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THERMAL ANALYSIS OF HEXACHLOROPLUMBATE AND CHLORIDES CONTAINING COMPLEX DIVALENT LEAD 2,2’-BIPYRIDINE CATIONS

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Abstract

Lead(II) 2,2’-bipyridine hexachloroplumbate tetrahydrate was synthesized and investigated by DTA, TG and DTG. IR spectroscopy and other methods enabled the identification of some of the decomposition products. Comparative studies on the corresponding chlorides: $[Pb(bipy)]Cl_2$ and $[Pb(bipy)_3]Cl_2$, which can be considered as precursors of the hexachloroplumbate, were also undertaken. X-ray measurements enabled the tentative determination of the crystal structure of $[Pb(bipy)]Cl_2$. Hexachloroplumbate decomposes with the liberation of chlorine, water and organic ligands, and the process is accompanied by the simultaneous transition of Pb(IV)→Pb(II). Chlorides release only ligands upon heating. Residues comprised always $PbCl_2$.

Keywords: lead(II) 2,2’-bipyridine hexachloroplumbate and chlorides, thermal analysis, X-ray structure

Introduction

Numerous salt-like derivatives of hexachloroplumbic acid and nitrogen organic bases have been known for some 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 evaluation based on Hess’s law and the Kapustinski–Yatsimirski 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].

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This publication describes syntheses and results of thermoanalytical and X-ray investigations on the salts containing the $PbCl_6^{2-}$ or chloride anions and complex $[Pb(bipy)_x]^{2+}$ cations (x equals 1 in the case of hexachloroplumbate and 1 or 3 for chlorides).

Experimental

Syntheses

$Pb(bipy)_3Cl_2$ was prepared by mixing stoichiometric amounts of solutions of $PbCl_2$ and 2,2'-bipyridine dissolved in water and water–ethanol (9:1) mixture, respectively. White precipitate was separated by filtration and dried in a vacuum over KOH. The $[Pb(bipy)]Cl_2$ was synthesized by the reaction of stoichiometric amounts of aqueous solutions of $PbCl_2$ and 2,2'-bipyridine. The reactant mixture was kept at 333 K overnight and then in the refrigerator for 3 days. The transparent needle crystals were filtrated and dried over KOH. Hexachloroplumbate was prepared by mixing stoichiometric amounts of aqueous solutions of hexachloroplumbic acid [1, 2] and Pb(II) 2,2'-bipyridine chloride cooled to 268 K [11]. Yellow precipitate was separated by filtration and dried in vacuum over KOH.

Elemental analyses were carried out on a Carlo Erba EA 1108 instrument, mercurometric determinations of Cl^- [12] and iodometric determination 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 carried out on a TG 209 (Netzsch) thermobalance connected to an IFS 66 (Bruker) infrared spectrophotometer (conditions: platinum crucible, dynamic atmosphere of nitrogen, m=13 mg, heating rate=20 K min^{-1}).

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

The crystal structure of $[Pb(bipy)]Cl_2$ was tentatively determined on a KM-4 four-circle diffractometer using SHELXS-90 [13] and SHELX-97 [14] programs.

Results and discussion

Carrying out syntheses we obtained crystals suitable for X-ray measurements only in the case of $[Pb(bipy)]Cl_2$. This gave us an opportunity to gain an insight into the structure of the compound in which the $[Pb(bipy)]^{2+}$ cation – the same as in $[Pb(bipy)(H_2O)_4]PbCl_6$ – occurs. The structure was measured and refined several times, but *R* (discrepancy factor) was always of the order of 0.12. With such *R* the structure can be considered to be determined only tentatively. We can, however, say that the compound crystallizes in the $P2_1/c$ space group with 4 molecules in the unit cell. Figure 1 shows molecular arrangement in the crystalline phase, from which we know that each Pb atom is surrounded by 4 chlorine atoms and binds one 2,2'-bipyridine molecule through 2 nitrogen atoms. Two chlorine atoms are somewhat closer to the Pb atom than the other two, which gives the impression that the crystal constitutes $[Pb(bipy)]Cl_2$ stoichiometric units. Atoms surrounding the Pb are located in the corners of a highly distorted octahedron. Pairs of chlorine atoms are shared by neighbouring octahedrons, which form a chain along a double inversion axis. Chains are bound in the crystal through dispersive interactions between hydrocarbon fragments of 2,2'-bipyridine ligands.

