Reaction of Tetraiodomercurate Anion with HSO_3Cl: Synthesis of and Physico-Chemical Studies on $M_2[Hg(SO_3Cl)_4]$ (M=Cu(I), K), $(Et_4N)_2[Hg(SO_3Cl)_2I_2]$, and $K_2[Hg(SO_3Cl)_nI_{4-n}]$ (n=1, 2, and 3)

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Reactions of $[M_2HgI_4]$ with excess of HSO_3Cl afford $M_2[Hg(SO_3Cl)_4]$ (M=Cu(I), K). However, the reactions of K_2HgI_4 with stoichiometric amounts of HSO_3Cl, i.e., in 1 : 3, 1 : 2, and 1 : 1 molar ratios, yield $K_2[Hg(SO_3Cl)_nI_{4-n}]$ (n=3,2,1). In these reactions HSO_3Cl acts as both chlorosulfating agent as well as medium of the reaction. Et_4NI reacts with $Cu^I_2[Hg(SO_3Cl)_4]$ suspended in CH_2Cl_2 affording $(Et_4N)_2[Hg(SO_3Cl)_2I_2]$ and $[CuSO_3Cl]_x$. All these compounds have been characterized by elemental analysis, electrical conductivity measurements, IR and electronic spectral studies.

Tetrahalometallate complex anions of the type $[MX_4]^{-2}$ (M=Mn^{II}, Fe^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Hg^{II}; X=Cl^-, Br^-, and I^-) and also of $[FeX_4]^-$ are quite well known.[1-7] The halogen complex anions of Mn^{II}, Fe^{II}, Fe^{III}, and Hg^{II} have been thoroughly investigated using IR,[8,9] electronic,[10] Raman,[11] Chlorine nuclear quadrupole resonances[8] and Mössbauer spectroscopic studies for analysing molecular structure and mode of bonding in these complex anions. Tetrakis (chlorosulfato)metallate anions, $[M(SO_3Cl)_4]^-$, [M=B^{III}, Al^{III}, and Ga^{III} are obtained,[14-18] by utilizing either the addition reactions of sulfuric acid anhydrides or the solvolytic reactions of chlorosulfuric acid with corresponding tetrachlorometallates. The preparation and characterization of complex (chlorosulfato) metallates of heavier transition metals, i.e., $Na_2[Pd(SO_3Cl)_4]$ and $Na_2[Ir(SO_3Cl)_6]$, have been reported[19] from this laboratory. Here we are communicatingg for the first time the synthesis and characterization of $M_2[Hg(SO_3Cl)_4]$, [M=K and Cu(I)], $(Et_4N)_2[Hg(SO_3Cl)_2I_2]$ and $K_2[Hg(SO_3Cl)_nI_{4-n}]$ (n=1, 2, and 3).

Experimental

Materials. Pure chlorosulfuric acid (Riedel) was used as such; HgI_2, Et_4NI, $CuSO_4\cdot5H_2O$, and KI all were commercially pure samples which were used after recrystallization. However, Cu_2HgI_4 and K_2HgI_4 were synthesized according to the reported methods.[20] The solvents diethyl ether, DMSO, CH_2Cl_2, hexane, and acetonitrile were used after drying.[21]

Preparation of $Cu_2[Hg(SO_3Cl)_4]$ (1). Solid $[Cu_2HgI_4]$ (0.9340 g or 1.11 mmol) was placed in a reaction flask and chlorosulfuric acid was added in excess (ca. 15 ml) at room temperature with magnetic stirring. A vigorous exothermic reaction took place with evolution of violet fumes. The reaction mixture was stirred for about three hours. The light brown colored solid material was filtered off through a sintered glass frit under N_2, washed with HSO_3Cl, and finally with thionyl chloride and then dried in vacuo at 60 °C to a constant weight (mp 300 °C, yield 0.75 g (ca. 80%) based on Cu_2HgI_4).

