

PHYSICAL METHODS  
OF INVESTIGATION

## Synthesis and Thermodynamics of Lead(II), Manganese(II), and Cobalt(II) Pivalate Complexes

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**Abstract**—Manganese and cobalt oxopivalates and lead pivalate have been synthesized, mass spectral and thermogravimetric analysis have been performed. Sublimation enthalpies of cobalt and manganese oxopivalates have been determined for the first time, while the sublimation enthalpy of lead pivalate has been found to agree well with literature data. Low sublimation enthalpy, high volatility, and monomolecular composition of gas phase allow one to use these complexes as precursors for preparing oxide films and materials by MOCVD method.

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Volatile metal complexes, in particular metal pivalates showing a unique set of physicochemical properties, are promising for preparing functional materials. One of these properties is the ability to transfer into gas phase at relatively low temperatures, which provides a possibility to use these compounds as precursors in chemical vapor deposition (CVD) method. This method, depending on deposition conditions, allows preparation of oxide, metallic, carbide films and coatings with interesting electrical, optical, magnetic, and catalytic properties. For example, thin films based on lead and manganese oxides are employed in the production of catalysts [1], gas sensors [2], magnetic colloidal suspensions [3], while metallic cobalt layers are widely used as electrically conducting, radio absorbing, anticorrosive, and protecting coatings [4, 5]. Therefore, it is necessary to perform systematic study of thermodynamic characteristics of volatile metal complexes; this information makes it possible to control the thickness of prepared films and synthesize films of prescribed composition. There are many different structures of carboxylate complexes, therefore not only composition but also the structure of volatile complexes used in CVD method is important for the synthesis of functional film materials. Therefore, the search for useful precursors is an urgent task for the preparation of functional materials. This work deals with the synthesis, structure analysis, and determination of certain thermodynamic characteristics of piva-

late complexes of lead(II), manganese(II), and cobalt(II).

The synthesis of all the compounds was accomplished by the reaction of freshly deposited hydroxides and pivalic acid in aqueous medium in molar ratio 1 : 2.



Reaction course was judged by the disappearance of transparent pieces of pivalic acid, water formation, and quick solidification of resultant gel-like phase. Thus obtained products were washed with large amount of water and dried under vacuum ( $p < 1 \times 10^{-4}$  Pa) at ambient temperature.

The prepared compounds were identified by mass spectral (MS) analysis on a Thermo Scientific DSQII commercial analytical quadrupole mass-spectrometer equipped with a Thermo Scientific DIP direct sample inlet system. As was shown in the works [6, 7], micro crucible of direct inlet system can be considered as an analog of Knudsen effusion cell. Therefore, investigation procedure for vaporization processes is the same as in the classical mass spectral experiment. Such experimental procedure allows one to employ widely distributed commercial devices instead of special mass spectral equipment.

The synthesized compounds were placed into direct inlet micro crucible. Temperature programming was as follows: a sample was kept at 323 K for 3 min, next the temperature was increased at minimal possible rate 10 K/min up to 673 K and maintained constant for 5 min. Temperature was measured with a Pt/Pt–Rh thermocouple and monitored using digital

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**Table 1.** Mass spectrum of gas phase over lead, cobalt, and manganese complexes ( $U_{\text{ioniz}} = 70$  eV)

Metal in complex	$[M]^+$	$[MPiv]^+$	$[M_3OPiv_3]^+$	$[M_4OPiv_5]^+$	$[M_4OPiv_6]^+$
Lead	23	100	—	—	—
Cobalt	—	—	14	100	2
Manganese	—	—	20	100	11

unit of direct inlet controller of mass spectrometer with accuracy  $\pm 1$  K. When heating began, mass spectra were registered in the range 50–1000  $m/z$ . Ionizing voltage was 70 eV. Ion source temperature was  $473 \pm 1$  K.

Table 1 represents the mass spectra of gas phase over the samples. According to mass spectrum, the gas phase over lead, manganese, and cobalt complexes contains  $Pb(Piv)_2$  molecules ( $[Pb(Piv)]^+$  and  $[Pb]^+$  ions),  $Mn_4OPiv_6$  ( $[Mn_4OPiv_5]^+$ ,  $[Mn_3OPiv_3]^+$ , and  $[Mn_4OPiv_6]^+$  ions), and  $Co_4OPiv_6$  ( $[Co_4OPiv_5]^+$ ,  $[Co_3OPiv_3]^+$ ,  $[Co_4OPiv_6]^+$  ions), respectively.

