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ORGANOTELLURIUM(IV) DERIVATIVES: SYNTHESIS AND CHARACTERIZATION OF METAL DIALKYLTETRAKIS(CHLOROSULPHATO)TELLURATE(IV), $M_2[R_2Te(SO_3Cl)_4]$ (M = Na, K) AND $Sn[R_2Te(SO_3Cl)_4]$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9)

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Abstract—The ability of $R_2Te(SO_3Cl)_2$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) compounds to behave as a SO_3Cl^- acceptors has been proved by the synthesis and characterization of new monomeric complexes of the type $M_2[R_2Te(SO_3Cl)_4]$ (M = Na, K) and $Sn[R_2Te(SO_3Cl)_4]$ by reacting stoichiometric amounts of R_2TeI_2 ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) with metal salts, namely NaI, KI and $SnCl_2$, in excess HSO_3Cl. The compounds are hygroscopic in nature but are stable under dry nitrogen. The IR spectra of the compounds suggest that the SO_3Cl^- is covalently bonded to the dialkyltellurium moiety. The observed molar conductance values of these compounds in DMSO confirm that they are 1 : 1 and 1 : 2 electrolytes. The ^1H NMR spectra are discussed in terms of inductive effects and since the chlorosulphate group is expected to be bound in monodentate manner the hexa-coordination around the tellurium atom is maintained.

Inorganic hexa- and penta-halotellurates(IV) are well known.[1,2] A large number of organyl tetrahalotellurates(IV) have also been prepared in high yields by refluxing organyl tellurium trihalides with ammonium, phosphonium, arsonium or tropylium halides in chloroform or by addition of an aqueous onium salt solution to a solution of the organyl tellurium trihalides in 6 M HCl or 3 M HBr.[3–5] However, the alkali and alkaline earth metal organyl tetrahalotellurates(IV) are less well known.[6] It has been established in the last 25 years that HSO_3Cl can act as a medium and as a chlorosulphonating agent for the synthesis of a variety of metal chlorosulphates,[7] mixed metal chlorosulphates,[8,9] oxychlorosulphates,[10] and organotellurium chlorosulphates.[11] It has also been shown by conductometric studies in HSO_3Cl that alkali metals, alkaline earth metals[12] and tin(II) chloride[13] act as strong electrolytes and undergo complete ionization in solution. However, dimethyl tellurium diiodide and diethyl tellurium diiodide[14] solutes act as weak electrolytes and are partially and incompletely ionized, producing corresponding dicationic species R_2Te^{2+} ($R = CH_3$, C_2H_5) in solution. Recently, we have reported[15] the ability of $R_2Sn(SO_3Cl)_2$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) to act as SO_3Cl^- acceptor by synthesizing dialkyl tetrakis(chlorosulphato)stannate(IV) complexes of the types $Li_2[R_2Sn(SO_3Cl)_4]$ and $M[R_2Sn(SO_3Cl)_4]$ (M = Ba, Sn; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) from organotin(IV) chloride in HSO_3Cl.

It was therefore thought worthwhile to expand the synthetic utility of HSO_3Cl by synthesizing a variety of dialkyltetrakis(chlorosulphato)tellurates(IV) of the types $M_2[R_2Te(SO_3Cl)_4]$ (M = Na,

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K) and $Sn[R_2Te(SO_3Cl)_4]$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) and characterizing them.

RESULTS AND DISCUSSION

The compounds $M_2[R_2Te(SO_3Cl)_4]$ ($M = Na$, K; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) were prepared by reacting $NaSO_3Cl$ or KSO_3Cl with $R_2Te(SO_3Cl)_2$, which were conveniently prepared *in situ* from the corresponding iodides in 1 : 2 molar ratio in HSO_3Cl according to the following reaction.

$$2M(SO_3Cl)+R_2Te(SO_3Cl)_2 \rightarrow M_2[R_2Te(SO_3Cl)_4]. \quad (1)$$

However, the compounds $Sn[R_2Te(SO_3Cl)_4]$ were synthesized by reacting an equimolar ratio of $Sn(SO_3Cl)_2$ and $R_2Te(SO_3Cl)_2$, both conveniently prepared *in situ* from the corresponding halides in HSO_3Cl, according to the reaction given below:

$$Sn(SO_3Cl)_2+R_2Te(SO_3Cl)_2 \rightarrow Sn[R_2Te(SO_3Cl)_4]. \quad (2)$$

The above reactions and the formation of the corresponding products may be explained in terms of the ability of $R_2Te(SO_3Cl)_2$ to act as SO_3Cl^- acceptor similar to the variety of dimethyltin(IV) fluorosulphate and dialkyltin(IV) chlorosulphate derivatives.[15–17]

