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Abstract

Full Text

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Synthesis and Analytical Properties of Tetra(α-thienyl)borate and Tetra(n-anisyl)borate Salts of Alkali Metals

(Presented by Academician A. N. Nesmeyanov, 7 XII 1956)

It is known that sodium tetraphenylborate ([1]) has recently been widely used as a reagent for the potassium ion. This compound also precipitates cesium and rubidium ions. Potassium, rubidium, and cesium tetraphenylborates are very sparingly soluble in water ([2]). Thus, at 20° (±0.5°), in 100 ml of water there dissolve 0.0053 g of the first salt, 0.0018 g of the second, and 0.0013 g of the third, which corresponds to 0.578 mg K, 0.38 mg Rb, and 0.43 mg Cs.

A. N. Nesmeyanov and one of us proposed a simple method for obtaining sodium tetraphenylborate ([3])—the action of phenylmagnesium bromide on sodium borofluoride:

$$NaBF_4 + C_6H_5MgBr \rightarrow NaB(C_6H_5)_4.$$

Potassium borofluoride also reacts readily with organomagnesium compounds (C_6H_5MgBr, n-$CH_3C_6H_4MgBr$ ([4]), $C_6H_5C{\equiv}CMgBr$ ([5]), etc.) with the formation of the corresponding tetraarylborate salts. It was further shown that this reaction is also possible in the heterocyclic series ([6]).

In the present work new salts of potassium, rubidium, cesium, and thallium are described, which are of interest for analytical chemistry. Our analytical data are preliminary in character and show that, using the tetrathienylborate ion, it may be possible to develop a method for separating cesium from other alkali metals and, probably, for the quantitative determination of thallium(I).

Under the action of α-thienylmagnesium iodide on potassium borofluoride, potassium tetra(α-thienyl)borate is formed:

$$KBF_4 + C_4H_3S{-}MgI \rightarrow KB(C_4H_3S)_4$$

Unlike potassium tetraphenylborate, the salt is soluble in water. Among the important properties of potassium tetra(α-thienyl)borate one should note its ability to precipitate cesium and rubidium ions from aqueous solutions:

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$$KB(C_4H_3S)_4 + CsCl \rightarrow\downarrow CsB(C_4H_3S)_4 + KCl$$
$$KB(C_4H_3S)_4 + RbCl \rightarrow\downarrow RbB(C_4H_3S)_4 + KCl,$$

while lithium and sodium ions do not interfere with these reactions.

In studying the dependence of the solubility in water of tetra(α-thienyl)borate salts of K, Rb, and Cs on temperature, the following data were obtained (salt content in grams per 100 g of aqueous solution):

Salt	0°	15°	25°	35°	45°	60°
$KB(C_4H_3S)_4$	0.668	0.804	1.038	1.459	1.953	2.890
$RbB(C_4H_3S)_4$	0.244	0.374	0.419	0.421	0.611	1.254
$CsB(C_4H_3S)_4$	0.051	0.053	0.091	0.098	0.122	0.209

The large difference in the solubility of the potassium and cesium salts makes it possible to use potassium tetra(α-thienyl)borate for the detection and separation of cesium from other alkali metals.

A solution containing 0.3 mg of Cs in 1 ml still gives a positive reaction for the presence of cesium upon addition of a 1% aqueous solution of $KB(C_4H_3S)_4$ (at room temperature).

Potassium tetra(α-thienyl)borate quantitatively precipitates thallium(I) ions in the form of $TlB(C_4H_3S)_4$.

A salt less soluble in water (in comparison with $KB(C_4H_3S)_4$) is obtained by the interaction of potassium borofluoride with iodide n-anisylmagnesium:

$$KBF_4 + \text{n-}CH_3OC_6H_4MgJ \longrightarrow KB(C_6H_4OCH_3)_4.$$

In our first communication ([4]), the reaction of n-anisylmagnesium bromide with KBF_4 was described, leading to tri(n-anisyl)boron, isolated in the form of the amminate. It was indicated there that, as an intermediate reaction product, tetra(n-anisyl)boropotassium apparently forms. Subsequently it was observed that certain ammonium and pyridinium tetraarylboron salts cannot be isolated, and instead the corresponding amminates and pyridinates of triarylboron are formed directly, unlike tetraphenylborammonium and -pyridinium, which can be isolated in pure form. By changing the method for isolating potassium tetra(n-anisyl)borate, we succeeded in obtaining this salt.