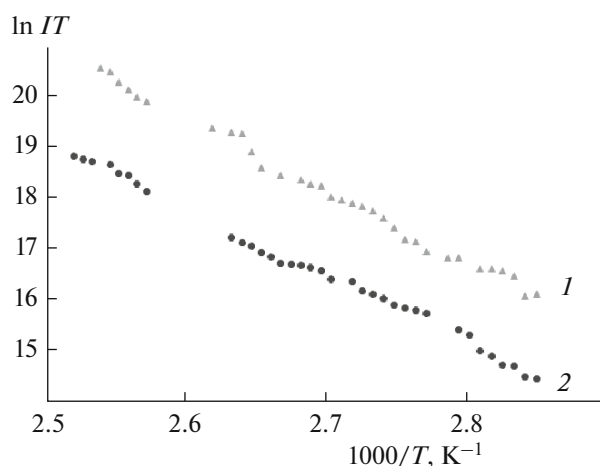
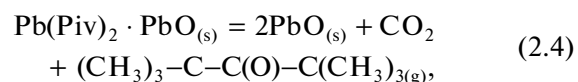
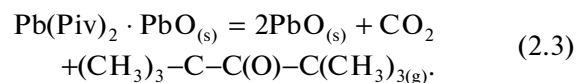
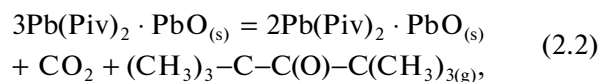
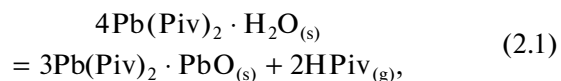
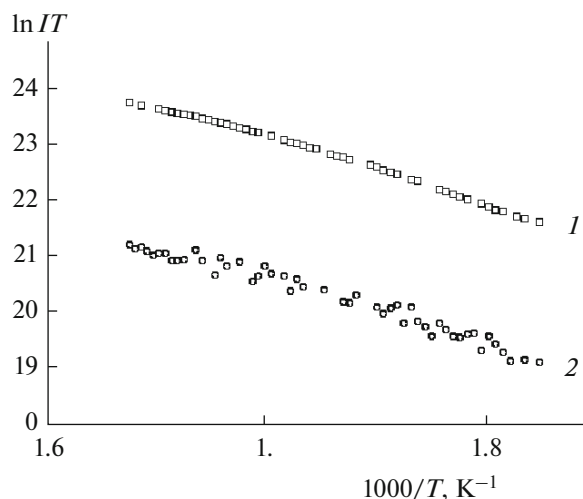
The energetic characteristics of vaporization processes for  $Pb(Piv)_2$ ,  $Co_4OPiv_6$ ,  $Mn_4OPiv_6$  molecules were calculated from the temperature dependences for ion current intensities of  $[PbPiv]^+$ ,  $[Pb]^+$ ,  $[Co_4OPiv_5]^+$ , and  $[Mn_4OPiv_6]^+$  mass spectra in a gas phase using Clausius–Clapeyron equation by least square method in temperature ranges 350–382, 408–452, and 446–479 K, respectively (Figs. 1–3).

Table 2 displays the average values of sublimation enthalpies for the complexes calculated from three independent experiments.

Thus, on the basis of results of mass spectral analysis, one can draw a conclusion that the reaction of the corresponding hydroxides with pivalic acid in aqueous medium leads mainly to complexes that produce gas phase containing lead pivalate  $Pb(Piv)_2$  and cobalt and manganese oxopivalates  $Co_4OPiv_6$  and  $Mn_4OPiv_6$ .

However, the results of thermogravimetric analysis (TGA) for the synthesized products dramatically differ from the mass spectrometry data. TGA was performed on a Q50 TGA analyzer in nitrogen flow (99.999%). Heating rate was 10 K/min at nitrogen flow rate 100 mL/min. Sample weights varied from 4 to 13 mg. The composition of initial compound was calculated from the obtained TG curves using procedure [9].

**Lead(II) compound.** The results of TGA study for the prepared lead(II) complex (Fig. 4), computations (Table 3), and analysis of literature data [10] allowed us to establish its composition and show that it decomposes in the temperature range 25–400°C in three stages through intermediate compounds of type  $xPb(Piv)_2 \cdot yPbO$  to give lead oxide  $PbO$ :

**Fig. 1.** Temperature dependence of ion current intensity for  $[PbPiv]^+$  (1) and  $[Pb]^+$  (2).**Fig. 2.** Temperature dependence of ion current intensity for  $[Mn_4OPiv_5]^+$  (1) and  $[Mn_4OPiv_6]^+$  (2).