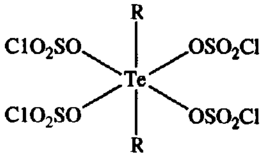
The results of elemental analyses (Table 1) are consistent with the stoichiometry of the compounds as $M_2[R_2Te(SO_3Cl)_4]$ [$R = CH_3$, C_2H_5, C_3H_7, C_4H_9, $M = Na$ (**1–4**); $M = K$ (**5–8**)] and $Sn[R_2Te(SO_3Cl)_4]$ [$R = CH_3$, C_2H_5, C_3H_7, C_4H_9, (**9–12**)]. The observed molar conductivities of these compounds in DMSO are comparable with those reported[18] for 1 : 1 and 1 : 2 electrolytes, consistent with the above proposed formulations. The compounds are stable under a dry N_2 atmosphere and soluble in most non-polar solvents.

IR spectra

The IR spectra of the compounds (Table 2) contain bands characteristic of the chlorosulphate group, in addition to the fundamental bands arising from the organic moiety. The bands corresponding to the chlorosulphate group may reasonably be assigned by comparing with the spectra of the free SO_3Cl^- anion (as in $CsSO_3Cl$)[19]. A positive shift in SO_3 symmetric stretch $\nu_1(A)$ and the splitting of the double degenerate (E) modes suggest an appreciable covalent interaction existing between the SO_3Cl^- anion and the R_2Te^{IV} cation. This covalent interaction lowers the symmetry of the chlorosulphate group from the C_{3v} expected to exist in ionic $CsSO_3Cl$ to C_s symmetry.[7–9] The other bands [S—Cl stretch, $\nu_2(A)$; S—Cl wag, $\nu_6(E)$; and SO_3 symmetric deformation, $\nu_3(A)$, of the SO_3Cl group] appeared as medium to strong intensity bands nearly at their estimated positions, as reported for other metal chlorosulphates.[7–9]

In all the compounds except ethyl derivatives, the ν(Te—C) asymmetric stretching frequency of alkyl groups appeared in the region 535–545 cm^{-1}, whereas the Te—C ethyl frequency appeared in the region 520–525 cm^{-1}. However, the positions of these bands are shifted to higher frequency as compared[20,21] with $(CH_3)_2Te$ and $(C_2H_5)_2Te$, respectively. The band position corresponding to the ν(Te—C) asymmetric stretching frequency of alkyl groups suggests that these groups are disposed *trans* to each other, similar to previous reports[22–25] for a variety of organotin(IV) derivatives involving organic donor bases. The bands in the region 280–290 cm^{-1} are assignable to Te—O stretching.[26] The other bands corresponding to alkyl groups appeared at their appropriate positions. The present investigation indicates that the SO_3Cl^- group is expected to be bonded in monodentate manner, maintaining hexa-coordination around the tellurium atom.

The present data help us to visualize these complexes as shown below.



^{1}H *NMR spectra*

The ^{1}H NMR spectra of the compounds (Table 3) $M_2[R_2Te(SO_3Cl)_4]$ ($M = Na$, K) and $Sn[R_2Te(SO_3Cl)_4]$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) have been recorded in DMSO-d_6 at room temperature. Compounds **1**, **5** and **9** exhibit a singlet in the region 4.24–4.26 ppm, due to CH_3 protons. Compounds **2**, **6** and **10**, with $R = C_2H_5$, showed two multiplets in the regions 2.68–2.70 and 4.48–4.54 ppm corresponding to CH_3 and CH_2Te protons, respectively. Similarly, a multiplet at 3.08 ppm and two triplets in the regions 2.04–2.08 and 4.54–4.56 ppm appeared due to CH_2, CH_3 and CH_2Te protons, respectively, for compounds **3**, **7** and **11**, with $R = C_3H_7$. The butyltellurium compounds **4**, **8** and **12** showed two multiplets, one at 2.36 and the other in the region 2.90–2.94 ppm for $(CH_2)_2$ protons and two triplets in the regions 1.90–1.96 and 4.54–4.58 ppm corresponding to CH_3 and CH_2Te protons,