Potassium tetra(n-anisyl)borate is more soluble in water than potassium tetraphenylborate, but considerably less soluble than potassium tetra(α-thienyl)borate; it precipitates rubidium and cesium ions.

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Below is given the dependence of the solubility of potassium, rubidium, and cesium tetra(*n*-anisyl)borates in water on temperature (salt content in grams per 100 g of aqueous solution):

	25°	40°	60°
$KB(C_6H_4OCH_3)_4$	0.0337	0.0653	0.166
$RbB(C_6H_4OCH_3)_4$	0.0260	0.0508	0.163
$CsB(C_6H_4OCH_3)_4$	0.0244	0.0286	0.0463

With cations of quaternary ammonium salts, potassium tetra(*n*-anisyl)borate also gives tetra(*n*-anisyl)boron salts. With ammonium and pyridinium salts, however, potassium tetra(*n*-anisyl)borate does not give the corresponding tetraarylboron salts; instead the amminate and pyridinate of tri(*n*-anisyl)boron are obtained.

Potassium tetra(*n*-anisyl)borate is decomposed by dilute hydrochloric acid to di-*n*-anisylboric acid in 40% yield.

Experimental Part

Potassium tetra(α-thienyl)borate. To iodide α-thienylmagnesium, prepared from 0.93 g of magnesium, 8 g of α-iodothiophene* and 40 ml of absolute ether, 1.2 g of KBF_4 is added. The reaction is carried out in a conical flask equipped with a calcium chloride tube (in the case of larger quantities—with a condenser) with vigorous stirring. The reaction proceeds with slight warming and ends with separation of the mixture into layers. As soon as the warming of the mixture ceases and two layers form (after 20–35 min.), the precipitate is filtered off through a No. 1 glass filter and washed several times with absolute ether. The weight of the precipitate is 2.3 g. To separate potassium tetra(α-thienyl)borate from KBF_4, it is dissolved in nitromethane. The solution is filtered and absolute ether (or benzene) is added until precipitation of the white precipitate ceases. The latter is filtered off and washed with ether; 1.3 g (36% of theory) of potassium tetra(α-thienyl)borate is obtained. After recrystallization from water and drying in a vacuum desiccator over P_2O_5, a substance with the following analysis is obtained.

$C_{16}H_{12}S_4BK$.	Found, %:	C 50.07; 50.30; H 3.28; 3.28; K 10.42
	Calculated, %:	C 50.25; H 3.16; K 10.23

* α-Bromothiophene may be used in the reaction.

Tetra(α-thienyl)boropotassium is readily soluble in nitromethane and acetone; insoluble in ether and benzene; soluble in water.

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Tetra(α-thienyl)borocesium. When an aqueous solution of tetra(α-thienyl)boropotassium is added to an aqueous solution of the chloride or sulfate salt of cesium, a precipitate of tetra(α-thienyl)borocesium is formed; after washing with water and drying in a vacuum desiccator over P_2O_5, it was analyzed:

Found %:	C 40.39; 40.60; H 2.41; 2.50; Cs 28.01
$C_{16}H_{12}S_4BCs$. Calculated %:	C 40.35; H 2.54; Cs 27.90

Tetra(α-thienyl)borocesium is considerably less soluble in water than the corresponding potassium salt.

Tetra(α-thienyl)bororubidium. When an aqueous solution of $KB(C_4H_3S)_4$ is added to a solution of rubidium chloride, a white precipitate of tetra(α-thienyl)bororubidium is formed; after washing with water and drying in a vacuum desiccator over P_2O_5, it was analyzed.

Found %:	C 44.80; 44.59; H 2.76; 2.75
$C_{16}H_{12}S_4BRb$. Calculated %:	C 44.82; H 2.82

Tetra(α-thienyl)bororubidium, in its solubility in water, occupies an intermediate position between the corresponding potassium and cesium salts.

