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# Chemistry

1961

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**Abstract**

**Full Text**

**Chemistry**

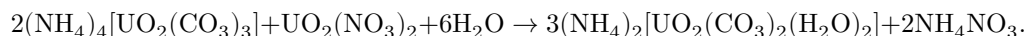
**D. I. Ryabchikov and E. K. Korchemnaya**

**Complex Uranyl Dicarbonate**

*(Presented by Academician A. N. Frumkin, 21 IV 1961)*

The uranyl ion, as is known, is a very energetic complex-forming agent, capable of forming coordination bonds with addends, in particular with the carbonate ion, predominantly through oxygen atoms. There is detailed literature on the complex formation of the uranyl ion with carbonate (<sup>1-7</sup>), where it is mainly indicated that already at a ratio  $\text{UO}_2^{2+} : \text{CO}_3 = 1 : 3$  and higher, a tricarbonat form of composition  $\text{Me}_4[\text{UO}_2(\text{CO}_3)_3]$  is formed, in which the six coordination sites of the uranyl ion are saturated by three  $\text{CO}_3^{2-}$  groups. The formation of this form of the compound is widely used in the processing of uranium ores (<sup>4,8</sup>).

It has been indicated (<sup>1</sup>) that compounds of the tricarbonat type are also formed with sodium bicarbonat. In our experiments, in the reaction of uranyl nitrat with sodium bicarbonat, a compound was invariably obtained that contained in the inner sphere only two coordinated  $\text{CO}_3^{2-}$  groups. It is interesting to note that a complex uranyl dicarbonat was obtained by I. I. Chernyaev and others (<sup>5</sup>) in another way, namely by the interaction of uranyl tricarbonat with uranyl nitrat according to the reaction:



However, the authors indicated that the ammonium form isolated by them is unstable and is readily destroyed. According to our data, the complex sodium uranyl dicarbonat is somewhat inferior in stability to the tricarbonat, but ammonia, for example, does not precipitate ammonium diuranat; on the contrary, it somewhat strengthens the complex, from which in this state the uranyl ion is not precipitated even by phosphate. It is more correct to regard uranyl dicarbonat as a compound of medium stability.

The compound was obtained in the following way. To a titrated solution of uranyl nitrat, prepared from metallic uranium, finely ground air-dry sodium bicarbonat was added in portions. The first portions were consumed in neutralizing the excess nitric acid. With subsequent addition, a precipitate began to form, which gradually dissolved in an excess of the reagent. Complete dissolution of the initially formed precipitate indicated the formation of the complex compound. The neutralization of the excess nitric acid and the formation of the

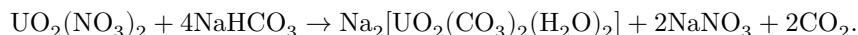
latter always consumed the same amount of sodium bicarbonate, equivalent to approximately 4 moles of it per 1 mole of uranium. From the aqueous solution, the resulting complex compound, upon addition of alcohol, was readily separated in the form of an oily liquid, which very rapidly in the aqueous-alcoholic medium turned into a finely crystalline powder. The filtered compound, washed with alcohol and ether and dried in air to constant weight, was analyzed.

According to the analytical data, the composition may be expressed by the formula  $\text{Na}_2[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ .

Found, %: U 49.51; C 4.27; H 1.01;  $\text{H}_2\text{O}$  6.78

Calculated, %: U 50.42; C 5.07; H 0.84;  $\text{H}_2\text{O}$  7.62

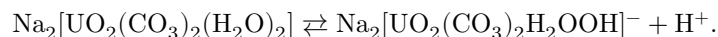
On the basis of the analytical data presented, the interaction between uranyl nitrate and sodium bicarbonate apparently proceeds according to the reaction:



The solubility of sodium uranyl dicarbonate is approximately 5 times greater than that of uranyl tricarbonate.

In the interaction with bicarbonate, only two  $\text{CO}_3^{2-}$  groups are placed in the inner sphere, while the remaining two coordination positions are replaced by two water molecules. This circumstance is probably the reason for the greater solubility of the aquo form  $\text{Na}_2[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ , in comparison with the tricarbonate form— $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$ . It is interesting that the isolated crystalline aquo form dissolves readily in water, but after prolonged exposure to air becomes sparingly soluble. An aqueous solution of the freshly prepared complex compound of the aquo form has a weakly acidic reaction.

For neutralization of a solution containing 2.12 g of  $\text{Na}_2[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ , an average of 23.0 ml of 0.096 N NaOH was consumed. This corresponds to approximately 12% of ionized hydrogen of the total amount entering into the composition of the complex compound in two molecules of water. It may be assumed that the formation of hydrogen ions in an aqueous solution of the aquo form of the complex dicarbonate compound of uranium occurs as a result of partial inner-sphere dissociation, proceeding according to the equation:



As a result of this process, an acidic form of the composition  $\text{Na}_2\text{H}[\text{UO}_2(\text{CO}_3)_2\text{H}_2\text{OOH}]$  is formed in solution, in which the hydrogen ions are detected by titration. This extremely interesting fact of the different mechanism of complex formation of the uranyl ion with sodium carbonate and bicarbonate has not found sufficient reflection in the literature.

Received  
20 IV 1961

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*Note: Figure translations are in progress. See original paper for figures.*

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