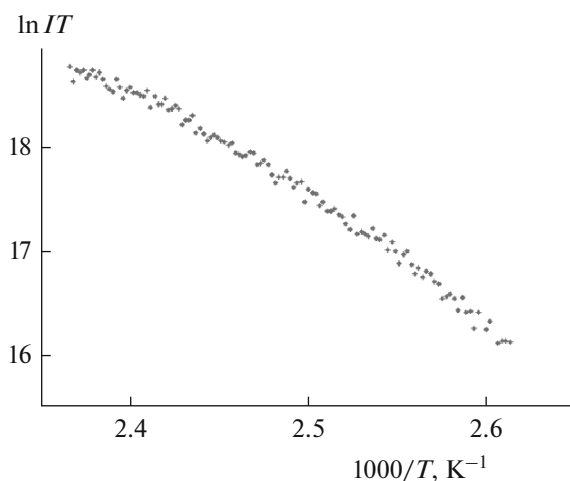


Fig. 3. Temperature dependence of ion current intensity for  $[\text{Co}_4\text{OPiv}_5]^+$ .

We carried out stoichiometric calculations as follows. Using initial sample weight (7.317 mg), we calculated the weight of PbO residue and weight loss for the each stage of curve from percentage ratio toward the initial compound (Table 3). The weight of PbO residue should correspond to the initial weight of  $\text{Pb}(\text{Piv})_2$  of 7.284 mg, consequently, the initial compound contains an additional component along with lead pivalate, which is most likely to be water, taking into account the low temperature of the first stage. Thus, the first stage of thermal process is hydrolysis resulting in formation of pivalic acid and compound  $[\text{3Pb}(\text{Piv})_2 \cdot \text{PbO}]$ . The amounts of decomposed lead pivalate and the corresponding reaction product of composition 3 : 1

Table 2. Average values of sublimation enthalpies for lead pivalate and cobalt and manganese oxopivalates

Compound	Temperature range, K	$\Delta_s H_T^\circ$ , kJ/mol
$\text{Pb}(\text{Piv})_2$	350–382	$113 \pm 10$ ( $104 \pm 3$ [8])
$\text{Co}_4\text{OPiv}_6$	380–425	$180 \pm 10$
$\text{Mn}_4\text{OPiv}_6$	446–479	$161 \pm 14$

Table 3. TGA data for lead(II) complex

Stage	Weight loss, mg	Amount of PbO, $\mu\text{mol}$	Amount of $\text{PbPiv}_{2\text{undecom}}$ , $\mu\text{mol}$	Condensed phase composition
1	0.852 (0.032 of which is HPiv)	4.41	13.40	$3\text{Pb}(\text{Piv})_2 \cdot \text{PbO}$
2	0.798	4.29	9.11	$2\text{Pb}(\text{Piv})_2 \cdot \text{PbO}$
3	1.695	9.11	0	PbO
Residue	3.972	17.81	—	

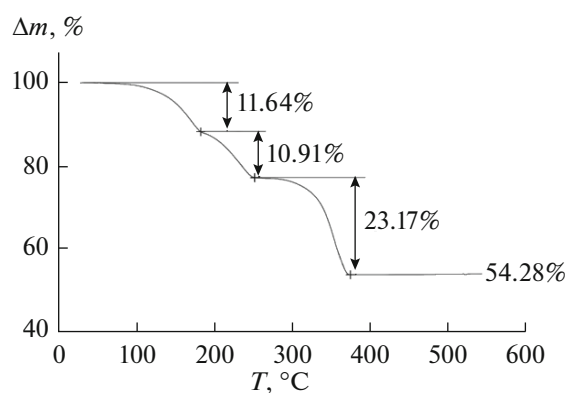


Fig. 4. TG curve for  $\text{Pb}(\text{Piv})_2$ .

were found from the weight loss of pivalic acid only. At the second stage of the process, the 3 : 1 adduct decomposes to form compound  $[\text{Pb}(\text{Piv})_2 \cdot \text{PbO}]$ , which, in turn, undergoes further degradation at the third stage to give lead oxide. In these cases, weight loss is caused by the formation of carbon dioxide and ketone [11, 12], which enabled us to find the amount of resultant 1 : 1 adduct, oxide, and their ratio. The small discrepancy between calculation and experiment of <1% is acceptable for such a study and can be explained by both accuracy of TG procedure and the possibility of other unaccounted degradation processes.