Tetra(α-thienyl)borothallium(I). To a solution of 0.0612 g of thallium(I) sulfate in 20 ml of water, a solution of 0.12 g of tetra(α-thienyl)boropotassium in 40 ml of water is added dropwise. A white precipitate of tetra(α-thienyl)borothallium(I) immediately separates; it is filtered off, washed several times with water, and dried in a vacuum desiccator over P_2O_5. They obtain 0.1331 g of $TlB(C_4H_3S)_4$; the calculated amount is 0.1328 g.

Found %:	C 34.98; 34.76; H 2.18; 2.18
$C_{16}H_{12}S_4BTl$. Calculated %:	C 35.09; H 2.21

Tetra(n-anisyl)boropotassium. To n-anisylmagnesium iodide, prepared from 10 g of n-iodoanisole, 1.1 g of magnesium, and 100 ml of abs. ether and decanted from the unreacted magnesium into a conical flask, 1.34 g of finely ground KBF_4 is added. The flask is closed with a stopper fitted with a calcium chloride tube. The reaction mixture is stirred vigorously for 20–25 min., after which it is filtered. The precipitate is washed twice with ether and dried in air. They obtain 2.62 g of crude substance. For purification, tetra(n-anisyl)boropotassium is dissolved in acetone, the solution is filtered from inorganic impurities, and the salt is reprecipitated from acetone with ether. They obtain 1.15 g (23% of theory) of tetra(n-anisyl)boropotassium.

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Found %: C 69.79; 70.01; H 5.95; 5.97
$C_{28}H_{28}O_4BK$. Calculated %: C 70.30; H 5.89

Tetra(n-anisyl)boropotassium is a colorless crystalline substance; on heating at about 95° it turns yellow, and at 280–300° it decomposes; it is readily soluble in acetone and pyridine, less readily in alcohol, slightly soluble in water, insoluble in ether, petroleum ether, and benzene; it recrystallizes from a mixture of alcohol with acetone. Aqueous solutions of the salt give a qualitative reaction for K^+ with a solution of sodium tetraphenylborate.

Di-*n*-anisylboric acid. 0.1 g of tetra(n-anisyl)boropotassium is dissolved in a minimal amount of acetone, and several drops of dilute HCl are added to the solution. After 2–3 min., water is added to the solution. The precipitated solid is filtered off, dried in a vacuum desiccator, and recrystallized from petroleum ether. They obtain 0.02 g (40% of theory) of di-n-anisylboric acid with m.p. 104–105° (in a sealed capillary). According to the literature, m.p. 107° (7).

Tetra(*n*-anisyl)bororubidium. An aqueous solution of RbCl is added to a saturated aqueous solution of tetra(n-anisyl)boropotassium. The precipitated—

the white precipitate of tetra(p-anisyl)bororubidium is filtered off, washed several times with water, and dried in a vacuum desiccator over P_2O_5.

Found, %: C 64.21; 63.98; H 5.36; 5.45
$C_{28}H_{28}O_4BRb$. Calculated, %: C 64.08; H 5.38

Tetra(p-anisyl)bororubidium is a colorless crystalline substance, thermally rather stable (at 260° it begins to turn yellow, above 280° it decomposes); readily soluble in acetone and pyridine, sparingly soluble in alcohol and water; insoluble in ether and benzene; reprecipitated from acetone solution with ether.

Tetra(*p*-anisyl)borocesium. An aqueous solution of CsCl is added to a saturated aqueous solution of tetra(p-anisyl)boropotassium. The resulting white precipitate of tetra(p-anisyl)borocesium is filtered off, washed several times with water, and dried in a vacuum desiccator over P_2O_5.

Found, %: C 58.97; 59.19; H 5.06; 5.09
$C_{28}H_{28}O_4BCs$. Calculated, %: C 58.77; H 4.93

Tetra(p-anisyl)borocesium is a colorless crystalline substance (at 270° it turns yellow, above 290° it decomposes); readily soluble in acetone and pyridine, sparingly soluble in alcohol and water; insoluble in ether and benzene; reprecipitated from acetone solution with ether.

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