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Abstract

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PREPARATION OF RHENIUM DICHLOROMONOACETATE AND ITS DERIVATIVES WITH PYRIDINE AND THIOUREA

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In the Laboratory for the Synthesis of Rare-Element Compounds under elevated gas pressures, V. G. Tronev and co-workers (7–8) obtained a series of new compounds of divalent, trivalent, and tetravalent rhenium. Thus, among compounds of divalent rhenium a product of the following composition, $(PyH)HReCl_4$, was first isolated and was then obtained in a coarsely crystalline form (3), which enabled V. G. Kuznetsov and P. A. Koz' min (9) to study the structure of the compound and establish the presence in it of a —Re—Re—bond.

As was shown (4), when the compound $H_2ReCl_4 \cdot 2H_2O$ is dissolved in glacial acetic acid, followed by evaporation of the solvent, a series of derivatives can be obtained. The most stable proved to be the product to which the formula $ReCl_2 \cdot CH_3COOH \cdot H_2O$ was assigned.

To obtain rhenium dichloromonoacetate in crystalline form and of a sufficient degree of purity, the dark-blue solution obtained as a result of reducing potassium perrhenate in hydrochloric acid with hydrogen under pressure at 330°, and containing mainly the ions $ReCl_6''$ and $ReCl_4''$, hydrogen chloride, and water, was kept at room temperature for 15 hours. During this time a considerable amount of potassium chlororhenate, K_2ReCl_6, precipitated from it and was removed by filtration. The dark-blue filtrate was treated with an equal volume of glacial acetic acid. Within 1-2 hours a dark-blue, almost black precipitate separated from the solution; it was filtered off and treated with acetone. The acetone solution was then allowed to crystallize at room temperature. Within 24 hours, lustrous dark-blue crystals in the form of irregular hexagonal prisms separated from it. In order to obtain a purer product, the precipitate was recrystallized. A mixture of acetic acid and acetone in a ratio of 1:1 was used as the solvent. Within 10–15 hours crystals separated from the solution; in individual cases they reached a size of 1–2 mm.

On examination of the crystals under the microscope, no impurities were detected in them. For analysis, the crystals were carefully pressed on filter paper and dried in a vacuum drying oven at 100° until constant weight was attained. Below, as in all other cases, are given the average values found by analysis for

Fig. 1

Figure 1: Fig. 1

the amounts of rhenium, chlorine, carbon, etc.

$ReCl_2CH_3COOH \cdot H_2O$.	Found, %: Re 55.57; Cl 21.83; C 7.42; H 1.95; H_2O_2 5.35
	Calculated, %: Re 55.6; Cl 21.45; C 7.17; H 1.79; H_2O_2 5.36

by the method of A. G. Elishur (10).

The oxidation number of rhenium, determined by the method of I. and V. Noddack (11), proved to be 1.91.

The presence of water was also confirmed by the thermogram of the product (Fig. 1a), on which the endothermic effect at 122° corresponds, as was shown (4), to the removal of water. Determination of water from the loss in weight also gave satisfactory results.

In studying the magnetic properties, V. I. Belova found that rhenium dichloromonacetate is diamagnetic ($-\chi \cdot 10^6 = 0.16$). Since this product is obtained by the interaction of acetic acid with the compound $H_2ReCl_4 \cdot 2H_2O$, which has a Re—Re bond(7) and is therefore diamagnetic, it may be assumed that the diamagnetic properties of $ReCl_2 \cdot CH_3COOH \cdot H_2O$ are also associated with polymerization of the molecules through the Re—Re bond.

The molecular weight of $ReCl_2 \cdot CH_3COOH \cdot H_2O$ was determined from the depression of the melting point of a mixture of bromocamphor with the substance, as compared with the melting point of pure bromocamphor. The value of the molecular weight found was 660. Calculated for the monomer: 335.2. For the dehydrated product $ReCl_2 \cdot CH_3COOH$: found, 620. Calculated for the monomer: 317.2. It can be seen that the molecular-weight values found correspond to a dimeric product of composition $(ReCl_2 \cdot CH_3COOH \cdot H_2O)_2$.

Fig. 1

As was assumed earlier, the hydrogen of the acetic acid in the compound under study retains its acidic character, which was manifested, for example, in interaction with pyridine(4).

A more detailed study of the reaction of rhenium dichloromonacetate with pyridine in aqueous solution showed that, apparently, what occurs is not addition of pyridine to the acid hydrogen, but replacement of water by pyridine. Thus, determination of the water content by the Elishur method and by loss in weight in the pyridine derivative gave negative results.

To obtain the pyridine derivative, pyridine was added dropwise to an aqueous solution of $(ReCl_2 \cdot CH_3COOH \cdot H_2O)_2$. The dark-blue precipitate that separated was washed with cold distilled water, then repeatedly with alcohol, dried at 100° in a vacuum drying oven, and then analyzed.

