The Ternary Compound
SbCl₅ · TiCl₄ · 3POCl₃

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In the system SbCl₅-TiCl₄-POCl₃, a compound is formed which has a higher melting point than any of the compounds SbCl₅-POCl₃, TiCl₄-POCl₃ or TiCl₄-2POCl₃. It is rather difficult to obtain the compound pure from excess SbCl₅, TiCl₄ or POCl₃ (depending upon the mole ratios of the original mixture), but all such experiments indicate a composition SbCl₅-TiCl₄-3POCl₃. (The high melting point shows that it cannot be a mixture of SbCl₅, POCl₃ and TiCl₄-2POCl₃.) We therefore tried to prepare a pure specimen by dissolving SbCl₅ and TiCl₄ in the mole ratio 1:1, in ethylene chloride and adding an excess of POCl₃. The volatile components were then removed by evaporation, 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 MgNH₄PO₄·6H₂O 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°C.

The high melting point indicates that the ternary compound cannot be a loose addition compound between SbCl₅ · POCl₃ and TiCl₄ · 2POCl₃. 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 [TiCl₄(OPCl₃)]⁺ containing Sb as well as Ti, can therefore have formed. A more probable alternative would be the formation of SbCl₅ and [TiCl₄(OPCl₃)]⁺ ions.

The latter suggestion has been tested by measurements of the specific conductances of 0.9 M solutions of SbCl₅·POCl₃, TiCl₄·2POCl₃ and SbCl₅·TiCl₄·3POCl₃ in ethylene chloride. The values are approximately (at +21°C):

- 2.4 × 10⁻⁴ ohm⁻¹ cm⁻¹ (SbCl₅·POCl₃)
- 3.7 × 10⁻⁴ ohm⁻¹ cm⁻¹ (TiCl₄·2POCl₃)
- 6.3 × 10⁻⁴ ohm⁻¹ cm⁻¹ (SbCl₅·TiCl₄·3POCl₃)

The evidence so far is thus in accord with the idea that the ternary compound is actually [TiCl₄(OPCl₃)]⁺(SbCl₅). Conclusive proof is, however, still lacking.

In the systems SbCl₅-SnCl₄-POCl₃ and SbCl₅-AsCl₅-POCl₃ no ternary compound could be found. The increase in specific conductance is obtained, however, but the magnitude of the conductances is smaller than with TiCl₄·2POCl₃:

- 3.6 × 10⁻⁴ ohm⁻¹ cm⁻¹ (SnCl₄·2POCl₃)
- 6.1 × 10⁻⁴ ohm⁻¹ cm⁻¹ (SbCl₅ · POCl₃ + SnCl₄ · 2POCl₃)

The greater tendency of TiCl₄ to act as a chloride ion donor in these systems is in agreement with the active base strength of TiCl₄ as determined by potentiometric measurements.

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