Preparation of $(Et_4N)_2[Hg(SO_3Cl)_2I_2]$ (2). Tetraethylammonium iodide (1.285 g or 5.42 mmol) was reacted with 1.9688 g (2.4 mmol) of **1** suspended in 25 ml dichloromethane and stirred for about 4 h. The wine red colored solution was filtered off leaving behind some colorless residue. The solution was then mixed with hexane and kept at ca. 10 °C for a week. Dark brown, hexagonal crystals appeared along with some dirty white powdery mass which settled at the bottom. The crystals were collected and again recrystallized in the same manner. The recrystallized material melts at 135 °C (Yield 1.38 g (ca. 70%) based on **1**). The white amorphous solid was washed several times with CH_2Cl_2 and vacuum dried. The result of the elemental analysis proved it $[CuSO_3Cl]_x$. Found: Cu, 35.12; S, 17.8; Cl, 19.90%. Calcd for $[CuSO_3Cl]_x$: Cu, 35.48; S, 18.87; Cl 19.82%, respectively.

Preparation of $K_2[Hg(SO_3Cl)_nI_{4-n}]$ [n=1, 2, 3, and 4; (6, 5, 4 and 3)]. For $K_2[Hg(SO_3Cl)_4]$ (**3**) solid K_2HgI_4 (0.7860 g or 0.001 mol) was mixed with excess of frozen HSO_3Cl. The temperature of the reaction mixture was slowly brought to room temperature with continuous magnetic stirring. The resulting dark red solution was poured dropwise in chilled dry diethyl ether in a closed vessel which resulted in the separation of colorless solid material. The solution was decanted off and the solid was repeatedly washed with ether till the washing did not show any color. The solid was vacuum dried, mp 197 °C, yield 0.55 g (ca. 70%) based on K_2HgI_4.

Compounds **4**, **5**, and **6** were prepared by mixing K_2HgI_4 with frozen HSO_3Cl in 1 : 3, 1 : 2, and 1 : 1 molar ratios, respectively, and the reaction mixture was allowed to warm up to room temperature with continuous stirring giving brownish-yellow colored solutions. These solutions separately resulted in the solid material when poured dropwise to chilled diethyl ether and the solid compounds were isolated in the manner as described above for **3**, melting points: **4** decomp 298—300 °C; **5** decomp 253—255 °C, **6** decomp 232—235 °C; yields: 2.7 g, 0.55 g, 3.79 g (70%, 70%, 80%, respectively based on K_2HgI_4).

Analysis. The results of C, H, N analyses were obtained from the microanalytical laboratory of I.I.T. Kanpur, whereas Cu, Hg, S, Cl, and I were determined by established methods.[22,23] The IR spectra (4000—250 cm^{-1}) were recorded as Nujol mulls using a Perkin Elmer Model 621 Spectrophotometer. Electrical conductivity was measured in 10^{-3} mol dm^{-3} solutions in DMSO or CH_3CN using a sys-

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tronic bridge model 302 thermostated at 25±0.1 °C. The electronic spectra were recorded in DMSO or CH_3CN using a PYE Unicam 8800 spectrophotometer.

Results and Discussion

For the synthesis of **1** and **3** the solvolytic reaction of $[M_2HgI_4]$ with HSO_3Cl has been utilized where HSO_3Cl also serves as the reaction medium and the formation may be typified by the following reactions.

$$M_2HgI_4 + 4HSO_3Cl \rightarrow M_2[Hg(SO_3Cl)_4] + 4HI \tag{1}$$

$$2HI + 2HSO_3Cl \rightarrow H_2SO_4 + 2HCl + I_2 + SO_2 \tag{2}$$

(M=K, Cu(I)).

Reaction of **1** with Et_4NI in CH_2Cl_2, where both the reactants are separately insoluble, seems to be an interesting one. It was anticipated to get the replacement of copper(I) ion by the bulky cation, Et_4N^+ together with the release of Cu(I)iodide. It is noteworthy that in this reaction the final products obtained (Experimental Section) have been characterized as **2** and $[CuSO_3Cl]_x$, but only **2** is soluble in CH_2Cl_2 giving a dark brown solution. This implies that during the course of the reaction, in addition to the exchange of the cation, an anion replacement also takes place which may reasonably be due to the soft nature of iodide ion.[24–26] The reaction may be represented by the following equation.

$$Cu_2[Hg(SO_3Cl)_4] + 2Et_4NI \rightarrow (Et_4N)_2[Hg(SO_3Cl)_2I_2] + 2CuSO_3Cl \tag{3}$$

Stoichiometric amounts of $[K_2HgI_4]$ and HSO_3Cl, i.e., 1 : 1, 1 : 2, and 1 : 3 molar ratios, have been used for the preparation of **6**, **5**, and **4** where chlorosulfuric acid is an efficient chlorosulfating agent[27] effectively displacing an iodine atom as shown below.

$$K_2HgI_4 + nHSO_3Cl \rightarrow K_2[Hg(SO_3Cl)_nI_{4-n}] + nHI \tag{4}$$

(n=1, 2, and 3).

