SYNTHESIS AND THERMAL ANALYSIS OF 2,2′-BIPYRIDINE DIVALENT TRANSITION METAL HEXACHLOROPLUMBATES

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Abstract

Several complex salts of the general formula $[M(II)\,(bipy)_x(H_2O)_y]PbCl_6$ (where x=2–3, y=0–2 and M=Mn(II), Fe(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II)) were synthesized and investigated by DTA, TG and DTG. Some of the decomposition products were identified by IR spectroscopy and other methods. The compounds decompose with the liberation of water (in the case of hydrates), chlorine (sometimes causing chlorination of organic fragments), organic molecules (sometimes chlorinated) and sometimes hydrogen chloride. The residues comprise metal(II) chlorides and $PbCl_2$.

Keywords: 2,2′-bipyridine transition metal salts, hexachloroplumbates, thermoanalytical investigations

Introduction

Numerous salt-like derivatives of hexachloroplumbic acid and nitrogen organic bases have been known for a long time [1, 2]. The existence of hexachloroplumbates containing mono-valent metals (potassium, rubidium or caesium) has also been well evidenced [1, 3]. On the other hand, synthesis of hexachloroplumbates of divalent metals came up against numerous difficulties [4], and the existence of such compounds was not actually proved [5]. Difficulties in synthesis of the latter derivatives explain simple thermochemical evaluations based on Hess's law and the Kapustinskii-Yatsimirskii relationship [6–10]. Such considerations carried out for hexahalogenohafnates, similar to hexachloroplumbates, revealed that salts of the $M(II)HfCl_6$ type would be stable if the diameter of M(II) was greater than 1.8 Å [8]. All known cations of divalent metals are smaller. However, if divalent cations attach ligands (as e.g. 2,2′-bipyridine) their dimensions increase and they should then be able to form salts with the hexachloroplumbate anion [11].

This communication describes syntheses and results of thermoanalytical investigations on salts containing the $PbCl_6^{2-}$ anion and complex $[M(II)(bipy)_x]^{2+}$ cations, as well as attempts to evaluate the heats of their primary decomposition.

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Experimental

Syntheses

Hexachloroplumbates were prepared by mixing stoichiometric amounts of aqueous solutions of hexachloroplumbic acid [1, 2] and 2,2′-bipyridine metal chloride cooled to –5°C [11]. Yellow precipitates (green-yellow in the case of Cu(II) salt) were separated by filtration and dried in vacuum over KOH.

Elemental analyses carried out on a Carlo Erba EA 1108 instrument, mercurometric determinations of Cl^- [12] and iodometric determinations of Pb(IV) [12] confirmed the expected composition of the compounds.

Measurements

TG, DTA and DTG analyses were carried out on an OD-103 (Monikon) derivatograph (conditions: platinum crucible, dynamic nitrogen atmosphere, m=100 mg, heating rate=5 K min^{-1}, sensitivities DTA and DTG=1/5 and 1/10, respectively, α-Al_2O_3 served as reference material). Thermogravimetric measurements were also performed on a TG 209 (Netzsch) thermobalance connected to an IFS 66 (Bruker) infrared spectrophotometer (conditions: platinum crucible, dynamic atmosphere of nitrogen, m=7–13 mg, heating rate=20 K min^{-1}).

Experiments carried out under isothermal conditions enabled identification of some reaction products, including chlorine which was quantitatively absorbed in aqueous potassium iodide solution and assayed iodometrically [12].

Results and discussion

The results of thermoanalytical investigations of selected compounds are demonstrated in Figs 1 (obtained using an OD-103 derivatograph) and 2 (employing TG 209 thermobalance), while Table 1 contains information concerning temperatures, mass losses, gaseous products and thermochemistry of the decomposition process.