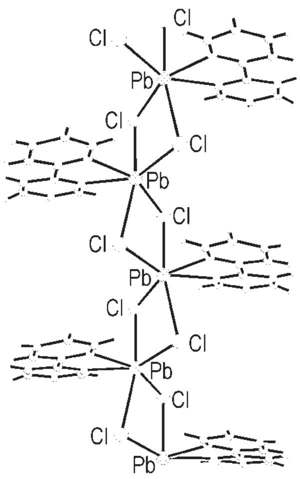

Fig. 1 Molecular arrangement in the crystalline phase of $[Pb(bipy)]Cl_2$

The results of thermoanalytical investigations of the compounds investigated are demonstrated in Figs 2 (obtained using an OD-103 derivatograph) and 3 (employing TG 209 thermobalance), while Table 1 contains information concerning temperatures, mass losses, gaseous products and thermochemistry of the decomposition process. Thermoanalytical curves in Fig. 2 differ slightly from those in Fig. 3, which can be attributed to different experimental conditions applied (mass of sample and heating rate).

Thermoanalytical curves for $[Pb(bipy)_3]Cl_2$ and $[Pb(bipy)(H_2O)_4]PbCl_6$ demonstrate patterns typical of multistep processes, while $[Pb(bipy)]Cl_2$ decomposes in one step. $[Pb(bipy)(H_2O)_4]PbCl_6$ is stable upon heating up to 380 K (Fig. 2C). The compound decomposes between 420 and 520 K in two slightly overlapping stages. Analysis of gaseous products and mass loss (13.5%) reveals that Cl_2 and H_2O are released in the initial stage, between 420 and 455 K. It can be expected that water as an unreactive entity is transferred to the gaseous phase unchanged. Between 455 and 520 K

Table 1 Thermal decomposition data for lead(II) 2,2'-bipyridine heaxachloroplumbate tetrahydrate and corresponding chloride salts

Compound (Formula)	Stage of the process		T_{peak}/K[a]		Mass loss		Gaseous products	$\Delta_d H^{0b}$/ kJ mol^{-1}
	No.	T_{range}/K[a]	DTG	DTA	found[a]	calc.		
[Pb(bipy)]Cl$_2$		450–545	528	528	35.5	36.0	bipy	179
[Pb(bipy)$_3$]Cl$_2$	I	380–450	443	443	36.5	41.8	2bipy	28
	II	450–530	518	521	25.0	20.9	bipy	129
[Pb(bipy)(H$_2$O)$_4$]PbCl$_6$	I	420–455	448	445	13.5	16.7	4H$_2$O, Cl$_2$	77
	II	455–520	503	508	22.0	18.3	bipy	86

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

[b] Values obtained on the basis of thermogravimetric curves recorded on an OD-103 derivatograph

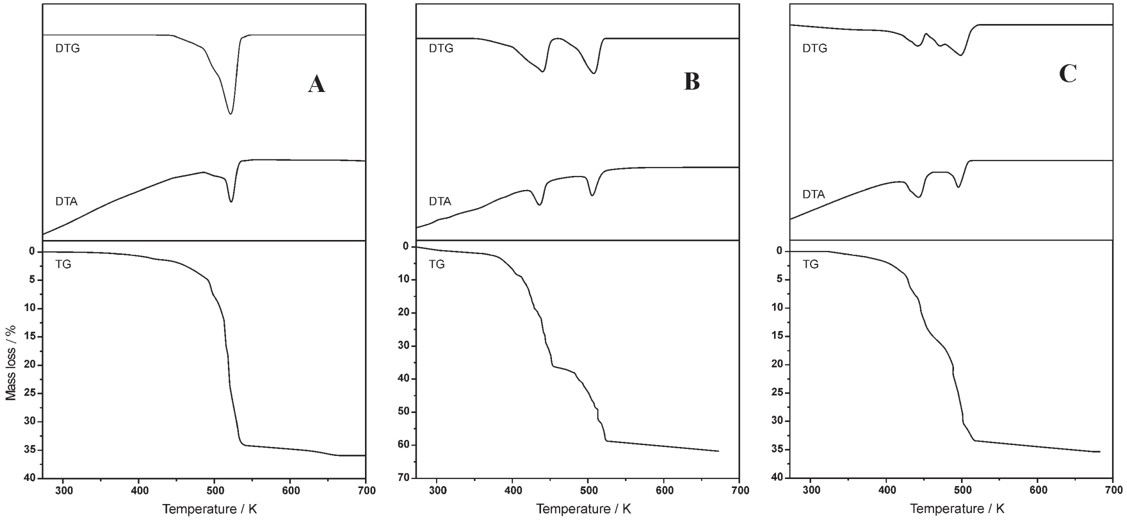

Fig. 2 Thermoanalytical curves for A – $[Pb(bipy)]Cl_2$, B – $[Pb(bipy)_3]Cl_2$ and C – $[Pb(bipy)(H_2O)_4]PbCl_6$ recorded on an OD-103 derivatograph