The magnitudes of the molar conductivity measured in DMSO for **3**, **4**, **5**, **6** and in CH_3CN for **1** and **2** (Table 1) suggest these to be strong electrolytes.[28]

Table 1. Elemental Analysis and Molar Conductance of the Compounds[a)]

Copounds		Melting points	Found (Calcd)/%					μM[b)]	Yield
		°C	S	Cl	I	Hg	Cu	cm^2 S^{-1} mol^{-1}	%
$Cu_2[Hg(SO_3Cl)_4]$	**1**	d.300	16.8 (17.4)	17.0 (17.2)	—	24.7 (25.4)	15.8 (16.26)	181	80
$(Et_4N)_2[Hg(SO_3Cl)_2I_2]$	**2**	130	8.1 (8.3)	8.5 (9.09)	31.6 (32.0)	25.1 (25.9)	—	140	70
$K_2[Hg(SO_3Cl)_4]$	**3**	197	18.4 (18.28)	19.1 (20.28)	—	29.3 (28.37)	—	250	70
$K_2[Hg(SO_3Cl)_3I]$	**4**	d.298—300d	12.01 (12.8)	13.77 (14.2)	18.02 (16.9)	25.4 (26.6)	—	200	70
$K_2[Hg(SO_3Cl)_2I_2]$	**5**	d.253—255d	7.99 (8.39)	8.98 (9.18)	32.80 (33.33)	25.7 (26.77)		145	70
$K_2[Hg(SO_3Cl)I_3]$	**6**	d.232—235d	4.17 (4.13)	4.39 (4.58)	49.75 (49.22)	24.1 (25.83)	—	161	80

a) Calculated values in parenthesis, d decomposition. b) for **1** and **2** in CH_3CN and for **3**, **4**, **5**, and **6** in DMSO.

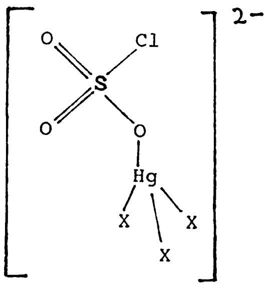
Table 2. Infrared Frequencies (cm^{-1}) and Electronic Spectral Bands (nm) of Compounds[a)]

Compounds		ν_6(E)	ν_2(A)	ν_3(A)	ν_5(E)	ν_1(A)	ν_4(E)	$\nu_{(Et_4N)}$	Electronic spectra
$Cu_2[Hg(SO_3Cl)_4]$	**1**	310 w 330 w	460 m	540 s	590 s 610 s	1075 s	1280 s 1300 s		230 m, 260 m, 280 s, 470 mb.
$(Et_4N)_2[Hg(SO_3Cl)_2I_2]$	**2**	310 w 320 w	420 m	545 m	590 s 610 s	1030 s	1170 s 1225 s	2980 m 2940 m 1450 b 1365 m 1005 s	230 w, 260 s, 280 sh, 360 mb.
$K_2[Hg(SO_3Cl)_4]$	**3**	310 w 330 w	460 m	520 s	570 s 590 s	1050 s	1170 m 1250 s 1290 s		230 m, 260 m, 280 sh, 350 s, 470 mb
$K_2[Hg(SO_3Cl)_3I]$	**4**	310 w 330 w	450 m	510 s	580 s 600 s	1070 s	1230 s 1290 s		230 m, 260 m, 280 sh, 360 sh.
$K_2[Hg(SO_3Cl)_2I_2]$	**5**	320 w 340 w	450 m	530 s	600 s 610 s	1060 s	1270 s 1300 s		230 m, 290 s, 360 m
$K_2[Hg(SO_3Cl)I_3]$	**6**	310 w 330 w	460 m	520 s	590 s 610 s	1056 s	1200 s 1230 s		270 s, 300 m, 370 sh

a) w=weak, m=medium, s=strong, b=broad, sh=shoulder, ν_1(A) sym·SO_3 stretch, ν_4(E) asym·SO_3 stretch, ν_5(E) asym·SO_3 def., ν_3(A) sym·SO_3 def., ν_2(A) S–Cl stretch, ν_6(E) S–Cl wag.