All thermoanalytical curves demonstrate patterns typical for multistep processes. Analysis of gaseous products and mass losses reveals that Cl_2 and H_2O (in the case of hydrates) are always released in the initial stage, which is clearly seen during decomposition of **2**, **4**, **5** and 7. The primary decomposition of **1**, **3**, **6** and **8** is additionally accompanied by partial release of 2,2′-bipyridine. It may be expected that water as an unreactive molecule is transferred to the gaseous phase unchanged. As regards chlorine, stoichiometric amounts of this were found in the gaseous phase only upon decomposition of 7 and **8**. During decomposition of other compounds, up to 40% of chlorine is consumed in secondary chlorination of 2,2′-bipyridine. As a result of such a process organochlorine compounds and HCl should be formed. The presence of the latter entity was indeed confirmed by

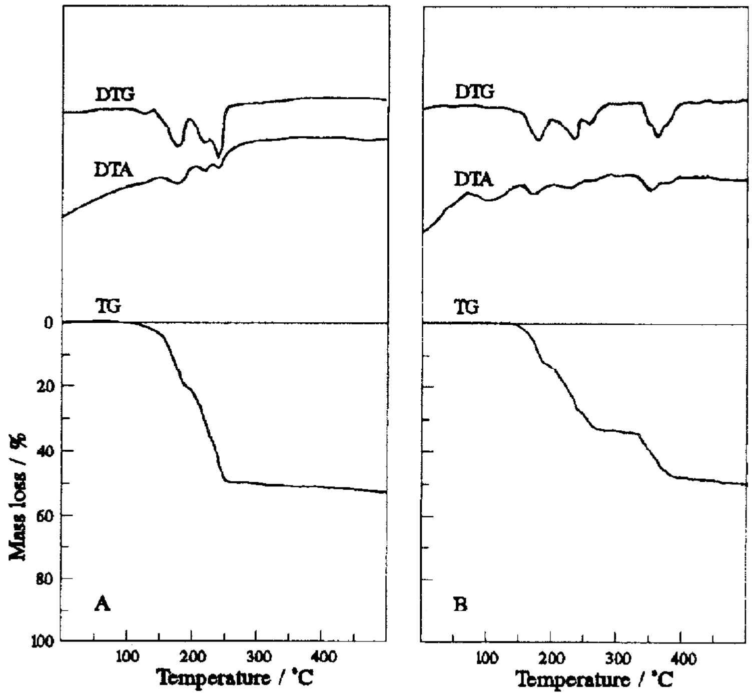

Fig. 1 Thermoanalytical curves for $[Zn(bipy)_2(H_2O)_2]PbCl_6$ (A) and $[Cu(bipy)_2(H_2O)_2]PbCl_6$ (B) recorded on an OD-103 Derivatograph

IR spectroscopy. We were unable, however, to identity organic products of chlorination in this way.

The solid products of the above described primary decomposition should be mixtures of $PbCl_2$ and $[M(II)(bipy)_x]Cl_2$. $PbCl_2$ remains unchanged upon heating up to 720 K (the upper limit of thermoanalytical investigations), while from $[M(II)(bipy)_x]Cl_2$ organic fragments are released in one (**1**, **2**, **3**, **6** and **8**) or several steps (**4**, **5** and **7**). Examination of thermogravimetric curves enabled stoichiometry of these steps to be tentatively ascribed.

The residues of decomposition comprise $PbCl_2$ and $M(II)Cl_2$ sometimes contamined with traces of carbonization products. Final mass losses extracted from thermogravimetric curves compare well with those predicted. A considerable discrepancy is noted only in the case of **8**, since $HgCl_2$ undergoes partial sublimation in experimental conditions.

Decomposition of $[bipyH_2]PbCl_6$ (**9**) proceeds in a manner different from that of other compounds which implies that its constitution differs from that of all complex salts.