Table 1. Analytical data and molar conductivity values of the compounds

Compounds		Found (Calc.) (%)						
		Cl	S	Te	Sn	C	H	μ_m ohm^{-1} cm^2 mol^{-1}
$Na_2[(CH_3)_2Te(SO_3Cl)_4]$	**(1)**	21.0	19.1	19.0	—	3.5	0.9	120
		(21.3)	(19.3)	(19.2)		(3.6)	(0.9)	
$Na_2[(C_2H_5)_2Te(SO_3Cl)_4]$	**(2)**	20.1	18.3	18.0	—	6.8	1.3	130
		(20.4)	(18.5)	(18.4)		(6.9)	(1.5)	
$Na_2[(C_3H_7)_2Te(SO_3Cl)_4]$	**(3)**	19.6	17.4	17.5	—	9.7	1.7	125
		(19.7)	(17.8)	(17.7)		(10.0)	(2.0)	
$Na_2[(C_4H_9)_2Te(SO_3Cl)_4]$	**(4)**	18.7	17.0	16.9	—	12.8	2.3	127
		(18.9)	(17.1)	(17.0)		(12.8)	(2.4)	
$K_2[(CH_3)_2Te(SO_3Cl)_4]$	**(5)**	20.2	18.1	18.0	—	3.2	0.8	110
		(20.3)	(18.4)	(18.3)		(3.4)	(0.9)	
$K_2[(C_2H_5)_2Te(SO_3Cl)_4]$	**(6)**	19.3	17.3	17.0	—	6.5	1.3	117
		(19.5)	(17.7)	(17.6)		(6.6)	(1.4)	
$K_2[(C_3H_7)_2Te(SO_3Cl)_4]$	**(7)**	18.7	16.9	16.1	—	9.4	1.7	114
		(18.8)	(17.0)	(16.9)		(9.6)	(1.9)	
$K_2[(C_4H_9)_2Te(SO_3Cl)_4]$	**(8)**	18.0	16.3	16.3	—	12.1	2.2	117
		(18.1)	(16.4)	(16.3)		(12.3)	(2.3)	
$Sn[(CH_3)_2Te(SO_3Cl)_4]$	**(9)**	19.0	17.2	17.0	15.8	3.2	0.8	60
		(19.2)	(17.4)	(17.3)	(16.1)	(3.3)	(0.8)	
$Sn[(C_2H_5)_2Te(SO_3Cl)_4]$	**(10)**	18.4	16.4	16.5	15.1	6.0	1.2	62
		(18.5)	(16.7)	(16.7)	(15.5)	(6.3)	(1.3)	
$Sn[(C_3H_7)_2Te(SO_3Cl)_4]$	**(11)**	17.6	15.9	15.8	14.7	9.0	1.6	64
		(17.9)	(16.1)	(16.1)	(14.9)	(9.1)	(1.8)	
$Sn[(C_4H_9)_2Te(SO_3Cl)_4]$	**(12)**	17.0	15.2	15.2	14.2	11.5	2.2	60
		(17.2)	(15.6)	(15.5)	(14.4)	(11.7)	(2.2)	

Table 2. IR spectra of the compounds (cm^{-1})

Possible assignment	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
ν_6 (*E*)	300m	310m	305m	305m	310m	310m	305m	300m	300m	310m	310m	310m
	330m	330m	330m	335m	335m	330m	335m	330m	330m	330m	335m	325m
ν_2 (*A*)	440m	450m	445m	445m	440m	450m	445m	445m	440m	440m	445m	440m
ν_3 (*A*)	560s	565s	560m	560s	560s	560s	560m	560m	560s	560s	565m	560m
ν_5 (*E*)	630s	630s	625s	635s	625s	630s	625s	630s	630s	630s	630s	630s
	670s	665s	670s	660s	660s	660s	670s	660s	655s	660s	660s	665s
ν_1 (*A*)	1070vs	1070vs	1080vs	1070s	1070vs	1075vs	1080s	1080vs	1080vs	1080vs	1080vs	1075vs
ν_4 (*E*)	1190s	1190s	1190s	1190s	1185s	1180s	1190s	1185s	1190s	1175s	1175s	1180s
	1270s	1270s	1275s	1270s	1265s	1270s	1275s	1285s	1280s	1280s	1275s	1275s
ν (Te—C)	540s	525s	545s	535s	540s	520s	545s	540s	540s	525s	545s	540s
ν (Te—O)	280m	290m	285m	285m	285m	285m	285m	280m	285m	285m	290m	290m
Alkyl group vibration	2950s	2980m	2985s	2985s	2950s	2970s	2980s	2980s	2960s	2980s	2985s	2980s
	2840s	2860s	2860s	2870s	2850s	2860s	2865s	2870s	2860s	2880s	2875s	2880s
	1390s	2900m	2920s	2910s	1380s	2910s	2900s	2915s	1380s	2910s	2925s	2900s
	1280m	2820m	2820s	2820s	1260s	2820s	2815s	2810s	1270s	2820s	2820s	2830s
		1380m	1390s	1380s		1385m	1385m	1374s		1380s	1380s	1380s
		1290s	1280s	1290s		1280s	1275s	1280s		1295m	1290m	1290m

m = medium ; s = strong ; vs = very strong.