**Cobalt(II) compounds.** TGA of two samples of cobalt complex was carried out. The first sample was a product obtained by the direct reaction of cobalt hydroxide and pivalic acid (Table 4), the second sample is the same substance resublimed in a quartz reactor at residual pressure of 1 Pa in temperature range 180–200°C (Table 5). Mass spectral and CHN analyses showed that the second sample is  $\text{Co}_4\text{OPiv}_6$ . Figure 5 represents the TGA curve for this sample corresponding to weight loss in one stage. Nonvolatile residue is cobalt(II) oxide in amount <10% (Table 4). These experiments allow us to represent the thermal behavior of cobalt oxopivalate under TG experimental conditions as the following two reactions:



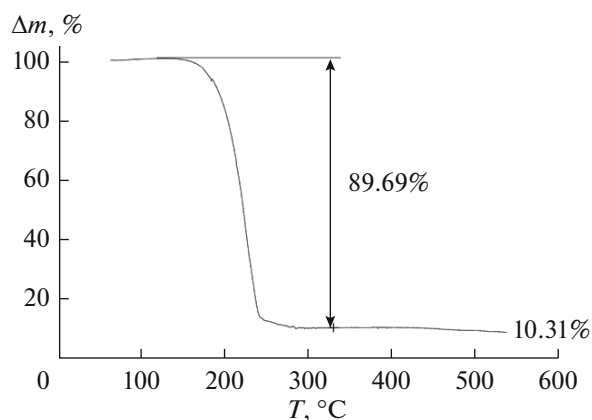
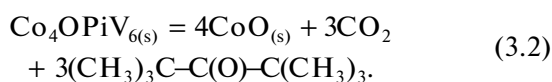
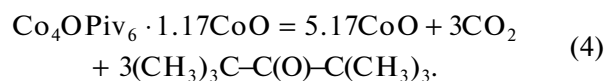


Fig. 5. TG curve for resublimed  $\text{Co}_4\text{OPiv}_6$ .



The TG curve for the initial cobalt compound (Fig. 6) corresponds to three processes of thermal degradation that result in cobalt(II) oxide as the final product like for resublimed compound (Fig. 5). Taking into consideration the high temperature range of 430–530°C, the third degradation stage of the initial cobalt compound can be described by the following scheme:



The second stage of weight loss on TG curve for the cobalt complex at 280–380°C corresponds mainly to the transition of  $\text{Co}_4\text{OPiv}_6$  molecules into gas phase

Table 4. TGA data for cobalt(II) oxopivalate

Cobalt(II) oxopivalate	Weight, mg	Substance amount, $\mu\text{mol}$
Initial weight	5.2480	—
Loss at the 1st stage	1.0401	5.5 (HPiv) 27 ( $\text{H}_2\text{O}$ )
Loss at the 2nd stage	1.9772	2.3 ( $\text{Co}_4\text{OPiv}_6$ )
Loss at the 3rd stage	1.3206	7.1 ( $\text{CO}_2$ ) 7.1 (ketone)
Residue	0.9151	12.2 (CoO)

Table 5. TGA data for resublimed cobalt(II) oxopivalate

Cobalt(II) oxopivalate	Weight, mg	Substance amount, $\mu\text{mol}$
Initial weight	0.872	1.016
Lost	0.782	0.911
Residue	0.090	0.105

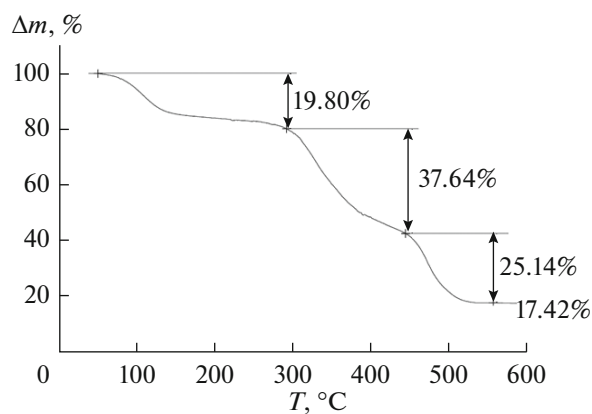
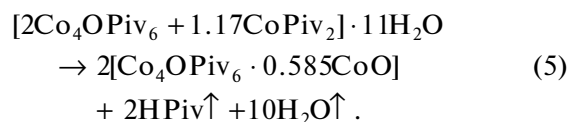


Fig. 6. TG curve for  $\text{Co}_4\text{OPiv}_6 \cdot \text{CoPiv}_2 \cdot 10\text{H}_2\text{O}$ .

and formation of compound  $\text{Co}_4\text{OPiv}_6 \cdot 1.17\text{CoO}$ . The formation of a chemical compound rather than a mixture of two individual phases is proved by the high temperature for the transition of cobalt oxopivalate molecules into gas phase as compared with pure  $\text{Co}_4\text{OPiv}_6$  phase, for which this temperature is 180–270°C (see Fig. 5). It is not excluded, however, that weight loss can be explained in part by the decomposition of cobalt complex to form carbon dioxide and ketone.

