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THE PREPARATION OF TRIOXO-TRIFLUORORHENATE (VII) AND OXO-PENTAFLUORORHENATE (VI)

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SUMMARY

The newly prepared $K_2ReO_3F_3$ is the first known complex of ReO_3F. New methods were applied for the synthesis of the Rb- and Cs-salts of $ReOF_5^-$, which could be isolated and identified unequivocally.

$K_2ReO_3F_3$

ReO_3F was prepared from ReO_3Cl and HF by Engelbrecht and Grosse [1], and later on by fluorination of $KReO_4$ with IF_5 at 97°C by Aynsley and Hair [2]. Though Aynsley and Hair got KF and IOF_3 as byproducts, they could not observe any complexation. Furthermore, attempts to get the complex ion $ReO_3F_3^{2-}$ by fluorination of $KReO_4$ in a KHF_2-melt were unsuccessful [3]. Thus, ReO_3F was not known to be a fluoride acceptor as yet.

We modified the method of Aynsley and Hair [2] by fluorinating a stoichiometric mixture of $KReO_4$ and KF at room temperature in an excess of IF_5 expecting the following reaction:

$$KReO_4 + KF + IF_5 \xrightarrow{IF_5} K_2ReO_3F_3 + IOF_3$$

After 30 min. stirring, the solid mixture was completely dissolved in IF_5, which was slightly yellow because of some small impurities. The excess IF_5 was pumped off, first at room temperature, then at 90°C. A white, polycrystalline solid remained in the reaction vessel.

Spectroscopic investigations showed this solid to be a mixture of the expected complex $K_2ReO_3F_3$ [4], IO_2F and KIO_3 [5] (see Fig.1).

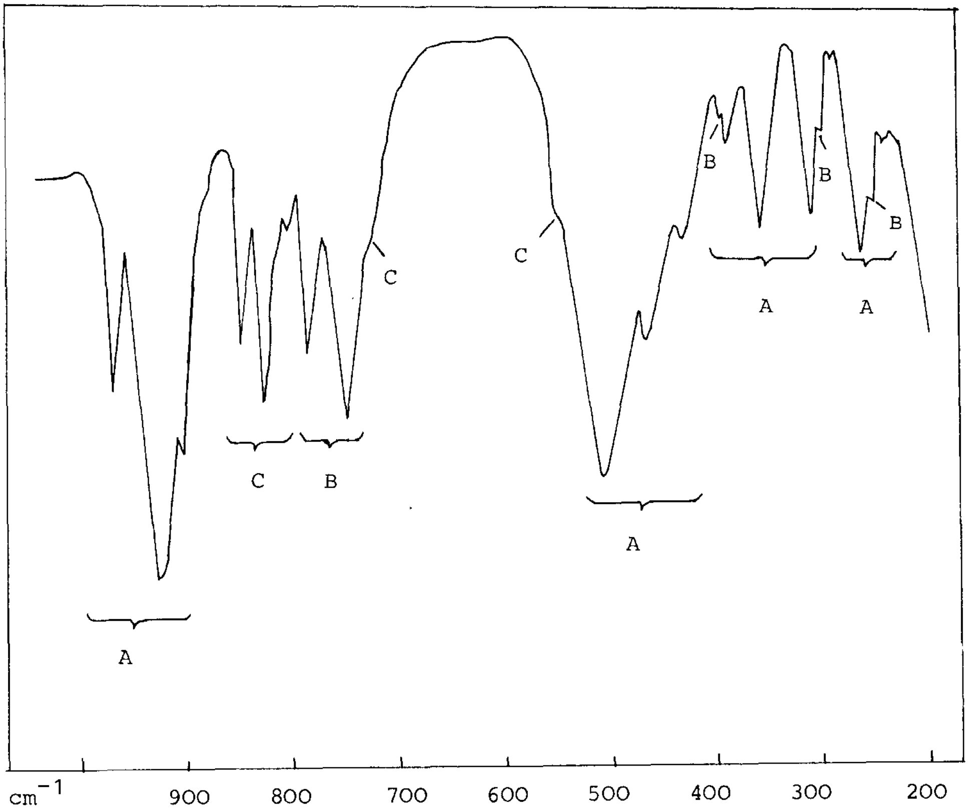

Fig. 1 Infrared spectrum of $5K_2ReO_3F_3$(A) + KIO_3(B) + IO_2F(C)

The stoichiometry of the reaction had therefore be corrected to

$$5KReO_4 + 6KF + 2IF_5 \xrightarrow{IF_5} 5K_2ReO_3F_3 + KIO_3 + IO_2F.$$

This mixture was always obtained without change using the proper amounts of starting materials.