Assuming that the stoichiometry of a given step is as shown in Table 1, one can evaluate heats of decomposition on the basis of the Van't Hoff equation [2, 3, 13]

Table 1 Thermal decomposition data for hexachloroplumbates containing 2,2′-bipyridine metal complexes

No.	Compound (Fomula)	Stage of the process		T_{peak}/K^a		Mass loss/%		Gaseous product	$\Delta_d H^o$/ kJ mol^{-1}
		No.	T_{range}/K^a	DTG	DTA	found^b	calc.		
1	$[Mn(bipy)_2(H_2O)_2]PbCl_6$	I	388–459	451	448	20.0	22.5	$2H_2O$, Cl_2, 0.5bipy	172
		II	459–522	508	488, 508	50.0	50.9	1.5bipy	113
2	$[Fe(bipy)_2(H_2O)_2]PbCl_6$	I	423–463	443	444	13.0	13.0	$2H_2O$, Cl_2	281
		II	491–568	551	488, 511	45.0	50.9	2bipy	139
3	$[Co(bipy)_2(H_2O)_2]PbCl_6$	I	413–513	473, 498	475, 499	22.0	22.4	$2H_2O$, Cl_2, 0.5bipy	144
		II	513–672	623	654	50.0	50.9	1.5bipy	66
4	$[Ni(bipy)_2(H_2O)_2]PbCl_6$	I	333–473	428, 466	466	9.0	12.9	$2H_2O$, Cl_2	65
		II	473–531	516	516	29.5	31.8	bipy	89
		III	531–748	658	654	52.0	50.7	bipy	38
5	$[Cu(bipy)_2(H_2O)_2]PbCl_6$	I	418–450	448	391, 449	12.0	12.9	$2H_2O$, Cl_2	336
		II	450–503	499	499	28.0	31.6	bipy	82
		III	503–531	523	523	35.0	41.0	0.5bipy	88
		IV	573–648	621	614	50.0	50.4	0.5bipy	50

Table 1 Continued

No.	Compound (Formula)	Stage of the process No.	T_{range}/K[a]	T_{peak}/K[a] DTG	DTA	Mass loss/% found[a]	calc.	Gaseous product	$\Delta_d H°$/ kJ mol^{-1}
6	$[Zn(bipy)_2(H_2O)_2]PbCl_6$	I	388–456	446	449	20.0	22.2	2H2O, Cl_2, 0.5bipy	176
		II	456–516	488, 508	488, 508	51.5	50.3	1.5bipy	114
7	$[Cd(bipy)_3]PbCl_6$	I	380–425	413	415	6.8	7.1	Cl_2	88
		II	425–468	464	465	23.0	22.7	bipy	83
		III	468–510	486, 503	503	37.5	33.3	bipy	108
		IV	535–625	615	616	46.0	46.1	0.5bipy	27
		V	625–710	695	695	54.5	53.9	0.5bipy	–
8	$[Hg(bipy)_2(H_2O)_2]PbCl_6$	I	413–473	468	468	32.0	27.2	$2H_2O$, Cl_2, bipy	268
		II	473–513	488, 503	488, 503	57.0	43.3	bipy	139
9	$[bipyH_2]PbCl_6$	I	373–461	448	448	18.0	24.9	Cl_2, 2HCl	115
		II	451–518	513	513	48.0	51.9	bipy	81

[a]Data extracted from thermoanalytical curves recorded on an OD-103 derivatograph

$$\ln\alpha = -\frac{\Delta_d H^o}{nR}\frac{1}{T} + \frac{\Delta_d H^o}{nR}\frac{1}{T_d} \qquad (1)$$

in which α represents the experimental extent of reaction at temperature $T(\alpha = m_o - m_T/(m_o - m_\infty)$; m_o – initial mass, m_T – mass at temperature T and m_∞ – final mass, all masses are relevant to a given step), R is the gas constant, n – number of gaseous molecules released to gaseous phase in a given step, and $\Delta_d H^o$ and T_d denote heat and temperature (at which pressure of gaseous products reaches atmospheric pressure) of decomposition, respectively. Evaluated by using Eq. (1) enthalpy changes are demonstrated in the last column of Table 1. They represent ba-