Table 3. ^{1}H NMR spectra of the compounds (ppm)

Compounds		$\delta(CH_2Te)$	$\delta(CH_2)/(CH_2)_2$	$\delta(CH_3)$
$Na_2[(CH_3)_2Te(SO_3Cl)_4]$	**(1)**	4.24s	—	—
$K_2[(CH_3)_2Te(SO_3Cl)_4]$	**(5)**	4.26s	—	—
$Sn[(CH_3)_2Te(SO_3Cl)_4]$	**(9)**	4.24s	—	—
$Na_2[(C_2H_5)_2Te(SO_3Cl)_4]$	**(2)**	4.54m	—	2.70m
$K_2[(C_2H_5)_2Te(SO_3Cl)_4]$	**(6)**	4.52m	—	2.70m
$Sn[(C_2H_5)_2Te(SO_3Cl)_4]$	**(10)**	4.48m	—	2.68m
$Na_2[(C_3H_7)_2Te(SO_3Cl)_4]$	**(3)**	4.56t	3.08m	2.08t
$K_2[(C_3H_7)_2Te(SO_3Cl)_4]$	**(7)**	4.54t	3.08m	2.06t
$Sn[(C_3H_7)_2Te(SO_3Cl)_4]$	**(11)**	4.56t	3.08m	2.04t
$Na_2[(C_4H_9)_2Te(SO_3Cl)_4]$	**(4)**	4.56t	2.90m 2.36m	1.90t
$K_2[(C_4H_9)_2Te(SO_3Cl)_4]$	**(8)**	4.58t	2.94m 2.36m	1.90t
$Sn[(C_4H_9)_2Te(SO_3Cl)_4]$	**(12)**	4.54t	2.92m 2.36m	1.96t

s = singlet; m = multiplet; t = triplet.

respectively. However, the positions of the resonance peaks in all the compounds are shifted to low field as compared with those observed[11,27] for the corresponding dialkyltellurium bis(chlorosulphates) and dialkyltellurium diiodides, suggesting a greater drainage of electron density from the tellurium atom towards the SO_3Cl^- group.

EXPERIMENTAL

Pure chlorosulphuric acid (Riedal) was used. The compounds dimethyltellurium diiodide, diethyltellurium diiodide, di-n-propyltellurium diiodide and di-n-butyltellurium diiodide were prepared according to literature methods.[28,29] The metal salts NaI and KI (both Aldrich) were used as received. $SnCl_2 \cdot 2H_2O$ (Aldrich) was used after dehydration with acetic anhydride.[30] The solvents DMSO and Et_2O were dried by standard methods. All manipulations were done in a glove box under dry nitrogen.

Metal dialkyltetrakis(chlorosulphato)tellurate(IV), $M_2[R_2Te(SO_3Cl)_4]$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9; M = Na, K)

Dialkyltellurium diiodide R_2TeI_2 (4.2 mmol; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) and 8.4 mmol of NaI or KI were added to about 15 cm^3 of distilled HSO_3Cl in a stoppered flask having two stoppered side tubes for continuous supply of dry nitrogen through one tube and evacuation of volatile products through the other. A vigorous reaction took place and the gas evolved was removed *in vacuo*. It was then magnetically stirred for 72 h at room temperature, resulting in clear solutions. White microcrystalline solids were immediately separated out when the solutions were added dropwise to 75 cm^3 of chilled Et_2O. These were isolated by filtering, followed by washing with dry ether and lastly drying *in vacuo*.

Tin(II) *dialkyltetrakis(chlorosulphato)tellurate*(IV), $Sn[R_2Te(SO_3Cl)_4]$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9)

An equimolar ratio of dialkyltellurium diiodide R_2TeI_2 (4.4 mmol; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9) and $SnCl_2$ (4.4 mmol) was added to about 20 cm^3 of HSO_3Cl in a closed reaction vessel, as described above. The reaction mixture was warmed to room temperature and the evolved byproduct HX (hydrogen halide) was removed *in vacuo*. Then the contents were magnetically stirred for 72 h, resulting in the formation of a clear solution. White microcrystalline solids were immediately separated out when the solutions were slowly added dropwise to 75 cm^3 of chilled Et_2O. These were isolated in the manner described above.

Elemental analyses for carbon and hydrogen were done in a microanalytical laboratory, while sulphur, chlorine, tin and tellurium were determined[31,32] according to established methods. The IR spectra of all the compounds were recorded as Nujol mulls in polyethylene envelopes sealed on all sides using a Perkin–Elmer model 621 spectrophotometer. The electrical conductivities were obtained for 10^{-3} M solutions in DMSO using a systronic type 302 conductivity bridge thermostatted at 25 ± 0.05°C. The ^{1}H NMR spectra were recorded on Bruker Ac 200E nuclear magnetic resonance spectrophotometer in DMSO-d_6 using TMS as internal reference at G.N.D. University, Amritsar, India.

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