Found, %: Re 46.61; Cl 17.89; N 3.56; C 20.62; H 2.51
$ReCl_2 \cdot CH_3COOH \cdot Py$. Calculated, %: Re 47.21; Cl 17.9; N 3.54; C 21.2; H 2.28

On the thermogram of the product (Fig. 1b) there are two endothermic effects at 316 and 380°. The endothermic effect at 126°, which was observed on the heating curve of $(ReCl_2 \cdot Cl_3COOH \cdot H_2O)_2$, is absent. It may also be noted that pyridine somewhat increases the thermal stability of the compound.

The value of the molecular weight, determined from the difference between the melting points of bromocamphor and of the mixture of bromocamphor with the substance, indicated dimerization. Thus molecular-weight values of 753 and 768 were found. Calculated for the dimeric product: 792.

The interaction of dichloromonacetate with pyridine in aqueous solution may be represented by the following scheme:

$$(ReCl_2 \cdot CH_3COOH \cdot H_2O)_2 + 2Py \rightarrow (ReCl_2 \cdot CH_3COOH \cdot Py)_2 + 2H_2O$$

$$\longrightarrow$$

$$\downarrow$$

To a solution of rhenium dichloromonacetate in acetone (sample ~ 0.2—0.3 g), a saturated acetone solution of thiourea was added. Gradually ob-

a precipitate formed, which was filtered off, washed repeatedly with acetone and ether, and kept in a desiccator until constant weight was attained. The isolated product was a yellowish-brown finely crystalline powder, readily soluble in water and alcohol. The results of analyses for its content of rhenium, chlorine, nitrogen, carbon, and hydrogen are given below:

$ReCl_2 \cdot CH_3COOH \cdot 2ThiO$. Found, %: Re 40.28; Cl 15.97; N 12.21; C 10.53; H 2.46
Calculated, %: Re 39.8; Cl 15.2; N 11.94; C 10.03; H 2.14

Measurement of the magnetic susceptibility showed that the compound with thiourea is also diamagnetic ($\chi_g \cdot 10^6 = -0.306$). Consequently, it may be assumed that in this product as well the bond —Re—Re—is retained. Unfortunately, it was not possible to measure the molecular weight in molten camphor, and doubling of the formula for the thio derivative has not been strictly proved.

In the thermal study of this product, no effects were observed up to a temperature of 250°. Final decomposition of the substance occurred at 380°.

Apparently, in the interaction of thiourea with dichloromonoacetate, not only did substitution of water by thiourea occur, but also addition of a second ThiO molecule.

Thus it was shown that the divalent rhenium dichloromonoacetate obtained in crystalline form is a dimerized product of the following composition $[ReCl_2CH_3COOH \cdot H_2O]_2$. Dimerization probably occurs through the —Re—Re—bond.

The interaction of rhenium dichloromonoacetate with pyridine and thiourea proceeds with replacement of water in the initial compound. The reaction products apparently also have a dimeric structure, $(ReCl_2 \cdot CH_3COOH \cdot Py)_2$ and $(ReCl_2 \cdot CH_3COOH \cdot 2ThiO)_2$.

According to thermographic investigation, the derivatives of $(ReCl_2 \cdot CH_3COOH \cdot H_2O)_2$ with pyridine and thiourea possess greater thermal stability than rhenium dichloromonoacetate.

In conclusion, the authors express their deep gratitude to V. G. Tronev for his attentive discussion of the results of the work and to V. I. Belova for the investigation of the magnetic properties.

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CITED LITERATURE

1. V. G. Tronev, S. M. Bondin, *DAN*, **68**, 87 (1952).
2. V. G. Tronev, S. M. Bondin, *Chemistry of Rare Elements*, **1**, 40 (1954).
3. V. G. Tronev, G. K. Babeshkina, *ZhNKh*, **3**, 2458 (1958).
4. A. S. Kotelnikova, V. G. Tronev, *ZhNKh*, **3**, 1016 (1958).
5. V. G. Tronev, G. K. Babeshkina, *ZhNKh*, **3**, 2278 (1958).
6. V. G. Tronev, Myao-Tsin-Shen, *ZhNKh*, **4**, issue 12, 2834 (1959).
7. V. G. Tronev, Myao-Tsin-Shen, *ZhNKh*, **4**, issue 8, 1768 (1959).

8. G. K. Babeshkina, V. G. Tronev, *ZhNKh*, **7**, issue 1, 215 (1962).
9. V. G. Kuznetsov, P. A. Kozmin, *Structural Chemistry*, **4**, 62 (1963).
10. A. G. Elitsur, *Proceedings of the Platinum and Other Noble Metals Section*, issue 22, 149 (1948).
11. J. and W. Noddack, *Zs. anorg. Chem.*, **215**, 129 (1933).

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