

The Ternary Compound



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In the system SbCl_5 — TiCl_4 — POCl_3 a compound is formed which has a higher melting point than any of the compounds $\text{SbCl}_5 \cdot \text{POCl}_3$, $\text{TiCl}_4 \cdot \text{POCl}_3$ or $\text{TiCl}_4 \cdot 2\text{POCl}_3$. It is rather difficult to obtain the compound pure from excess SbCl_5 , TiCl_4 or POCl_3 (depending upon the mole ratios of the original mixture), but all such experiments indicate a composition $\text{SbCl}_5 \cdot \text{TiCl}_4 \cdot 3\text{POCl}_3$. (The high melting point shows that it cannot be a mixture of $\text{SbCl}_5 \cdot \text{POCl}_3$ and $\text{TiCl}_4 \cdot 2\text{POCl}_3$). We therefore tried to prepare a pure specimen by dissolving SbCl_5 and TiCl_4 in the mole ratio 1:1, in ethylene chloride and adding an excess of POCl_3 . The volatile components were then removed by evacuation, the solid residue was further purified by sublimation and the resulting crystals were analyzed. (Found: Cl 67.5; Ti 5.00; P 10.0. Calc. Cl 67.3; Ti 5.05; P 9.8.)

Titanium was determined spectrophotometrically by the peroxide method with an excess of phosphoric acid in order to make the determination insensitive to the amount of phosphoric acid in the dissolved sample.

Phosphorus was determined by precipitation as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in the presence of EDTA and hydrogen peroxide (to keep titanium in solution) and titration by EDTA of the magnesium content in the washed precipitate.

Antimony did not interfere in these determinations.

The crystals sublime before melting at about $+200^\circ\text{C}$.

The high melting point indicates that the ternary compound cannot be a loose addition compound between $\text{SbCl}_5 \cdot \text{POCl}_3$ and $\text{TiCl}_4 \cdot 2\text{POCl}_3$. Since co-ordination around Sb and Ti is already as large as possible in

those two addition compounds, however, no halogen bridged compound of the same type as in $[\text{TiCl}_4(\text{OPCl}_2)_2]_2$, containing Sb as well as Ti, can therefore have formed. A more probable alternative would be the formation of SbCl_6^- and $[\text{TiCl}_2(\text{OPCl}_2)_2]^+$ ions.

The latter suggestion has been tested by measurements of the specific conductances of 0.9 M solutions of $\text{SbCl}_5 \cdot \text{POCl}_3$, $\text{TiCl}_4 \cdot 2\text{POCl}_3$ and $\text{SbCl}_5 \cdot \text{TiCl}_4 \cdot 3\text{POCl}_3$ in ethylene chloride. The values are approximately (at $+21^\circ\text{C}$):

$$\begin{aligned} 2.4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1} & (\text{SbCl}_5 \cdot \text{POCl}_3) \\ 3.7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} & (\text{TiCl}_4 \cdot 2\text{POCl}_3) \\ 6.3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} & (\text{SbCl}_5 \cdot \text{TiCl}_4 \cdot 3\text{POCl}_3) \end{aligned}$$

The evidence so far is thus in accord with the idea that the ternary compound is actually $[\text{TiCl}_2(\text{OPCl}_2)_2]_2(\text{SbCl}_6)$. Conclusive proof is, however, still lacking.

In the systems SbCl_5 — SnCl_4 — POCl_3 and SbCl_5 — AsCl_3 — POCl_3 no ternary compound could be found. The increase in specific conductance is obtained, however, but the magnitude of the conductances is smaller than with $\text{TiCl}_4 \cdot 2\text{POCl}_3$:

$$\begin{aligned} 3.6 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1} & (\text{SnCl}_4 \cdot 2\text{POCl}_3) \\ 6.1 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} & (\text{SbCl}_5 \cdot \text{POCl}_3 + \\ & \text{SnCl}_4 \cdot 2\text{POCl}_3) \end{aligned}$$

The greater tendency of TiCl_4 to act as a chloride ion donor in these systems is in agreement with the active base strength of TiCl_4 as determined by potentiometric measurements².

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