ppm corresponding to CH_3 bands in compound (2) and was a slight shift to low field of the peak for compound (3) due to CH_3O protons. However, the positions of the resonance peaks in all the compounds are shifted to low field as compared with those observed[5] for the corresponding acetato derivatives, suggesting a greater drainage of electron density from the tellurium atom towards the SO_3Cl^- group.

The UV spectra of these compounds dissolved in methyl cyanide exhibit two well resolved maxima which may reasonably be assigned to the expected η-σ^* (Te 5px-$4a_1$,$3b_2$) transition.

Experimental

Pure chlorosulphuric acid (Riedal) was used. The compounds diorganotellurium(IV)diacetates $R_2Te(COOCH_3)_2$ were prepared according to literature method. All manipulations were done in glove box under dry nitrogen.

Synthesis of diorganotellurium(IV) dichlorosulphates, $R_2Te(SO_3Cl)_2$ [$R=C_6H_5$, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$C_2H_5OC_6H_4$, (4-$C_2H_5OC_6H_4$)C_6H_5].

Diorganotellurim diacetates, $R_2Te(COOCH_3)_2$ (4.2 mmol) was added to about 20 cm^3 of distilled HSO_3Cl in a stoppered flask having two stoppered sidetubes for continuous supply of dry nitrogen through one tube and an evacuation of volatile products through the other. The reaction content was magnetically stirred for several hours. The microcrystalline solids where immediately separated out when the solutions were added dropwise to 50 cm^3 of chilled diethylether. These were filtered, washed with dry ether and vacuum dried.

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