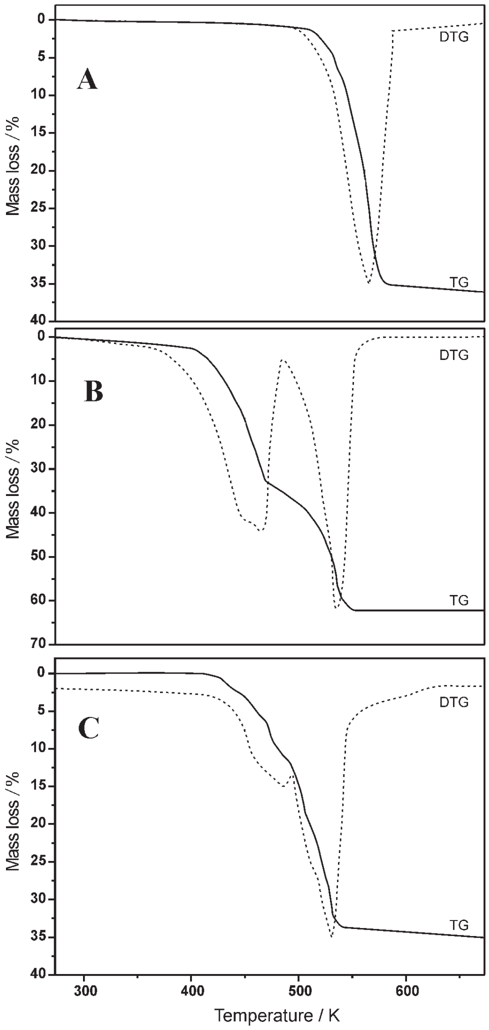

Fig. 3 Thermogravimetric curves for A – [Pb(bipy)]Cl_2, B – [Pb(bipy)$_3$]Cl_2 C – [Pb(bipy)(H_2O)$_4$]$PbCl_6$ recorded on a TG 209 thermobalance

there is a 22% mass loss which corresponds to the loss of 2,2'-bipyridine. In isothermal experiments, carried out at 520 K, ca 80% of chlorine is evolved. The remaining chlorine is consumed in secondary chlorination of 2,2'-bipyridine. The second stage shows a similar pattern to that characteristic of the decomposition of corresponding chloride salt. As a result of chlorination, organochlorine compounds and HCl should be formed. The presence of the latter entity was indeed confirmed by IR spectroscopy; typical bands due to HCl, between 3420–3500 cm^{-1}, were recorded. We were unable, however, to identify organic products of chlorination in this way. There is almost no further mass loss above 520 K; at each point there is a residue comprising of

$PbCl_2$. The final mass loss extracted from thermogavimetric (white powder) curves compare well with that predicted.

Thermoanalytical curves for Pb(II) 2,2’-bipyridine chloride demonstrate that their decomposition proceeds in one step (Fig. 2A). Between 450 and 545 K, there is a 35.5% mass loss, which corresponds to liberation of 2,2’-bipyridine. $[Pb(bipy)_3]Cl_2$ decomposes in two steps (Fig. 2B). Between 380 and 450 K, there is a 36.5% mass loss corresponding to the loss of nearly two molecules of 2,2’-bipyridine, which are weakly bonded with Pb(II). Between 450 and 530 K the mass loss equals to 25% and corresponds to the loss of the remaining 2,2’-bipirydine molecules which are more strongly coordinated with Pb(II). The residue in both cases is $PbCl_2$.

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, 15]

$$\ln\alpha = -[\Delta_d H^0/(nR)]/T + [\Delta_d H^o/(nR)]/T_d \qquad (1)$$

in which α represents the experimental extent of reaction at temperature $T(\alpha)=(m_0-m_T)/(m_0-m_\infty)$; m_0-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 given in the last column of Table 1. They represent basic thermodynamic characteristics for decomposition of the compounds investigated.

Summarising, we synthesised salts containing lead(II) 2,2’-bipyridine complex cations and $PbCl_6^{2-}$ or Cl^- anions. Hexachloroplumbate contains a molecule of 2,2’-bipirydine and four molecules of water per 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. It is possible to obtain hexachloroplumbate from both chloride salts. However, the complex cation of Pb(II) with one molecule of 2,2’-bipyridine is more suitable for the preparation of $[Pb(bipy)(H_2O)_4]PbCl_6$.

Thermal stability of divalent lead 2,2’-bipyridine hexachloroplumbate reflected by temperatures DTG and DTA peaks, as well as initiation of decomposition is similar to that of hexachloroplumbates containing Mn(II), Fe(II) and Zn(II) 2,2’-bipyridine complex cations described earlier [16].

Since $[Pb(bipy)(H_2O)_4]PbCl_6$ contains Pb(IV) and Pb(II), transfer of the charge from the Pb(IV) to Pb(II) is possible, and this unique feature makes the compound interesting from the cognitive and perhaps applicative point of view. Further insight into the chemistry and thermochemistry of this compound will be possible by carrying out theoretical studies on their stability. This is currently underway.

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