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THERMAL DECOMPOSITIONS OF $[Co(py)_4Cl_2]_2PbCl_6$ AND $[Ru(dipy)_3]PbCl_6$

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The thermal decompositions of $[Co(py)_4Cl_2]_2PbCl_6$ and $[Ru(dipy)_3]PbCl_6$ were examined by dynamic thermoanalytical methods and under isothermal conditions permitting quantitative determination of some of the reaction products. A comparative study of the corresponding chloride salts was also performed. Both groups of compounds decompose with the liberation of chlorine and organic ligands (and H_2O in the case of the hydrates of the chlorides), and the process is accompanied by the simultaneous transitions $Pb(4+) \rightarrow Pb(2+)$ and $Co(3+) \rightarrow Co(2+)$. The ruthenium complex salts initially decompose without a change in the oxidation state of the Ru atom, but upon thermal treatment of the hexachloroplumbate certain chlorination products of the organic ligands are formed.

Hexachloroplumbic acid (H_2PbCl_6) forms a large group of salt-like derivatives with numerous nitrogen-containing organic bases [1]. Among the hexachloroplumbates of metals, only the existence of the salts of potassium, rubidium and caesium has so far been proved. Several compounds of H_2PbCl_6 with mono- and divalent complex cations are also known [1]. Investigations of the thermal properties and thermochemistry of hexachloroplumbic acid derivatives were conducted earlier in this laboratory on the hexachloroplumbates of alkali metals [2] and numerous nitrogen-containing bases [3, 4]. The present communication reports the results of an analogous study of two hexachloroplumbates of complex cations $[Co(py)_4Cl_2)_2]PbCl_6$ and the newly synthesized $[Ru(dipy)_3]PbCl_6$, as well as the corresponding chloride salts.

Experimental

Bis[dichloro-tetrapyridine-cobalt(III)] hexachloroplumbate, *A*, was obtained according to [5]. [Tris(2,2′-dipyridyl)ruthenium(II)] hexachloroplumbate, *B*, was synthesized by mixing aqueous solutions of $[Ru(dipy)_3]Cl_2 \cdot 7H_2O$ (obtained

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according to [6]) and H_2PbCl_6 [1]. Free chlorine, which is always present in solutions of hexachloroplumbic acid [7], may oxidize orange $[Ru(dipy)_3]^{2+}$ to green $[Ru(dipy)_3]^{3+}$ [8], and hence the synthesis of $[Ru(dipy)_3]PbCl_6$ must be carried out carefully and rapidly to avoid the competing redox reaction. This was accomplished by an appropriate choice of temperature and acidity. The compositions of both compounds were confirmed analytically.

Thermal analyses were performed on an OD–103 derivatograph. Isothermal decompositions with subsequent quantitative analyses of the reaction products were carried out by the procedure described previously [9].

Results and discussion

Thermal analyses of both hexachloroplumbates and the corresponding chlorides are shown in Fig. 1. Thermal decomposition of hexachloroplumbic acid derivatives is always accompanied by a liberation of chlorine, this process being a consequence of the spontaneous transition Pb(4+) →Pb(2+) [10]. The chlorine released may initiate various secondary processes, which means that hexachloroplumbates usually exhibit a complex thermal decomposition pattern [3, 4, 9].

The first two distinct endothermic signals occurring upon the thermolysis of *A*, below 460 K (Fig. 1a), correspond to the release of two molecules of chlorine from one molecule of hexachloroplumbate, together with a major part of the pyridine from the complex cation. In isothermal experiments, the stoichiometric amounts of chlorine were evolved by 390 K. Two subsequent endothermic effects, at 525 K and

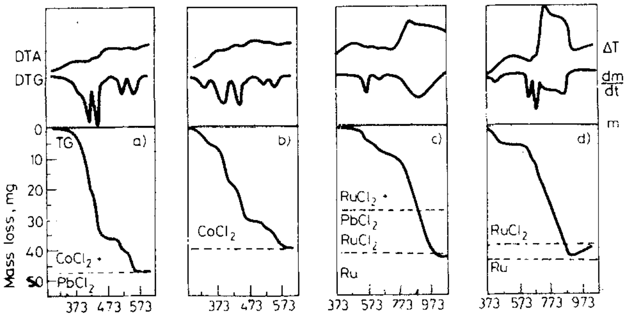

Fig. 1 Thermal analyses of $[Co(py)_4Cl_2]_2PbCl_6$ (a), $[Co(py)_4Cl_2]Cl \cdot 6H_2O$ (b), $[Ru(dipy)_3]PbCl_6$ (c), and $[Ru(dipy)_3]Cl_2 \cdot 7H_2O$ (d); Mass of samples, 80 mg (a) and 50 mg (b, c, d); Heating rate, 5 deg/min (a, b) and 10 deg/min (c, d); Galvanometer sensitivities: 1/10, 1/3, and 50 mg, for DTG, DTA, and TG, respectively: reference material, α-Al_2O_3; sample holder, platinum plate; atmosphere, dynamic N_2

565 K, are connected with liberation of the remaining pyridine and this thermal analysis fragment shows a similar pattern to that characteristic for the thermolysis of the corresponding chloride salt (Fig. 1b). Decomposition is completed below 600 K, and the residue of heating is a mixture of $2CoCl_2$ and $PbCl_2$.

