TABLE 1—PHYSICAL PROPERTIES AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	m.p., °C	(Found), Calc. (%)			
			Metal	N	C	H
Cu(4MeOHPEN)	Gray	264–66(d)	(14.90) 15.26	(6.41) 6.77	(63.90) 63.83	(6.40) 6.28
Ni(4MeOHPEN)	Orange	249–51(d)	(13.88) 14.37	(6.59) 6.85	(65.00) 64.58	(6.50) 6.36
Co(4MeOHPEN)	Brown	41–43(d)	(14.24) 14.41	(6.65) 6.85	(64.70) 64.56	(5.90) 6.36
VO(4MeOHPEN)	Green	286–87(d)	(12.01) 12.21	(6.61) 6.72	(63.81) 63.33	(5.89) 6.24
UO_2(4MeOHPEN)	Bright	234–36(d)	(38.16) 38.39	(4.91) 4.52	(41.28) 42.58	(3.91) 4.19

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Halocations of Selenium & Tellurium in Chlorosulphuric Acid

R. C. PAUL†, D. KONWER & J. K. PURI*
Department of Chemistry, Panjab University, Chandigarh 160 014

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Selenium and tellurium form $SeCl_3^+$, $SeBr_3^+$, $TeCl_3^+$ and $TeBr_3^+$ cations in chlorosulphuric acid in the presence of Cl_2 and Br_2. However selenium monochloride forms $Se_2Cl_3^+$ and $Se_2Cl_2Br^+$ in HSO_3Cl in the presence of chlorine and bromine respectively.

†Present address : Vice-chancellor, Panjab University, Chandigarh.

SELENIUM[1-3] and tellurium[4-6] form coloured solutions in strong acids. The green and yellow solutions of selenium are attributed to Se_8^{2+} and Se_4^{2+} cations and the red and yellow solutions of tellurium to Te_4^{2+} and Te_2^{2+} cations respectively. In the present note we report the formation of some halocations of selenium and tellurium in chlorosulphuric acid.

Chlorosulphuric acid (BDH) was purified as reported earlier[7]. Selenium and tellurium metals were of AR grade. Selenium monochloride was prepared by the standard method[8].

Chlorine and bromine behave as non-electrolytes[9] in chlorosulphuric acid. Selenium metal does not form any green solution in chlorosulphuric acid containing chlorine. UV and visible spectra of the solution rule out the presence of Se_8^{2+} or Se_4^{2+} ions. The solutions become stable after sometime. However, from the conductance data (Fig. 1), the possible mode of reaction may be represented by Eq. (1),

$$M + 2Cl_2 + HSO_3Cl \longrightarrow MCl_3^+ + SO_3Cl^- + HCl \quad ...(1)$$
$$(M = Se \text{ or } Te)$$

Beyond Se/Cl_2 molar ratio of 1:2, further addition of selenium metal results in a green solution (due to Se_8^{2+} cation) which slowly changes to yellow solution (due to Se_4^{2+} cation).

Selenium metal, in the presence of Br_2 in chlorosulphuric acid, does not form Se_8^{2+} or Se_4^{2+} cations. The reaction is always accompanied by the evolution of SO_2 gas, as confirmed by UV spectrum of the solution (λ_{max} at 280 nm). On the basis of the conductance data (Fig. 1) and the UV spectrum of the solution, the reaction in the presence of Br_2 may be represented by Eq. (2),

$$2M + 3Br_2 + 4\ HSO_3\ Cl \longrightarrow 2MBr_3^+ + 2SO_3Cl^- + H_2SO_4 + 2HCl + SO_2 \ldots(2)$$
$$(M = Se \text{ or } Te)$$

Beyond Se/Br_2 molar ratio of 2:3, further addition of selenium metal results in a greenso lution (due to Se_8^{2+}) which slowly changes to yellow (due to Se_4^{2+}).

Selenium monochloride disproportionates in chlorosulphuric[10] acid as $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$.