Our calculations, the low temperature range of 70–110°C, and the mass-spectral analysis of gas phase allowed us to suggest the composition of initial synthesis product and show that its weight loss at the first stage of thermal degradation is caused by hydrolysis:



Let us note that the proposed description of thermal behavior for primary synthesis product is debatable but it adequately reflects the experimental results of mass spectral and TG studies.

**Manganese(II) compounds.** The TG study (Fig. 7, Table 6) of manganese(II) compound showed that its thermal transformation proceeds in one stage to afford manganese(II) oxide as a final product. Taking into consideration the low temperature of onset thermal degradation, we admit that weight loss is associated mainly with hydrolysis of hydrated manganese piva-

Table 6. TGA data for manganese(II) oxopivalate

Manganese(II) oxopivalate	Weight, mg	Substance amount, $\mu\text{mol}$
Initial weight	18.6770	
Loss	13.3298	15.83
Residue	5.3472	75.31

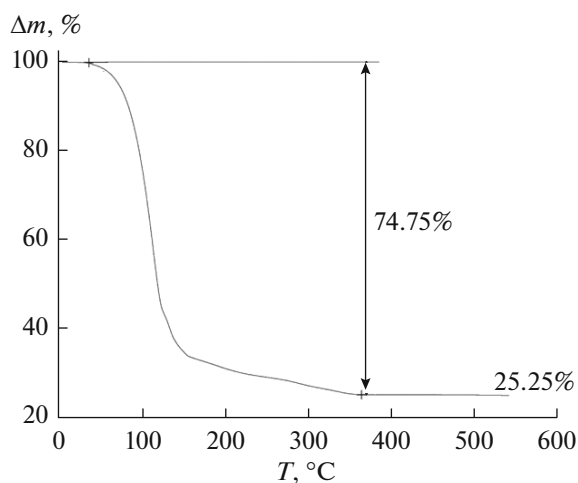
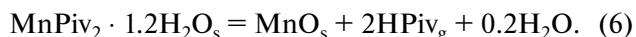


Fig. 7. TG curve for  $\text{Mn}_4\text{OPiv}_6$ .

late. Experimental data provide a possibility to represent this process as the following reaction:



The decrease of weight loss rate in the temperature range 150–350°C may be caused by the formation of dense manganese oxide layer on the surface of sample, which hampers vaporization, or by the high-temperature degradation of small non-hydrolyzed amounts of manganese complexes, for example,  $\text{Mn}_4\text{OPiv}_6$  and  $\text{MnPiv}_2$ .

Our study has shown that the thermal behavior of the prepared pivalate complexes is considerably dependent on vaporization conditions. The obtained complexes, except for the lead complex, are hydrated to a considerable extent. The heating of the cobalt and manganese compounds under atmospheric pressure leads to their deep hydrolysis to give the corresponding metal oxide as a final product. The thermal behavior of the hydrated complexes in vacuum is fundamentally different, a considerable amount of crystal water is removed under these conditions, which is accompanied by the slight hydrolysis to form volatile metal oxopivalates  $\text{M}_4\text{OPiv}_6$ .

Our study has shown that the synthesis of volatile lead, cobalt, and manganese compounds is rather sim-

ple and can be conventionally divided into two independent stages. The first stage consists in the reaction of the corresponding metal hydroxides with pivalic acid and formation of hydrated complexes. The second stage includes the resublimation of hydrated products preliminary dried in vacuum ( $p_{\text{res}} = 1 \text{ Pa}$ ) in the temperature range 150–300°C.

The found sublimation enthalpy of lead pivalate  $\text{Pb}(\text{Piv})_2$  agrees well with the known literature data [8]. The sublimation enthalpies of cobalt and manganese oxopivalates were determined for the first time. The low values of these parameters, high volatility, and monomolecular composition of gas phase allows one to use these complexes as precursors for the preparation of oxide films and materials by MOCVD technique.

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