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Abstract

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SYNTHESIS AND SOME PROPERTIES OF PYRIDINIUM PYRIDINEPENTAHALORHENATES (IV)–PyH[RePyCl$_5$] AND PyH[RePyBr$_5$]

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It was indicated earlier (^{1}) that the thermal decomposition of $(PyH)_2[ReCl_6]$ at 300° probably proceeds in two stages, according to the type of Andersen reaction known for Pt^IV (^{2}), i.e., from the decomposition of pyridinium hexachlororhenate we have:

$$(PyH)_2ReCl_6 \rightarrow HCl + PyH[RePyCl_5], \qquad (I)$$

$$PyH[RePyCl_5] \rightarrow HCl + [RePy_2Cl_4]. \qquad (II)$$

But since on the heating curves of $(PyH)_6[ReX_6]$ $(X = Cl, Br)$ there is one endothermic effect, we assumed that stages (I) and (II) proceed almost simultaneously; therefore (^{1},^{3}) only the final products of the second stage were isolated –dipyridinetetrahalorhenates $(RePy_2Cl_4)$ and $(RePy_2Br_4)$–and it was not possible to obtain the intermediate pentahalorhenates. In the synthesis of $[RePy_2Cl_4]$ and $[RePy_2Br_4]$ by the new method (^{3},^{4}), upon interaction of $(PyH)_2[ReX_6]$ with anhydrous pyridine, in some experiments at a lower temperature (195°) incomplete conversion of $(PyH)_2[ReX_6]$ into $[RePy_2X_4]$ was observed.

When the temperature was lowered to 190°, it proved possible to isolate the pentahalorhenates from solution in pyridine in pure form, to analyze them for Re, Cl, Br, C, and H content, and also to determine their magnetic susceptibility. Determination of solubility and electrical conductivity showed that the pentahalorhenates are two-ion electrolytes; their structure is confirmed by the preparation of the corresponding silver compounds–$Ag[RePyX_5]$.

The synthesis of these representatives of a new class of complex compounds of tetravalent rhenium makes it possible to suppose that, under appropriate conditions, varied classes and series of coordination paramagnetic compounds of Re IV can be obtained, analogous to the Werner-Miolati series known for compounds of Pt, Co, Cr, and other typical complex-forming metals.

Experimental Part

Synthesis and properties of $PyH[RePyCl_5]$**.** A sample of $(PyH)_2[ReCl_6]$ (0.5 g) and 10 ml of anhydrous pyridine were heated at 190° for two hours in an autoclave in an inert-gas atmosphere. The amber-yellow solution formed in the reaction was separated from the solid phase, which was almost always present in greater or lesser amount in all experiments. As established, it is dipyridinetetrachlororhenate $[RePy_2Cl_4]$, the formation of which occurs at almost this same temperature.

From the solution obtained, after addition of a tenfold amount of ethyl alcohol, a yellow finely crystalline precipitate separated, which was washed on the filter with fresh portions of alcohol, ether, and dried to constant weight at 105°.

The analytical data correspond to the proposed composition of the compound.

$PyH[RePyCl_5]$. Found, %: Re 34.75; Cl 33.54; C 22.76; H 2.76
Calculated, %: Re 35.62; Cl 33.91; C 22.97; H 2.12

The determination of electrical conductivity in aqueous solution was carried out at 25° at dilutions of 2000, 3000, and 4000 l per 1 mole of substance. It was not possible to prepare solutions at lower dilutions because of the poor solubility of the substance (~0.25 g/l). The results of the measurements are given in Table 1. Over time the electrical conductivity increased only slightly.

Table 1

Molecular conductivity of $PyH[RePyCl_5]$ **at 25°**

Dilution, l/mole	Molecular conductivity, ohm^{-1}
2000	100
3000	125
4000	140

Upon addition to an aqueous solution of $PyH[RePyCl_5]$ of a 3% solution of $AgNO_3$, an orange, finely crystalline precipitate of the silver salt separated, which was thoroughly washed free of excess $AgNO_3$, and then washed with alcohol and ether. The substance was dried to constant weight in a desiccator over P_2O_5.

$Ag[RePyCl_5]$. Found, %: C 10.87; H 1.52
Calculated, %: C 10.91; H 0.91

According to V. I. Belova, $\chi_g \cdot 10^{-6} = 9.25$. The effective magnetic moment is $\mu = 3.45\ \mu_B$.

Synthesis and properties of $PyH[RePyBr_5]$**.** Upon heating $(PyH)_2[ReBr_6]$ with anhydrous pyridine at 150°, the main reaction product is $PyH[RePyBr_5]$, which, analogously to $PyH[RePyCl_5]$, is salted out from the pyridine solution by an excess of ethyl alcohol. The substance consisted of orange-red small crystals, sparingly soluble in water. Hydrolysis of a saturated aqueous solution, observed visually, occurs at 40–45°, i.e., the compound is less stable in water than $PyH[RePyCl_5]$ (60–70°).

$PyH[RePyBr_5]$. Found, %: Re 24.31; Br 54.39; C 16.84; H 1.93
Calculated, %: Re 24.99; Br 53.63; C 16.12; H 1.48

The compound is paramagnetic, $\chi_g = 7.37 \cdot 10^{-6}$; the effective magnetic moment is $\mu = 3.66\ \mu_B$.

The synthesis of $Ag[RePyBr_5]$ was carried out by adding a 3% solution of $AgNO_3$ to an aqueous solution of $PyH[RePyBr_5]$ cooled to 10°. The product obtained was dried in a desiccator over P_2O_5.

$Ag[RePyBr_5]$. Found, %: C 8.44; H 0.66
Calculated, %: C 7.77; H 0.65

Thus, the synthesis has been accomplished of representatives of a new class of complex compounds of tetravalent rhenium, $PyH[RePyCl_5]$ and $PyH[RePyBr_5]$.

The study of some properties of these compounds—their electrical conductivity and magnetic susceptibility, and also the preparation of the derivatives $Ag[RePyX_5]$—confirms the proposed structure.

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