The pure complex $K_2ReO_3F_3$ was isolated by reduction of KIO_3 and IO_2F with KI in absolute CH_3CN, in which $K_2ReO_3F_3$ is insoluble and remains unchanged.

The white complex $K_2ReO_3F_3$ decomposes at 220-230°C, above the boiling point of ReO_3F (164°C) and hydrolizes in moist air according to:

$$K_2ReO_3F_3 + H_2O \longrightarrow KReO_4 + HF + KHF_2$$

$MReOF_5$ (M=Rb,Cs)

In 1962, Ippolitov [6] reported a blue product obtained by the hydrolysis of ReF_8^{2-}, which he thought to be $ReOF_5^-$. Quite recently, Holloway and Raynor [7] studied the hydrolysis of ReF_6 in aqueous HF. They obtained a green solution, in which they identified $ReOF_5^-$ by Raman spectroscopy, but without isolating the product. Holloway and Raynor were not able to verify the results of Ippolitov.

We synthesized and isolated the complexes $MReOF_5$ (M always Rb and Cs) by the two following routes:

1. Less than 100 mg pure $MReF_7$, were dissolved in 10 ml absolute CH_3CN. The pale yellow solution (from which $MReF_7$ can be recovered unchanged) turns immediately light green, if the proper amount of water according to

   $$MReF_7 + H_2O \xrightarrow{CH_3CN} MReOF_5 + 2HF$$

   is added. After pumping off CH_3CN and HF, pure light green $MReOF_5$ (M=Rb,Cs) remained in the reaction vessel.

2. Excess ReF_6 was condensed on MF (M=Rb,Cs) containing the proper amount of water. The blue colour immediately observed is due to the formation of $ReOF_4$:

   $$ReF_6 + H_2O \longrightarrow ReOF_4 + 2HF \text{ [8].}$$

   The mixture was dissolved in freshly distilled IF_5 an stirred for 30 min., yielding a blue-green solution. After pumping of the solvent, the light green complex $MReOF_5$ remained.

It may be supposed, that the blue compound reported by Ippolitov [6] was a mixture of $ReOF_4$ and $ReOF_5^-$, because he used ReF_8^{2-} as starting material, which is synthesized according to

$$2MReF_7 \longrightarrow M_2ReF_8 + ReF_6 \quad [9]$$

and the formed ReF_6 hydrolizes to $ReOF_4$. This was also discussed by Holloway and Raynor [7]. The Raman spectra of our solid complexes agree with that of their solution concerning the overall number of lines and their intensities, but some frequency shifts are observed (see subsequent paper).

ANALYTICAL RESULTS

Re and the alkali ions were determined by gravimetric methods, Re as nitron-perrhenate and the alkali ions as tetraphenylborates. For the determination of the F^--content, the solution of the compound was mixed with an excess, but known amount of $Th(NO_3)_4$, and then conductometric titrated with NaF [10]. This method yields only good results, if Re remains in one oxidation state. Therefore the determination of F^- was only possible for $ReO_3F_3^{2-}$, but not for $ReOF_5^-$, which disproportionates to ReO_4^- and ReO_2 on hydrolysis.

	alkali ions		Re		F^-	
	calc.	exp.	calc.	exp.	calc.	exp.
$K_2ReO_3F_3$	21,2 %	21,4 %	50,4 %	51,2 %	15,4 %	15,9 %
$RbReOF_5$	22,3 %	22,6 %	48,6 %	48,2 %		-
$CsReOF_5$	30,9 %	31,4 %	43,3 %	42,2 %		-

The complexes were also identified by their vibrational spectra (see subsequent paper).

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