The IR spectra of the compounds (Table 2) show bands which may reasonably be assigned to the characteristic SO_3Cl^- group vibrations. The chlorosulfate group is known[19,30] to coordinate to a metal ion in a uni- or bidentate manner exhibiting considerable cation–anion interaction. The free SO_3Cl^- ion has C_{3v} symmetry[27] which would comprise of six IR active fundamentals, namely $\nu_1(A)$, $\nu_2(A)$, $\nu_3(A)$, $\nu_3(E)$, $\nu_5(E)$, and $\nu_6(E)$ with three of these being degenerate. It has been observed[29–31] that $\nu_1(A)$ frequency in transition metal and rare earth metal chlorosulfates lies to a higher energy by about 35 cm^{-1} from that indicated[27] in ionic $CsSO_3Cl$, owing to an increased cation–anion interaction leading to a reduced C_s symmety. The lowering of the symmetry from C_{3v} to C_s causes the splitting of the degenerate modes exhibiting in all nine IR active fundamentals.[27] The present IR data are consistent with a covalent bonding of the SO_3Cl^- group to the Hg^{2+} ion. The nature and the positions of the bands in the IR spectra of all these compounds are identical, suggesting the formation of similar species with most likely tetrahedral geometry.

Goodgame et al.[32,33] have reported that in $K_3[Hg(NO_2)_4](NO_3)$ and $K_2[Hg(NO_2)_4]$ there are four chelating NO_2 groups surrounding the Hg^{2+} ion in an approximately tetrahedral array. The characteristic stretching frequency for (Hg–I) bond expected[34] at ca. 120 cm^{-1} could not be recorded as it occurs beyond the range of our instrument. The probable tetrahedral geometry of the anion $[Hg(SO_3Cl)_2I_{4-n}]^{2-}$ (n=1, 2, 3, and 4) may reasonably be represented as shown below, where X is I or SO_3Cl.



It has been reported that the two bands observed in the UV-region (250—300 nm) for transition metal chlorosulfate,[35] are due to charge transfer as well as the $n\rightarrow\sigma^*$ transition of the SO_3Cl^- group, irrespective of the IR geometry. Wolfsberg and Helmholtz[36] have proposed the LCAO-MO scheme to account the electronic spectra of the molecules like MnO_4^-, CrO_4^{2-}, $CoCl_4^{2-}$, and ClO_4^- etc. (Td symmetry). The observed lowest energy band of the $[Hg(SO_3Cl)_4]^{2-}$ anion (Table 2) in qualitative terms reasonably corresponds to the transition, HOMO [filled nonbonding π-orbital]$\rightarrow$LUMO [unfilled antibonding π^*-orbital]. The possibility of a Jahn–Teller distortion[37] in the molecule could not be ruled out as the spectrum contains closely spaced bands in the UV-region. The electronic spectra[38] of $[HgI_4]^{2-}$ and of $[HgI_3]^-$ anion[26,34] are similar showing maxima at 270 and 320 nm, characteristic of a tetrahedral geometry of the complex anion.[39] Although the exact nature of the transitions responsible for these bands has not authoritatively pronounced, they were considered to be due to promotion of a nonbonding electron to the available two unfilled orbitals. It has been indicated[40] that the substitution of halogen for oxygen atoms in CrO_4^{2-} (CrO_3F^-, CrO_3Cl^-, CrO_2Cl_2) shifts the absorption band to longer wavelengths suggesting that the $[Hg(SO_3Cl)_4]^{2-}$ anion also would exhibit a similar red-shift on substituting iodine atoms in place of a SO_3Cl^- group. However, no such information is revealed in the electronic spectra of **2**, **4**, and **5** rather the band occurring in the visible region of **1** and **3** does not appear in the former cases.

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