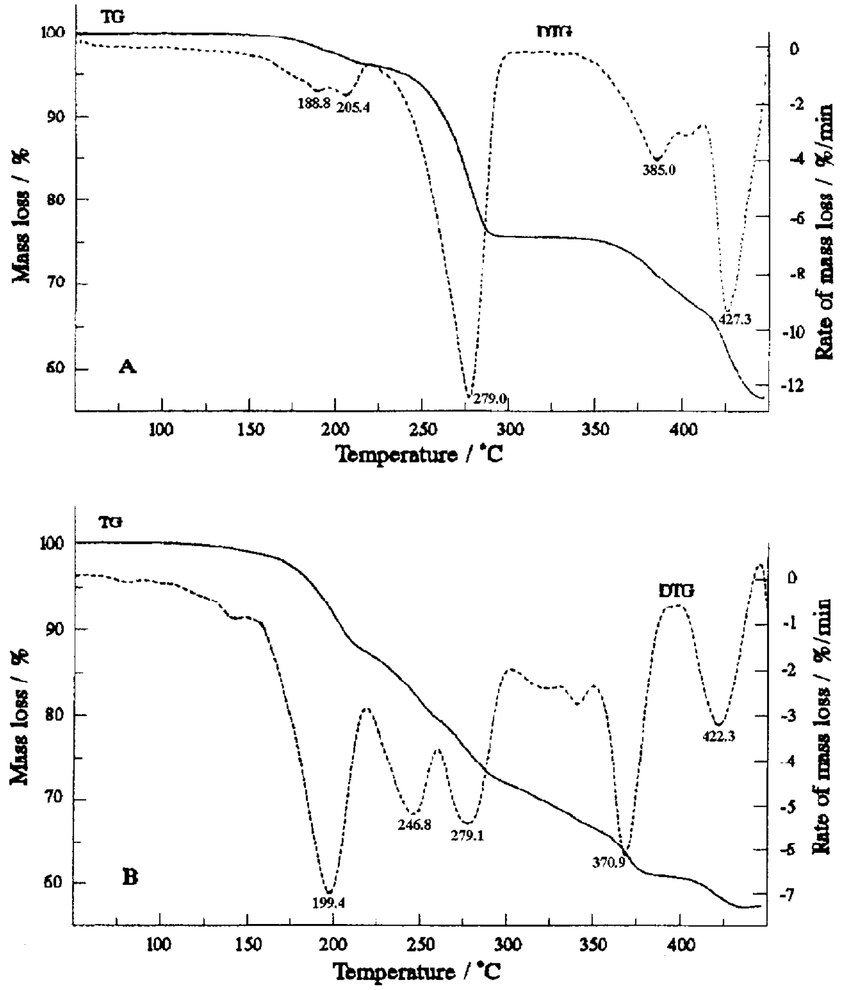

Fig. 2 Thermogravimetric curves for $[Ni(bipy)_2(H_2O)_2]PbCl_6$ (A) and $[Cu(bipy)_2(H_2O)_2]PbCl_6$ (B) recorded on a TG 209 thermobalance

sic thermodynamic characteristics for decomposition of the compounds investigated.

Summarizing, we synthesised eight unknown salts containing 2,2′-bipyridine divalent transition metal complex cations and $PbCl_6^{2-}$ anion. Such compounds, with the exception of **8**, contain two 2,2′-bipyridine molecules in a complex cation and additionally two H_2O molecules in the stoichiometric unit. We proved, therefore, that an increase of dimensions of divalent cations by attachment of ligands creates favourable conditions for the formation of hexachloroplumbates.

Thermal stability, reflected by temperatures DTG and DTA peaks, as well as initiation of decomposition are similar for all the compounds, including $[bipyH_2]PbCl_6$ (e.g. temperatures of DTG peaks comprise between 413–473 K). More differentiated are temperatures throughout the whole process, as well as heats of decomposition. It is difficult however, to find any relations between these quantities and the constitution of the compounds investigated.

Further insight into the chemistry and thermochemistry of divalent metal hexachloroplumbates will be possible by carrying out theoretical studies on their stability. We will focus our attention on this problem in the near future.

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