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Abstract

Full Text

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ON CERTAIN COMPOUNDS OF TRIVALENT TITANIUM AND PARAMAGNETIC RESONANCE IN THEM

(Presented by Academician A. E. Arbuzov, 14 XII 1961)

Familiarity with the literature shows that trivalent titanium compounds have been studied very little. We have carried out an investigation of these compounds by the method of paramagnetic resonance (^{1,2}). Methods were developed for obtaining titanium(III) carbonate and certain complex compounds. As far as we know, neither titanium carbonate nor the complexes synthesized by us have been described in the literature. To obtain titanium(III) carbonate, crystalline sodium carbonate is gradually added, with frequent stirring, to a saturated solution of titanium(III) chloride. In the reaction vessel titanium carbonate rapidly precipitates in the form of a black coarse-grained mass. The precipitate obtained is transferred to a Büchner funnel, suction-filtered, and repeatedly washed with cold water until chloride ions are removed. It may also be washed by decantation. For better precipitation one should avoid an excess of sodium carbonate, since in an alkaline medium trivalent titanium is readily converted into tetravalent titanium. Titanium(III) carbonate is a black amorphous mass which, in air, gradually becomes white in color, passing into tetravalent titanium. Titanium carbonate reacts with inorganic acids and with acetic acid, forming the corresponding salts. It must be stored either in an atmosphere free of oxygen and traces of moisture, or in a Dewar vessel with liquid nitrogen. For this purpose the amorphous mass is pressed into rods, which are wrapped with a gauze ribbon and lowered into a Dewar with liquid nitrogen.

The purity of the preparation was checked by the method of paramagnetic resonance. The point is that titanium(III) chloride at $T = 77^\circ\text{K}$ gives a measurable resonance effect, whereas titanium carbonate obtained from the chloride, after thorough washing, gives no effect.

In view of the low stability of the titanium(III) carbonate obtained by us, finding its general chemical formula was extremely difficult. On the basis of chemical analysis we succeeded in establishing the ratio between the amount of CO_3^{2-} ions and Ti^{3+} ions in one and the same sample. This ratio proved to be equal to 1 : 1 with an accuracy of up to 3%. The analysis was carried out as follows: a freshly prepared sample of titanium carbonate, after thorough washing and checking for the absence of TiCl_3 , was subjected to the action of HCl ; the amount of carbon dioxide evolved was determined with the aid of Berg's burette (³). In the solution

Fig. 1

Figure 1: Fig. 1

obtained after the action of HCl, titanium was determined gravimetrically in the form of TiO_2 . For this purpose titanium was precipitated with a 3% solution of cupferron. The yellow precipitate obtained, after thorough washing, was ignited in the full flame of a gas burner to constant weight. On the basis of the ratio found we may assert that our salt is basic in character and corresponds to one of the formulas: $\text{Ti}(\text{OH})\text{CO}_3$ or $\text{Ti}_2\text{O}(\text{CO}_3)_2$.

Experimental part

Several pieces of titanium carbonate are placed in a porcelain dish, and with frequent stirring at room temperature, molten-

acid. As a result of the reaction, a grass-green solution is formed. A solution of analogous color is obtained when a small amount of hydrofluoric acid is allowed to act, without heating, on crystalline titanium chloride. When hydroiodic acid acts on titanium carbonate, a solution likewise of grass-green color is obtained. When hydrobromic acid and hydrochloric acid act on titanium carbonate, however, a violet solution is obtained. The solutions obtained were studied by the method of paramagnetic resonance.

As a result of the study of these complexes by the EPR method ⁽⁴⁾, it was established that the green solutions give a measurable resonant paramagnetic absorption, whereas the violet solutions give no effect. Evidently, the solutions that have a green coloration contain a low-symmetry complex of composition $[\text{TiF}_n(\text{H}_2\text{O})_{6-n}]^{3-n}$, while the solutions that have a violet coloration contain the high-symmetry complex of composition $[\text{Ti}(\text{H}_2\text{O})_6]$.

Besides green solutions of complexes, we obtained brown solutions. Thus, when hydrofluoric acid is allowed to act on crystalline titanium chloride at room temperature, a brown solution is first formed. With further action of the acid, this solution gradually turns green. However, both solutions, the green and the brown, give practically identical EPR signals.

Fig. 1

Figure 1 shows the EPR line from an aqueous solution of brown-colored complexes, with concentration 0.25 M/l, obtained at an oscillating magnetic-field frequency $\nu = 9320$ MHz and at room temperature; $\delta H = 18$ oersted.

The very presence of the effect makes it possible to consider that the brown complex, like the green ones, belongs to the low-symmetry forms. At the same time, the almost complete identity of the EPR spectra in both cases shows that the distance between the lower orbital singlet and the nearest doublet is practically the same in both cases.

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