The first step in the thermal decomposition of $[Co(py)_4Cl_2]Cl \cdot 6H_2O$ (Fig. 1b) presumably corresponds to the release of water. In the subsequent four stages, 4 moles of pyridine and half of mole of chlorine are evolved from one mole of the substrate. Isothermal investigations revealed that the liberation of chlorine proceeds below 400 K, accompanying the $Co(3+) \rightarrow Co(2+)$ transition. The total mass loss on heating up to 600 K corresponds to a residue of $CoCl_2$, and the composition of the residue was confirmed analytically.

The first stage in the thermal decomposition of $[Ru(dipy)_3]PbCl_6$ is connected with a mass loss of ca. 7% of the sample. This would correspond to the release of one molecule of Cl_2. The DTA and DTG peak temperatures for this effect are typical for the thermal decomposition of hexachloroplumbates [2–4, 9]. Isothermal experiments revealed that ca. 2/3 of the stoichiometric amount of chlorine is evolved at the temperature corresponding to the first step. Since the oxidation of ruthenium, i.e. $Ru(2+) \rightarrow Ru(3+)$, was not confirmed, one could expect that some chlorine is consumed in secondary chlorination processes. Indeed, the GC analyses revealed the presence of 2-chloropyridine, 3-chloropyridine and 2,5-dichloropyridine among the gaseous products leaving the reaction zone. The solid product of the first step of decomposition of *B* loses 2,2′-dipyridyl upon further heating, and this process is followed by the volatilization of $PbCl_2$. Since the latter processes occur at fairly high temperatures, they are accompanied by the destruction of ligand molecules. Thus, besides 2,2′-dipyridyl, pyridine was also identified in the gaseous phase. The residue upon heating up to 1000 K presumably consists of Ru, ruthenium chloride and oxide, and lead oxide, contaminated with carbonization products of the organic ligands.

The course of the thermal decomposition of $[Ru(dipy)_3]Cl_2 \cdot 7H_2O$ is similar to that described earlier [11].

The interesting feature is that the thermolysis of *B* proceeds at a much higher temperature that of the corresponding chloride salt. Moreover, $[Ru(dipy)_3]PbCl_6$ is thermally more stable than $[Co(py)_4Cl_2]_2PbCl_6$. This is a rather unusual finding, since the hexachlorometallates of divalent cations are less stable than monovalent ones. The relatively large 2,2′-dipyridyl ligands presumably stabilize the crystal lattice of the hexachloroplumbate.

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Zusammenfassung — Mit Hilfe dynamischer thermoanalytischer Methoden und unter die quantitative Bestimmung einiger Reaktionsprodukte ermöglichenden isothermen Bedingungen wurde die thermische Zersetzung von $[Co(py)_4Cl_2]_2PbCl_6$ und $[Ru(dipy)_3]PbCl_6$ untersucht. Eine vergleichende Betrachtung der korrespondierenden Chloride wurde ebenfalls durchgeführt. Die Zersetzung beider Verbindungsgruppen geschieht unter Freisetzung von Chlor und organischen Liganden (bei den Hydraten der Chloride auch vonWasser)und ist von den übergängen Pb(4+) →Pb(2+) bzw. (Co(3+) →Co(2+) begleitet. Die Komplexsalze des Rutheniums zersetzen sich anfangs ohne Änderung der Oxydationsstufe des Rutheniumatoms, es bilden sich allerdings infolge von Wärmezufuhr aus dem Hexachloroplumbat verschiedene Chlorprodukte der organischen Liganden.

Резюме — Термическое разложение комплексов $[Co(py)_4Cl_2]_2PbCl_6$ и $[Ru(dipy)_3]PbCl_6$ было изучено динамическими термоаналитическими методами и при неизотермических условиях, что позволило провести количественное определение некоторых продуктов реакции. Проведено также сравнительное изучение соответствующих хлоридных солей. Обе группы соединений разлагаются с выделением хлора и органического лиганда, а также и воды в случае гидратов хлоридных солей. При этом процесс разложения сопровождается одновременно восстановлением четырехвалентного свинца до двухвалентного и трехвалентного кобальта до двухвалентного. Комплексная соль рутения сначала разлагается без изменения валентного состояния рутения, но при термическойъобработке гексахлорсвинцивой соли образуются некоторые продукты хлорирования органических лигандов.