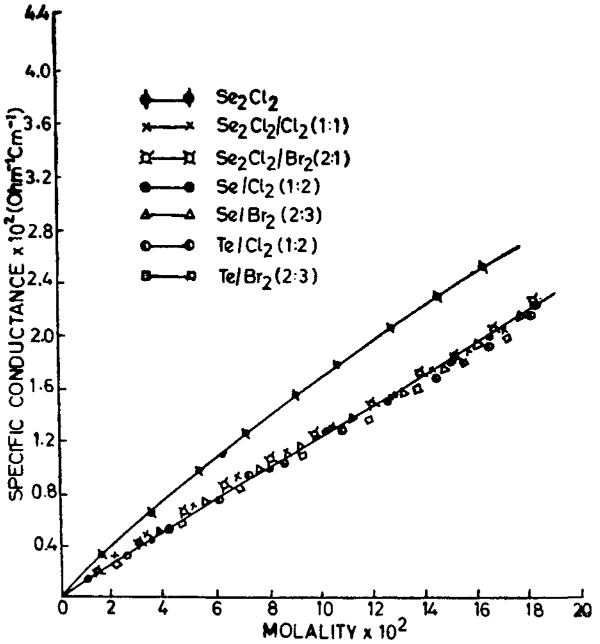

Fig. 1 — Specific conductivities of some selenium and tellurium compounds in chlorosulphuric acid at 25°C.

Elemental selenium gets oxidised further to form Se_8^{2+} cation which slowly changes to Se_4^{2+} cation and $SeCl_4$ forms $SeCl_3^+$ ion in this solvent[11].

Selenium monochloride in chlorosulphuric acid in the presence of chlorime, forms a light-green solution which immediately changes to yellow. A break in the conductance-composition curve at Se_2Cl_2/Cl_2 molar ratio of 1:1 is also obtained. From the conductance data the mode of reaction may be represented by Eq. (3),

$$Se_2Cl_2 + Cl_2 + HSO_3Cl \longrightarrow Se_2Cl_3^+ + SO_3Cl^- + HCl \quad \ldots(3)$$

Formation of the yellow solution may be due to the disproportionation reaction, $Se_2Cl_3^+ \longrightarrow SeCl_3^+ + Se$. Elemental selenium then further reacts with the solvent to form a green solution (due to Se_8^{2+}) followed by the appearance of yellow colour (due to Se_4^{2+}). Since only very small quantity of free selenium metal seems to be formed as a result of disproportionation reaction, it contributes very little to the γ value.

Selenium monochloride in the presence of bromine in chlorosulphuric acid does not form any green solution. UV and visible spectra of the above solution exhibit maximum absorption at 280 nm (ϵ_{max} 1050) suggesting the formation of SO_2 gas during the reaction. The conductance data are best represented by the reaction (4),

$$2Se_2Cl_2 + Br_2 + 4\ HSO_3\ Cl \longrightarrow 2Se_2Cl_2Br^+ + 2SO_3Cl^- + H_2SO_4 + HCl + SO_2 \quad \ldots(4)$$

When all the bromine has been consumed, further addition of selenium monochloride results in the formation of the green solution (due to Se_8^{2+}) which slowly changes to yellow (due to Se_4^{2+}). In the presence of excess of bromine, selenium monochloride does not form any green solution, suggesting that the cation $Se_2Cl_2Br^+$ is quite stable or possibly the green colour is masked by the reddish-brown colour of bromine in this solvent. Such type of species have also been reported in other strong acids[12].

Tellurium metal in chlorosulphuric acid in the presence of Cl_2 or Br_2 does not form any red colour. UV and visible spectra of the solutions rule out the presence of Te_4^{2+} or Te_2^{2+} cations. The solution in the presence of chlorine is found to be quite stable as there is no change in the conductance of the solution with time. From conductance data, the mode of reaction may be represented as in Eq. (1). Beyond Te/Cl_2 molar ratio of 1:2, further addition of tellurium metal causes the formation of a red solution (due to Te_4^{2+}) which slowly changes to an yellow solution (due to Te_2^{2+}).

The solution of tellurium metal in chlorosulphuric acid in the presence of bromine is not very stable as revealed by the variation in conductivity with time. However, the conductance data, when extrapolated to zero time and compared with that of a strong base in chlorosulphuric acid, show that the possible mode of reaction may be represented by Eq. (2). The UV spectrum of the solution exhibits absorption band at 280 nm due to the presence of SO_2 gas. Formation of $TeBr_3^+$ cation seems to be quite reasonable as such species has already been shown to form on dissolving $TeBr_4$ in chlorosulphuric acid[11].

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